Science and Technology for the Conservation of Cultural Heritage

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M.A. Rogerio-Candelera
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European Cultural Heritage is the product of the historical development of the myriad of civilizations that contributed over millennia to the creation of the historical, geographical and cultural concept of Europe. This cultural heritage plays a capital role in enriching and enhancing the quality of life of European peoples, in aiding in the understanding of our historical origins, problems, solutions and self-conscience as a differentiated historical entity, as well as in the development of a pool of solutions to environmental and construction-related problems.

Europe has shown itself skilled at turning pure scientific research for cultural heritage into innovative products, developing a lead over other world regions where a demand for European technologies does exist. Being conscious of the risk of oversimplification of the reality implied by the deterministic approaches and eagerness for standardization and recognizing the non-existence of universal solutions, we cannot forget that Europe has the scientific knowledge to validate the answers to concerns over the sustainability of our current approaches to cultural heritage conservation, as is attested by its world leading role in this field. The current crisis context within the European Union, especially in the Mediterranean countries richest in cultural heritage, i.e. Greece, Italy, Spain and Portugal, challenges the institutions and scientists concerned with cultural heritage conservation, thereby fostering the application of imaginative solutions for the exploitation of the synergies generated through international cooperation.

The international dimension and the importance of the challenges that threaten our cultural heritage have been recognized at European level by the launch in 2010 of the Joint Programming Initiative (JPI) "Cultural Heritage and Global Change: a Challenge for Europe" (http://www.jpi-culturalheritage.eu/). The coordinated work of the 26 countries currently involved in the JPI (18 members plus 8 observers) has allowed to define a common vision for the area of research on cultural heritage in a changing world, the definition of a common Strategic Research Agenda to address the challenges and objectives identified, and to set up common coordinated activities with the common aim of preserving our cultural heritage.

TechnoHeritage, the Spanish Network on Science and Technology for the Conservation of Cultural Heritage, funded by the Spanish ministry harboring the competences of scientific research (Ministerio de Economía y Competitividad) by means of a Complementary Action (HAR2010–11432-E), began its activities in March 2011. Currently, the number of member groups of the Network totals eighty, distributed in four areas: (i) Spanish National Research Council (CSIC) groups; (ii) Spanish University groups; (iii) Cultural institutions, foundations and museums; and (iv) private companies. The declared aim of the Network is fostering the collaboration between the elements of the science-technology-enterprise system in order to share ideas and experiences to allow the resolution of conservation problems, and the transfer of technology as a way of contributing to the common goal of the conservation of Cultural Heritage.

From the 2nd to the 5th of October 2012 an International Congress on Science and Technology for the conservation of Cultural Heritage was held in Santiago de Compostela, Spain, organized by the Universidade de Santiago de Compostela on behalf of *Technoheritage* Network. The congress was attended by some 160 participants from 10 countries, who presented a total of 145 contributions, comprising plenary lectures, as well as oral and poster communications. The main goal addressed by the congress was contributing to create an interdisciplinary forum for discussion on all aspects of cultural heritage conservation, providing at the same time an up-to-date and comprehensive picture of the state-of-the-art of investigations. The congress was dedicated to eight topics, namely (1) Environmental assessment and monitoring (pollution, climate change, natural events, etc.) of Cultural Heritage; (2) Agents and mechanisms of deterioration of Cultural Heritage (physical, chemical, biological), including deterioration of modern materials used in Contemporary Art and information storage; (3) Development of new instruments, non invasive technologies and innovative solutions for analysis, protection and conservation of Cultural Heritage; (4) New products and materials for conservation and maintenance of Cultural Heritage; (5) Preservation of industrial and rural heritage from the 19th and 20th centuries; (6) Security technologies, remote sensing and Geographical Information Systems for protection and management of Cultural Heritage; (7) Significance and social value of Cultural Heritage; and (8) Policies for conservation of Cultural Heritage.

For this volume we have edited a total of ninety-three contributions which reflect some of the most recent responses to the challenge of cultural assets conservation. It is worth pointing out that one of the main objectives of the congress, i.e. the promotion of networking among European research groups to strengthen the foundation of scientific and technological research, has been satisfactorily achieved as shown through the presentation of a significant number of investigations resulting from the collaboration between different groups. As a final remark, we (and possibly all the Network members and especially its coordinator, the congress participants and all of the book's contributors) hope to be able to maintain and reinforce such collaborations.

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Environmental assessment and monitoring of cultural heritage

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ABSTRACT: Our heritage has always been threatened by the environment. The Great Sphinx was buried by sand which was cleared away several times in the ancient world. Earthquakes, storms floods and war are all capable of causing immediate damage, but the effects of climate and air pollutants typically accumulate over time and these seem likely to change in the twentieth century. The monitoring assessment of the environment and the damage it causes is important in the strategic management of heritage assets. The processes that cause damage are likely to change over the coming century with frost damage being less frequent in Europe, but damage by salts or insect infestations may be more common.

1 INTRODUCTION

We live in a period of great environmental change. This is not simply that our climate is likely to alter because of increased concentrations of carbon dioxide and other gases in the atmosphere. The environment, as a whole, seems to be changing more rapidly than any time in the recent history of our planet. These changes are driven by an increased population and developing technology that has led to strong desires for enhanced material welfare. The changing environment has had an impact on heritage. As an example the expansion of cities in which people want to enjoy the enhanced opportunities that modern life can bring. Such urbanization is often be bought at the expense of both tangible and intangible assets. Nevertheless we soon regret the loss of heritage and recent times have also seen a profound increase in the desire to preserve the signs of the past.

Welcome news indeed, but it needs to be captured within strategies that use resources efficiently as we cannot preserve everything against all of the threats all of the time. Thus assessing and monitoring becomes so important to the long term management of heritage.

It is not just physical preservation either. Tangible assets have subtleties and aesthetics that are every bit as complex as than intangible heritage. It is not only the physical nature of this material heritage that is to be protected. We need to protect the skills and knowledge to can maintain and repair historic objects. Additionally aesthetics is a key consideration, so this paper reviews the physical and aesthetic changes and how to detect them. It will question how we monitor and assess changes and addresses the question of monitoring and modelling of potential threat and damage. As it is often the long term change requires that monitoring is stable, robust and simple.

2 MODES OF DAMAGE TO CULTURAL HERITAGE

It is not only environment pressures that damage our material heritage. We can make a long list of damaging factors; war and vandalism, urban development, changing architectural styles or poor restoration. These can be immediate and severe and occur as an impulse that can be thought of in a probabilistic sense. Similarly there are environmental impacts that are similarly probabilistic and take place as single, often catastrophic events, such as earthquakes or typhoons and hurricanes (Brimblecombe 1994). Again we measure their occurrence as a probability.

The gradual changes induced by climate or the impacts of air pollution can be quite different. Climate can be a changing parameter in which the daily of seasonal cycles of climate cause repeated stresses through its change, for example, in temperature or relative humidity. Air pollution impacts tend to be cumulative as there is an increasing deposit on material surfaces over time.

One element of assessment is to consider the appropriate procedures to lower risk. The distinctions in the paragraph above become important because the damage appears in such different ways that it leads to distinctive management strategies. Impulses, being probabilistic are ameliorated by lowering the probability or the intensity. Cyclic changes are often amenable to buffering and doses can be lowered by filtering. Thus we lower the probability it of an impulse by planning carefully to reduce accidents or the intensity of an earthquake by decreasing the shock with adequate building supports. Climate can be ameliorated by buffering objects against temperature or humidity cycles. Cumulative damage can be reduced by filter damaging light or pollutants so that they do not reach the surface of an object.

3 CHANGING THREAT

Although climates have always changed we see especially rapid changes evident and although the changes as a result of global warming are likely to be more dramatic over the next century it is hard to remain unaware of some subtle changes as warnings of longer term shifts in the threat to our heritage. Polar regions are particular sensitive to climate change so already show indications of higher temperatures. Snow packs in the Canadian Arctic once permanent have now become perennial, Viking middens in Greenland, for centuries frozen, now thaw and on Spitsbergen metal of abandoned railway stock is frequently above freezing point so the surfaces become wet and rust. The changes are not limited to high latitudes. Already some plant varieties flourish in gardens of Cornwall in southern England that would have struggled a few decades back. In the Central Yucatan changing humidity regimes are allowing the *Trentepohlia*-dominated biofilms to create more extensive red and black patinas on Mayan monuments (e.g. Ortega-Morales 2012). Heavier bursts of summer rain overwhelm the guttering of roofs in Europe, while milder, but wetter winters allow moisture to penetrate more into porous building stone (Smith et al. 2011).

These are cumulative processes, but those such as frost shattering or salt weathering involve phase changes water-to-ice or brine-to-salt-crystals and these are especially sensitive to small changes in temperature or humidity cycles. It seems likely that the changing temperature will decrease the damage in most regions of Europe that arises from frost weathering (Grossi et al. 2007), but increase the damage from salt weathering or at least change its seasonality (Grossi et al. 2011).

It should be note that the impact of climate on material heritage is often best describe in terms of non-classical parameters as it is important to think in terms of a heritage climate because although traditional approaches such as those of Köppen as so often mapped in school atlases are useful but they are limited because these are based on temperature and rainfall whereas material heritage may be more affected by factors such as humidity or wind driven rain or sand (Brimblecombe 2010a).

Pollution has also undergone great changes over the last century and it seems very unlikely that modern air pollution regulations will allow the traditional pollutants to increase in the future despite the increased industrial sources. Of course that has not been true everywhere and China particularly has struggled to combine industrial growth and a rising automobile fleet with lowered air pollution, but even there concern has mounted. In Europe, the concentrations of the most aggressive pollutants, sulphur dioxide and smoke have declined and along with this the rate of damage to building stones and metals (Brimblecombe & Grossi 2009). It may well be that some changes in the urban atmosphere such as the increasing production of photochemical pollutants under longer sunlight hours is not welcome, This may be a special problem for continental locations in Europe, although even considering this possibility it is likely that overall pollutant impacts on heritage will decrease (Brimblecombe & Grossi 2010, Grøntoft 2011).

Aesthetics is also an important consideration in measuring damage as the improvements brought about by the decreases in aggressive pollutants from coal smoke. However, the gains here might not necessarily be matched by a reduction in aesthetic damage. In particular the cleaner buildings that have resulted may have raised expectations and the rising deposit of diesel soot may now because an undesirable degree of blackening. Rain-washed surfaces, perhaps as the result of climate change, may cause disfiguring patterns on facades (Davidson et al. 2000, Grossi & Brimblecombe 2004). The colour of facades may also be changing (Grossi and Brimblecombe 2008) and the traditional blackening of buildings experienced up until recently may have changed in the more oxidative photochemically polluted atmospheres. Here it seems that the soot on buildings could be oxidized to warmer tones (Grossi & Brimblecombe 2008). The White Tower of the Tower of London creates a special perception problem if it were to appear yellow (Grossi & Brimblecombe 2005) though of course it has never really been white either. There are also numerous Black Towers, such as the one in Prague, and they would also hardly be well presented in yellow.

Changing climate can also be propagated indoors, especially in historic buildings without climate control. It seems that temperature increases will be found there, making the environment less comfortable for visitors and too hot for some objects. Humidity variations in southern English interiors do not look set to change very much (Lankester & Brimblecombe 2011, 2012b), but it could be that some increases (mould growth) and decrease (humidity driven dimensional change to wood) in material damage resulting from these changes. Perhaps more important is that the warmer temperatures seem to make the interiors more amenable to a range of insects (Brimblecombe & Lankester 2012) and that insect infestations may demand a continued application of focussed integrated pest management approaches.

4 MANAGING AND ASSESSING CHANGE

Long term monitoring and assessment heritage and its environment can be difficult because the timescales are long in terms of the lifetime of most instruments and research programmes. In the end very accurate surveys or simple passive devices and markers that are left as a legacy for future researchers may ultimately reveal century long change (Brimblecombe 2010b). The relative stability of official meteorological and air pollution monitoring could offer the most reliable source of environmental information as these agencies have long term commitments. The problem is that their weather stations are not always well located to provide information about heritage sites, but calibration against shorter onsite monitoring records is possible.

As stressed in the introduction there are not just physical processes that may be altered by climate change that are relevant to heritage management. Changes in the seasonality in gardens and flood and water damage to footpaths can alter visitor times and their appreciation of historic sites. It is possible that visitor behaviour could alter in response to a changing climate, but little is known about their likely response. Sunnier weather might encourage them to spend time outdoors, but if it was very hot the cool buffered interiors of historic properties might be more attractive (Grossi et al. 2010). Higher temperatures might encourage a shift in opening season to spring and autumn or perhaps night-time visits.

The shifting nature of the 21st century environment means that we have to adapt methods of monitoring and assessment. However the slow pace of environmental change means that the resulting damage appears only slowly and might not be a priority for managers.

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Environmental risks assessment and preventive conservation strategy for the Pórtico de la Gloria, Santiago de Compostela Cathedral

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ABSTRACT: In the framework of the Santiago de Compostela Cathedral Program a multidisciplinary investigation of the Pórtico de la Gloria was carried out between 2009 and 2011 to identify the main environmental risks and to develop a preventive conservation plan to be integrated in the general management strategy of the Cathedral. This study included historic and archivist research, structural studies, mineralogical analyses, biological sampling, cleaning tests, microclimatic monitoring. The main weathering factors and the related damage processes were identified. Results have shown that the main responsible for the observed damage was the infiltration of rainwater through the roof, due to cracks in the structure of the Cathedral. Other environmental factors having a remarkable impact on the state of conservation of the polychrome and its substrate were the solar radiation, the thermo-hygrometric cycles, the particle deposition and the biological growth. Solutions were suggested to improve the environmental conditions, thus reducing further damage.

1 THE MULTIDISCIPLINARY INVESTIGATION OF THE PÓRTICO DE LA GLORIA

The "Santiago de Compostela Cathedral Program" (2006–2012), financed by the Foundation Pedro Barrié de la Maza, contemplated the following work phases for the Pórtico de la Gloria to be executed between 2009–2011: preliminary study, monitoring and diagnosis, risk assessment, preventive conservation and restoration plan.

The Program started with a preliminary research in the archive documents about the construction phase, employed techniques, previous studies on the materials, evolution of their state of conservation and past restoration work.

The monitoring and diagnostic phase was focused on the characterization of the materials and their state of conservation. In particular, the following analysis were performed by COO.BE.C.: static monitoring to investigate the main structural problems; ultrasonic tomography of the stone elements and mechanical laboratory tests of quarry specimens; infrared thermographic analysis of the vaulted coverage; video-endoscopic studies of the stone elements, walls and floors; georadar and magnetometric investigations on the statues; mapping of the surface biological attack, dust deposits, sub-efflorescences and efflorescences; microscopic, mineralogical—petrographic studies and other analysis (SEM-EDXS, XRD, FT-IR, GCMS) for the characterization of the materials, microorganisms, dust composition, soluble salts.

Then, as the polychromies and stones of the Portico are exposed to complex environmental dynamics that affect their state of conservation, a microclimatic analysis was conducted in order to investigate the on-going processes between the atmosphere and the surfaces (Camuffo 1998) and thus contributing to the assessment of a preventive conservation plan (Bernardi 2009, Camuffo *et al.* 1999). The monitoring consisted in the measurement of the thermo-hygrometric conditions of the atmosphere at different distances from the surface, including surface temperature, following a specific methodology described elsewhere (Bernardi 2009).

All the results of the research phase were adapted into site applicable measures, by developing an environmental risk analysis and evaluation assessment (Tecnalia & CNR-ISAC) that permitted establishing future management and intervention actions; and were the basis of the future preventive conservation strategy and restoration plan of the Portico.

2 RESULTS

The structural study put in evidence that the Portico suffered of serious structural problems, mainly due to the instability of the South tower of the façade affected by inclination movements and land subsidence (Coo.Be.C. 2009). This effect inside the Portico was visible in superficial lesions and deep fissures, from which rainwater infiltrated. Other cracks and lesions were due to internal defects occurred in the plant construction consequently to the installation and the settling of the stone blocks.

The Portico was realized with three types of stones: marble, coarse-grained granite and fine-medium grained granite, with different mineralogical composition. Mortars and plasters are no more original materials but they belong to different ages and interventions. The stone materials and the plasters suffered of a quite large number of damage processes such as discoloration and stains caused by the remains of organisms, dust and dirt associated with percolation; efflorescences of nitrates and chlorides coming from percolations of water into the structure and deposition of marine aerosol; seritic alteration, arenization, pulverization, fractures and loss of fragments of material (Fig. 1) (Coo.Be.C. 2011).

The visible paint layer belongs to different epochs, as result of the restoration interventions occurred over time, hence it differs in quality and technology. The most recent one is of the 17th century and it is based on oil technique. The main damage was the detachment and falling of painting, mainly due to the crystallization of soluble salts and to the weathering of the preparatory layer. White and dark discoloration due to deposition of gypsum and oxalates were also observed, as well as sub-efflorescences and efflorescences of several saline species, such as sulfates, nitrates, chlorides (Fig. 1) (Coo.Be.C. 2011).

The video-endoscopic investigations behind the statues of the tympanum revealed the presence of vegetal substrates of soil and zone of accumulation of water drops. The biological growth covered also the surface of stone and plaster materials with a degree of contamination generally medium-low, only exceptionally high, consisting of green and black patinas, dark active colonies, presence of lichens and of algae in the layer of dust. The microorganisms responsible for this degradation were mainly fungi, yeasts and algae (Coo.Be.C. 2011).

Most of the surfaces of the Portico were subject to a considerable deposition of dust. Three types of powder were identified, with different size and degree of coherence: thick layer (>2 mm) consistent and hardened; layer less thick and adherent (>1 mm–<2 mm); thin and incoherent layer (<1 mm). The dust layers were subjected to humidification/dehumidification cycles, due to the presence of moisture within the wall as on the surface especially in the area close to the rainwater infiltration; the powder formed a compact layer well adherent to the surface and the presence of water enhanced the development of microorganisms.

Solar radiation has a notable influence on the thermal behavior the tympanum. In fact, the Portico is oriented toward west and, in the second part of the day, the sun hits the stone surface of the tympanum through the windows of the main façade; the portion of the surface

Figure 1. Deterioration processes affecting the Portico de la Gloria, from left to right: efflorescences on the edges of polychromy; arenization due to seritic alteration of the granite; microfractures.

irradiated and the intensity of the radiation depend on the hour, on the season and on the climatology. As for the conservation of the polychrome the thermal variations are much more dangerous than high thermal levels, a statistical analysis of the daily thermal variations was performed in the north and south sides of the tympanum. The risk of thermal stress was more remarkable in spring and summer for the high relief of the south side, as the solar maps made by Coo.Be.C. documented (Coo.Be.C. 2009). In this point the daily variations were more frequent in the range 1–2°C; for a third of the total time (1 year) they were higher than 2°C, with a maximum of 5°C. In the moments of direct solar irradiation in summer (around 20–20:30) the surface temperature of the south point sometimes increases of more than 1°C in about one hour (Tecnalia & CNR-ISAC).

The hygrometric values in the Portico were generally quite high, with an annual average of 73% RH and maxima frequently reached in autumn and winter. For 55% of total time (1 year) the relative humidity was higher than 65%, reference value for the risk of biodeterioration (Michalski 2000). The annual distribution of the hygrometric cycles, that may cause the dissolution/crystallization of the soluble salts, indicates that the cycles of 75% RH occurred for 6 % of the total time (about 140 cycles in 1 year, with a rate of sampling of 3 hours). 75% is about the equilibrium RH value of NaCl, responsible for the seritic alteration of the granite, a damage process mainly evident in the thin elements of the figures (fingers, curls) (Fig. 1) (Goudie & Viles 1988).

The study of the thermo-hygrometric conditions close to the surface of the tympanum allowed to evaluate the deposition of particles on the surface, in particular the impact of two phoretic processes (Friedlander 1977, Seinfeld 1986). Results shown that for most of the year the termophoresis was inhibited, because for the most of the time surface temperature was higher than air temperature. Contrariwise the diffusiophoresis was slightly favored (60% of total time) and it was more probable in winter and early spring. Moreover, during the whole year of monitoring, the study of the vertical thermal profile showed that the upper part of the Portico was characterized by instability, thus favoring vertical motions of air masses and so transport of suspended particles (Tecnalia & CNR-ISAC). The removal of the scaffolding, necessary to make the higher part of the Portico accessible to the scientific investigations, would enhance stability favored by the entrance of external air from the front doors, generally characterized by lower temperature. Nevertheless, the absence of thermal equilibrium between air and surfaces would always favor vertical air flow along the walls where the geometry of the high-reliefs will cause local turbulence, so inertial deposition of the fine particles (1–2 μm) (Seinfeld 1986).

3 ENVIRONMENTAL RISKS AND PREVENTIVE CONSERVATION PLAN

The multidisciplinary study allowed an integrated assessment of the main environmental risks for the conservation of the Portico de la Gloria and their prioritization according to their potential of damage (Tecnalia & CNR-ISAC). The main environmental phenomena having a remarkable impact on the state of conservation of the polychrome and its substrate were singled out:

- rainwater infiltration through the roof, due to failures in the structure of the cathedral, that mobilized the soluble salts and favored the capture by the surfaces of the suspended particles;
- impact of the solar radiation, that enhanced thermal stress, that forced the evaporation of the filtrated water and the crystallization of the soluble salts, with phenomena of sub-efflorescences and efflorescences, crackling, detachment and loss of material (especially of the paint layer);
- particle deposition, responsible for blackening and chemical interaction with the substrate, in particular in presence of water (infiltration or condensation);
- biodeterioration, favored by the presence of water and the high values of relative humidity.

Once the environmental factors responsible for the most important damage processes at the Portico had been identified and prioritized, several actions listed hereunder were suggested in order to stop these processes or at least reduce the circumstances favoring them.

First of all the technical direction of the Program during the development of the project produced a plan for the repair of the cover between the two towers and the gallery above the Portico, in order to stop the rainwater infiltration. The work was made between December 2010 and January 2011 and this intervention improved quickly the situation.

Then, to stabilize the microclimate, it was suggested to reduce the exchange between the internal and external atmospheres; for example repairing the windows and doors, especially the south one that presented deep fissures. Moreover the use of the doors (especially the north one) should be controlled, reducing it on the occasion of special events, in line with the management of the access to the Cathedral. A better management of the opening/closing of the doors will surely contribute to reduce the turbulence, so the inertial deposition, caused by the atmospheric instability in the upper part of the Portico. The short term analysis performed during the occasional removal of the scaffolding showed more stability but higher ventilation, two opposite conditions for the risk of the inertial deposition. Anyhow, deeper analysis by mean of a fluid dynamic model would be useful to draw final conclusion on the management of the openings.

The impact of IR and UV radiations on the surface of the tympanum, the most dangerous for conservation purposes (Camuffo 2004), should be stopped by the installation of specific filters on the windows of the façade.

Last, but not least, a better management of the pilgrims' access to the Cathedral is advisable, as they are one of the main vector of pollutants and water (especially in rainy days).

The suggested interventions, in order to be effective and sustainable, need to be integrated in the general management strategy for the conservation of the whole Cathedral.

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Basic descriptive statistical methods for monitoring and evaluation of microclimates in Cultural Heritage

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ABSTRACT: Inappropriate temperatures and relative humidity (RH) conditions quite often affect the conservation state of heritage buildings and outdoor archaeological sites. In such cases, a long-term microclimate monitoring is the first step to assess the conservation risks and to propose corrective actions. When a set of temperature and RH sensors are installed for this purpose, the amount of recorded data is usually high, and a suitable statistical methodology is necessary for the data analysis. A case study dealing with this issue is presented here. A set of 26 RH data-loggers and 26 temperature data-loggers were installed in four rooms of Ariadne's House (Pompeii, Italy) at different heights and wall orientations during 372 days. A negative correlation was found between mean values of temperature and RH. Plots of mean daily trajectories show that ambient conditions are different in each room, which provides guidelines about corrective measures to be taken. Principal components analysis was also applied to better characterize the data variability.

1 INTRODUCTION

The preventive conservation of cultural heritage requires prior knowledge about microclimate conditions (La Gennusa et al., 2005). It is well known that wall paintings, as many other artworks, are especially affected by changes in temperature and humidity (Nevin et al., 2008). Therefore, before undertaking a restoration work, long-term monitoring studies are needed to assess the risks affecting the artwork. When a set of temperature and RH sensors are installed for microclimate monitoring, the quantity of recorded data can become huge. Thus, appropriate statistical methods are necessary to analyze the data and obtain relevant information. In previous works, principal components analysis (PCA) was applied to analyze the data recorded by RH sensors for the conservation of renaissance frescoes in the Cathedral of Valencia (García-Diego & Zarzo 2010, Zarzo et al., 2011).

A case study is presented here to illustrate the advantages of PCA and basic graphic tools for the analysis of microclimate data recorded in open-air archaeological sites.

2 METHODS

A set of 26 thermohygrometric probes comprised by one RH data-logger (Datalog Hygrochron DS1923) and one temperature data-logger (Datalog Thermochron DS1922L) were installed in four rooms of Ariadne's House (Pompeii). This building is of great archaeological value due to the fresco paintings decorating several rooms. Three probes were placed in room 4 (codes #2 to #4), eight in room 3 (#5–#12), eight in room 2 (#13–#20), six in room 1 (#21–#26) and one outside the building (#1) serving as a control. Probes were located at different wall orientations and distance to the floor in order to study the effect of these factors. The experiment started on July 23th 2008 and ended on July 30th 2009, resulting a period of 372 days (Pérez et al., 2012).

Mean daily trajectories of temperature and RH were plotted in order to assess the differences among sensors according to their position. Average values of temperatures and RH were also compared by means of a bivariate plot. Temperatures recorded in summer were also analyzed by means of PCA.

3 RESULTS

3.1 *Mean daily trajectories*

Given the amount of data, average trajectories were generated with a software developed by our research group (Fernández-Navajas 2012). It allows an easy data management in long-term monitoring systems.

Figure 1 shows the mean daily trajectories recorded by temperature and RH data-loggers during the monitoring period. The thicker line corresponds to the average. The maximum temperature is reached around midday. It can be observed that temperatures in rooms 1 and 3 tend to be above the average (Fig. 1a), and the opposite applies to those in rooms 2 and 4 (Fig. 1b). Interestingly, rooms 1 and 3 are covered with transparent polycarbonate roofs and they are delimited by three walls, resulting ambient conditions more similar to the outdoor environment.

Daily cycles of RH are also observed (Fig. 1c, d), and the relative minimum corresponds to midday. Thus, results show a negative correlation between temperature and RH, which suggests that the measurement of both parameters is redundant in this case. The shape of all trajectories is quite similar except in a few cases. The abnormal pattern of #2 and #9 seems to be caused by direct sunshine radiation that heats the data-logger at certain time frames.

This type of plot is commonly applied in the control of batch chemical processes because it allows an easy identification of deviations with respect to the target trajectory. However, this kind of plot is not frequently used in microclimate monitoring studies of cultural heritage. The chart provides useful information when daily cycles are clearly marked, as it is the case here. Moreover, it allows an easy identification of outliers.

3.2 *Bivariate plots*

Figure 2 compares the average RH recorded by each data-logger in summer (July 24th to September 22nd) with respect to the average temperature. A negative correlation is observed, which again indicates that the measurement of both parameters is somewhat redundant. Nonetheless, deviations from the fitted regression line might reveal a different performance. This is the case of data-loggers #13, #14 and #16, whose RH recordings are slightly higher than other sensors with a similar mean temperature like #3 or #15. Data-loggers #13, #14 and #16 are located at the ground level, and their higher RH recordings might be caused by diffusion of water vapor by capillarity through the floor to the boundary layer in contact with the sensor. Generally speaking, sensors on the floor tended to record higher RH values except in the case of #8.

Temperatures registered in the same summer period were also analyzed with PCA following the methodology applied in a previous study (García-Diego & Zarzo 2010). Given that all trajectories are quite parallel, the first principal component (PC1) accounts for the differences among trajectories according to their average value.

The projections of observations (data-loggers in this case) over the direction determined by PC1, which are usually called t_1 scores, are strongly correlated with the average temperature, as it can be deduced by comparing Figures 2 and 3. Thus, data-loggers #9 and #10 are the ones with highest mean temperature and t_1 values, while the opposite applies to sensors #13 and #14.

The second principal component (PC2) accounts for the differences in the shape of trajectories. The scatterplot of t_2 vs t_1 (Figure 3) suggests that the trajectory of data-loggers #8, #9

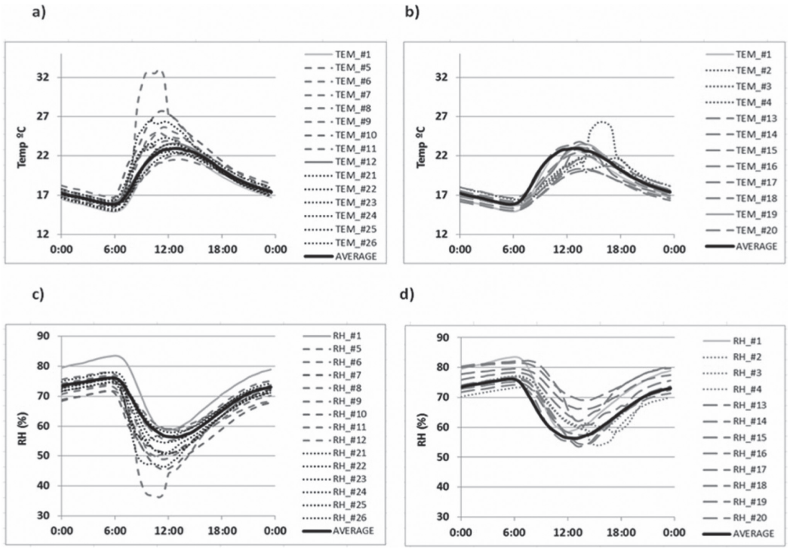

Figure 1. Mean daily trajectories of temperature and RH recorded from 07/23/2008 to 07/30/2009 in Ariadne's House (**a**, **c**: data-loggers in rooms 1 and 3; **b**, **d**: rooms 2 and 4).

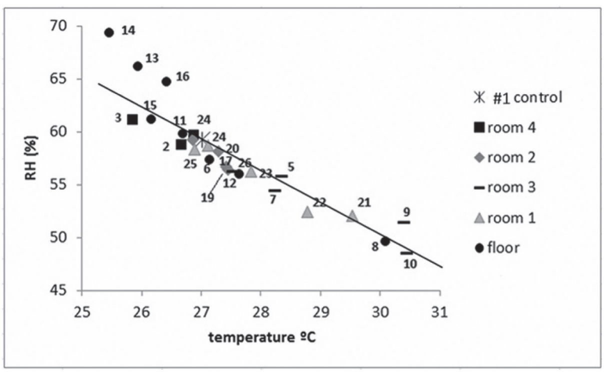

Figure 2. Bivariate plot of average RH vs average temperatures recorded in summer 2008 (07/24/2008 to 09/22/2008) in Ariadne's House (Pompeii). The regression line is indicated.

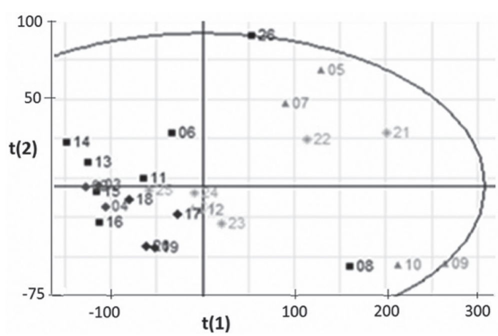

Figure 3. PCA results of temperatures recorded in summer 2008: bivariate plot showing the projection of data-loggers over the direction determined by the first principal component (t_1) and over the second principal component (t_2). Sensor codes as in Figure 2.

and #10 had certain different shape with respect to #5, #7 and #26. Such slight differences are not easily identified by visual inspection of Figure 1, which highlights the advantages of PCA for the interpretation of data in monitoring studies.

According to Figure 3, the most dissimilar shape with respect to the average trajectory corresponds to data-loggers #8, #9, #10 (room 3) and #26 (room 1). This result is intuitively appealing because rooms 1 and 3 are comprised by three walls and their ambient conditions are more affected by outside variations. PCA was also applied to RH data collected in the summer period, and it was found again that sensors in room 3 (#5, #8, #9) presented a higher variability with respect to PC2 (figure not shown). The effect of wall orientation was also studied, but no clear results were obtained.

4 CONCLUSIONS

In a previous study, PCA was successfully applied for the analysis of microclimate conditions aimed at assessing the conservation state of fresco paintings. The same methodology was used here. When all trajectories are quite parallel, which is often the case in microclimate monitoring, PC1 accounts for the average value and PC2 explains the basic differences of the trajectory shape. Despite the advantages of PCA, the interpretation of results may result a bit complex for those unfamiliar in the use of multivariate statistics.

The present work shows that a chart based on daily trajectories can also provide useful information in order to discuss the similarities and dissimilarities of recorded trajectories according to the position of data-loggers. This type of plot is easily obtained, but it is not commonly used in monitoring studies aimed at preventive conservation.

Results reported here show that daily temperature cycles in rooms 1 and 3 are more pronounced than in rooms 2 and 4, which is unfavorable for the conservation of fresco paintings.

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Evaluation of environmental conditions of the Museo del Ejército (Toledo, Spain) by means of Sol-Gel optical sensors

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ABSTRACT: Environmental evaluation is the key factor for preventive conservation in museums. Gaseous acid pollutants are dangerous threats for most of materials. However, no device can be found in the market for measuring the air acidity. Optical pH sensors based on Sol-Gel technology have been applied to the *Museo del Ejército*, a state-owned museum with the most advanced exhibition conditions. Throughout 7 months the sensors were installed inside showcases, as well as exposed to exhibition halls and outdoor air. For this purpose a portable device was designed and patented. Results indicate that indoor pH average is 7.2, while outdoor one is 5.0, which could induce acid shock. These results are discussed in terms of pollutants' concentration and relative humidity percentage, both indoor and outdoor, considering also the architectural building characteristics. The museum conditioning, preservation and security systems are addressed as the main factors to provide the optimal conservation conditions recorded.

1 INTRODUCTION

Full preventive conservation of Cultural Heritage items is connected to environmental evaluation or air quality control. Gaseous pollutants enhance most of degradation processes of materials due to its high acidity (low pH) (Grzywacz 2006). Although the pH electrodes technology is well developed for measuring this parameter in liquid phases and humid solids, no device can be found in the market able to measure quantitatively the whole concentration of acid-basic chemical species in the air. The TechnoHeritage groups C02 and IC2 have developed pH chemical sensors to measure both qualitative and quantitatively acidity/basicity of the air. Such sensors provide an optical response, i.e. absorption in the visible range, that varies the sensor colour depending on the whole acidity/basicity of the environment. These sensors have been proved in several Cultural Heritage sites (García-Heras et al. 2005, Peña-Poza et al. 2011). The optical response of the sensors was recorded with a conventional spectrophotometer and, hence, for long evaluation periods such as one year, the field work was not only time-consuming but subjected to the spectrophotometer moving and the electrical supply.

These former experiences led to the research team to develop a portable and autonomous measurement unit, able to record the optical response of the sensors and to transform it into an electrical signal that, by means of the sensors calibration curve, give the quantitative pH value detected (Villegas et al. 2010). In addition, the electronic device patented incorporates a conventional sensor for measuring the temperature of the surrounding environment. Both the sensors and the measurement device described were used to evaluate the environmental pH of the Museo del Ejército. This is a state-owned museum, attached to the Ministry of Defense and holding a wide variety of items and materials from 15th century AD, distributed over 8000 m^2. The museum building since 2010 is the Alcázar of Toledo; a fortified palace rebuilt upon Arabian, Medieval and further Renaissance castles. The great variety of materials in the museum (metals, textiles, paper documents, woods, leathers, paints, etc.) open an interesting horizon for the study of their preventive conservation, especially from the standpoint of microclimates that could arise in showcases and in the particular indoor environmental conditions of a large historical building. Therefore, the objective of the present work is the environmental monitorisation of the air acidity and temperature inside the showcases, in the air of the exhibition rooms and in the outdoor air. For such purpose both the pH sensors and the portable electronic measurement device developed by the research team were used.

2 EXPERIMENTAL

Acidity sensors were synthesised by the Sol-Gel method. A thin coating from a sol was deposited by dipping upon common glass slides. The sol contains, among other components, an organic dye sensitive to pH that remains encapsulated in the thin coating (Peña-Poza et al. 2011). After a soft thermal treatment to transform the sol into a gel, the coated slides were cut and polished conveniently to be used with the measurement device ($4.0 \times 2.5 \times 0.1$ cm in size). Calibration of sensors was carried out by recording their visible spectra after immersion into buffered solutions Hydrion Buffer Salt® (Aldrich). The spectral intensities at 575 nm were taken as reference optical response for each pH tested. A conventional spectrophotometer Ocean Optics model HR4000 was used for first calibration. Further calibration of sensors was conducted with the electronic measurement device, once it was technically validated.

The electronic measurement device consists of the following main components: a LED to produce a visible radiation (λ = 590 nm), a photodiode that detect the light intensity after crossing through the sensor, an ultra-low-power microcontroller, a processor, a power supply and a temperature sensor (Villegas et al. 2010). The device is provided with an user friendly software to manage and store the data recorded. Likewise, data can be sent to a PC by an USB connection. Validation of the measurement device was accomplished by a quality protocol applied for several pH values, using the spectrophotometer mentioned above, and a sensors series previously calibrated, whose accuracy respect the nominal pH values of the buffered solutions is $\leq$0.05 units of the pH scale.

Among the 8000 m^2 of exhibition space of the museum, several representative showcases of different sizes and content were selected for sensors installation. Other sensors were installed in the free air of the selected rooms, as well as on the four outdoor main façades of the building. Most of sensors were installed inside a protective plastic bag provided with a circular perforation by both sides and a clip to be hanged if necessary. When the space to place the sensor was small and no hanging was required, it was supported in such a way that both sides remain in direct contact with the air. Sensors were always placed in non-visible places to do not disturb the visual appearance of the items exhibited. Table 1 shows a summary on the sensors installation features. The optical response of the sensors installed was recorded from October 4th, 2011 to April 11th, 2012. Replacement of sensors was accomplished at about 3 months after start the data recording to confirm the measurements accuracy or to substitute the sensors damaged by handling or another circumstance. Data of environmental pH and temperature were recorded periodically using the electronic device described.

3 RESULTS AND DISCUSSION

Figure 1 shows the average results of environmental pH obtained during the whole evaluation period. Indoor pHs range between 6.2 and 8.2, while outdoor average pHs vary in a wider range (3.0 to 6.9). These later ranges are expected for an urban area with road traffic and with close bus and taxi stations over several façades of the Alcázar building. The outdoor pH average is very low and, hence, acid shock risk barely exists.

Table 1. Features of selected positions for sensors installation.

Position	Room	Sensors	Features
1	Vexilia	2	Inside two different showcases containing flags
2	Artillería	1	Behind a cannon exposed to the room air
3	Etnografía	1	Inside a showcase containing a Japanese armour
4	Pla Dalmau	1	Under a showcase exposed to the room air
5	Condecoraciones	1	Inside a showcase containing medals
6	Miniaturas	1	Inside a showcase containing miniatures
7	Uniformidad	1	Under a support inside a showcase containing uniforms
8	Medinaceli	4	Inside four different showcases containing armours and weapons
9	M. Hispánica	2	Inside two showcases containing textiles
10	M. Ilustrada	1	Beside a showcase exposed to the room air
11	Lib-Absol (L.A.)	4	Inside showcases containing several materials and to the room air
12	Estado Liberal	7	Inside an Arabian tent and showcases containing several materials
13	Restauración	6	Inside showcases containing weapons, flags and paper documents
14	Siglo XX	5	Inside showcases containing textiles, metallic and wooden pieces
15	Outdoor	4	Four outdoor positions at the museum façades

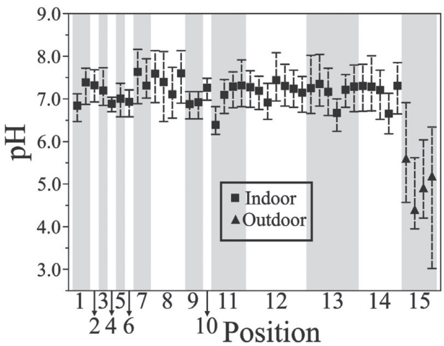

Figure 1. Average pHs recorded (symbols). Bars indicate maximum and minimum values.

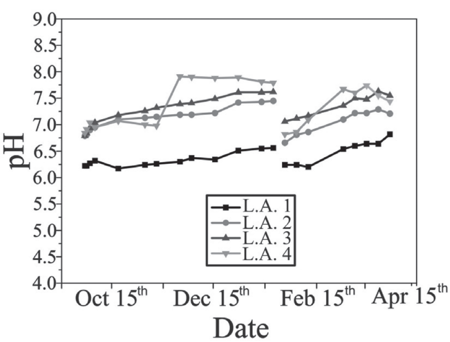

Figure 2. pH evolution in the positions of the room named *Liberales y Absolutistas* (L.A.).

As the indoor pH average values concern, these are all around the neutral condition, being the room *Pla Dalmau* (Table 1) the one with the most stable pH (ΔpH = 0.3), while the room *Medinaceli* (Table 1) shows the higher pH range (ΔpH = 1.6). Even in the latter case, no dangerous environment is accounted since absolute pH values are close to the theoretical neutral pH.

Some additional relation can be stated taking in mind, on the one hand, the sensors position (inside a showcase or in the room free air), and on the other hand, the content of showcases, i.e. the different nature of the items and materials exhibited. Related to the pH average differences between the sensors response sensitised inside showcases and in the rooms' free air, negligible variations were recorded. This is easily explained by the showcases ventilation system, which is installed in all the museum showcases, except in those of the flags room (*Vexilia*), in which the showcases position is very close to the rear wall. The ventilation system is installed in the rear side of the cases, which in general are partially open by such side, and whose air input is from the room free air. This ventilation system allows the air homogenisation and could also create a slight over-pressure indoor, which minimises uncontrolled infiltration from outdoor. Two kinds of filters are installed in the showcases: for solid particles and of activated carbon. Concerning the possible influence of the nature of the materials exhibited in showcases, no clear tendency or dangerous synergic effect was recorded.

The whole average pH results from indoor indicate very low acid shock risk, which could be additionally avoided due to the own architectural features of the Alcázar building. Its extensive surface area (more than 8000 m^2) and high ceilings, great variety of building materials, and the wide archaeological area included (original foundations and shreds of former civilisations) contribute to a huge absorbent active surface formed by stone, granite, bricks, plaster, paint, etc. Therefore, acid pollutants species, both from outdoor or, if any, from indoor sources (heritage items or showcases materials) have been neutralised and/or absorbed by the building materials.

In Figure 2 an example of the pH evolution detected by sensors installed in different positions of one exhibition room can be observed. The first sensor set was installed on October 4th, 2011 and the second one on January 25th, 2012 (note the discontinuity in the graph). In both cases, a sensor stabilisation period can be estimated on a maximum of 1 month and after that the pH values recorded vary in a narrow range about the neutral conditions. The sensors stabilisation period is explained by the low relative humidity indoors (35%), since humidity is needed to generate acid species from outdoor gaseous pollutants. In other words, the low relative humidity indoors hinders the formation of acid species and delays the sensors response. In Figure 2 the lowest pH values were recorded for the sensor labelled L.A.1 installed inside a small showcase containing several military instruments made mainly of woods and metals. Such relative acid pHs should be attributed to the presence of some acid emissive woods in the limited space of a small showcase. The sensor labeled L.A.4 is exposed to the room free air and has the higher pH variation, which can be explained because such room usually receives many visitors.

Temperature additional recordings were made automatically by the measurement device. Average indoor data are in the range (19.2 to 25.9). One showcase of the room *Monarquía hispánica* is the most stable from the thermal standpoint ($\Delta T = 1.6$ °C), while the free air of the room *Artillería* presents the highest temperature variation ($\Delta T = 5.9$ °C). Although some temperature conditioning malfunction could have been recorded, the whole variations are in the range recommended for conservation of Cultural Heritage items. Outdoor temperature range ($\Delta T = 19.8$ °C) was taken from the Spanish State Meteorology Agency, and corresponds to the average daily temperatures of Toledo during the days in which indoor measurements were taken. Note the significant difference of indoor and outdoor temperature ranges, which confirms the adequate conditioning of the museum.

4 CONCLUSIONS

pH sensors based on Sol-Gel technology and a portable electronic measurement device, both designed and produced to evaluate the environmental acidity, have been successfully applied to the Museo del Ejército (Toledo). Average pH and temperature data were recorded from showcases, the rooms' free air and the outdoor air. Results obtained during seven months of continuous monitorisation indicated average indoor pH values close to the theoretical neutral conditions (7.2), while outdoor values ranged between a very acid pH (5.0), due to urban gaseous pollutants. Features of the historical museum building (Alcázar of Toledo) are addressed as the main factors contributing to the neutrality, probably as a consequence of the building materials behaviour as active absorbent surfaces of any gaseous pollutant. Besides, the ventilation system of most of showcases homogenises the neutral air indoors. Therefore, the Museo del Ejército control systems have been sufficient to exclude outdoor and eventual indoor acid pollutants.

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Microclimatic assessment and modelling for salt crystallization control in the Crypt of the Duomo of Lecce (South Italy)

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ABSTRACT: It is known that unsuitable microclimatic conditions can raise the risk of damage in ancient monuments where even small fluctuations can activate deterioration processes, such as soluble salts crystallization. Therefore the importance to monitor the environmental conditions in cultural buildings is widely recognized. Furthermore, in the last decades, many modeling tools have been developed in order to better control the indoors in a preventive way. A microclimatic monitoring was performed over a one year in the Crypt of the Duomo of Lecce (South Italy) where efflorescence is one of the main decay evidence. The data were then used to develop a 3-dimensional Computational Fluid Dynamic (CFD) model to investigate the indoor thermo-hygrometric parameters and determine the most appropriate microclimatic asset. A number of possible microclimatic scenarios, given by ventilation through the windows, were considered. The simulations allowed establishing the most suitable scenario to preserve the building limiting salt crystallization.

1 THE CRYPT OF THE DUOMO OF LECCE

The studied Crypt (40°20'N, 18°07'W, Fig. 1a) was built in 1114 by the Normans in the historical center of Lecce (South Italy). It is actually closed to the public and it can be only accessed to scheduled ceremonies or weddings.

Crypt's deterioration mainly consists of efflorescence, in the form of white salt crystals covering the walls, columns and the Baroque decorations (Fig. 1c). The efflorescence diffusion appeared to be prompted by the indoor microclimate and the outdoor exchange through ventilation.

Therefore a CFD model was performed to find the most suitable microclimatic scenario for limiting the indoor decay.

2 MATERIALS AND METHODS

A CFD code based on the finite element method (FEM) solved all the equations needed to predict the indoor airflow as well as temperature and relative humidity distribution to evaluate both the current microclimatic status and a number of forecast scenarios.

The model was implemented in the Fluent code v.12.1 based on the FEM, to solve the momentum, mass and energy equations (Fluent Inc. 1998). Possible ventilation scenarios corresponding to a combination of different outdoor climatic conditions and airflow inlets were analyzed.

The Crypt is in fact linked with the outside through 9 windows (Fig. 1b) that are currently opened without considering the connected microclimatic effects. The climatic and microclimatic

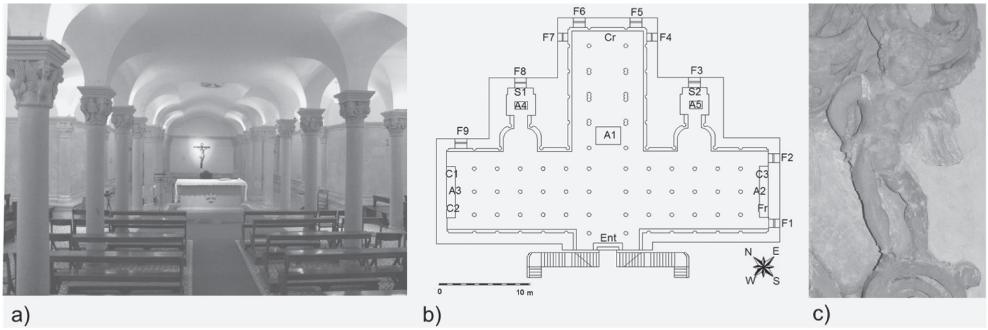

Figure 1. a) The Crypt of the Duomo of Lecce, b) the Crypt's plan with the windows (F1…F9) localization, c) efflorescence on artworks.

data were collected by instrumentation placed outside and inside the Crypt, in the period from April 2009 to April 2010.

The microclimatic monitoring program was planned to record automatically the main thermo-hygrometrical parameters, including air (T) and surface temperature (Ts), relative humidity (RH), dew point and airflow velocity (v).

The indoor Crypt microclimate seemed to be affected by the outdoor conditions, especially regarding the thermal gradients. During the monitoring period, T was between 8 °C and 27 °C and RH between 66% and 81%.

A typical spatial distribution of the indoor T and RH showed how many gradients occur in the lateral apses and the main nave of the Crypt. Dew point temperature was never reached in the Crypt, so condensation never occurred.

The main outdoor wind direction was N-NNE and WSW while indoor v measurements showed values in the range between 0.2 m/s and 0.4 m/s. The best ventilation assessment was checked by the CFD simulations considering that the most delicate artworks are placed in the lateral apses in order to retain here stable airflow patterns.

In this study, six main possible opened and/or closed windows scenarios (named from A to F) were taken into account together with two main wind blows: from North and South. The wind direction leads the air into or out of the Crypt in an opposite way both through each window.

Two main seasons (Winter and Summer) were taken into account, for a total of 24 scenarios to be simulated. In the scenario A, all the windows are opened; in the scenario B, F2, F4 and F7 are closed. The scenario C has F5, F6 and F9 closed while scenario D has F2, F4, F5, F6 and F9 closed. Scenario E has all the windows closed apart from F3, F4, F7 and F8 while scenario F has all windows closed.

The boundary conditions were set from considering averaged values for each season, given from the outdoor/indoor measurements. In Winter, outdoor T was between 11.0 °C (North wind) and 11.8 °C (South wind), RH between 81.2% (North wind) and 86.8% (South wind). Wind velocity was between 1.8 m/s (North wind) and 2.6 m/s (South wind) while in Summer it was between 1.2 m/s (North wind) and 1.6 m/s (South wind). In Summer, outdoor T was between 26.1 °C (North wind) and 28.2 °C (South wind), RH between 70.2% (North wind) and 76.4%(South wind). In Winter, indoor Ts was 12.1 °C and RH was 77.8% while in Summer Ts was 23.3 °C and RH was 71.3%.

The geometrical 3D model contains an air volume of 1880 m^3 that was approximately divided into 7.500.000 tetrahedral cells, each representing about a $10 \times 10 \times 10$ cm^3 volume.

The model was validated comparing the outputs of the CFD simulations with the experimental data obtained in specific surveys using an electronic TECHNOEL psychrometer (accuracy 0.1 °C, resolution 0.01 °C). The outputs of the CFD simulations were analysed on 27 plans on X,Y,Z axis across the Crypt at three different heights from the floor (Z = 1, 2, 3 m) with 2 m space.

3 RESULTS

In the analysis of the results, a particular attention was given to identify the airflow patterns and the microclimatic gradients (Table 1). Scenarios A and B produced an indoor microclimate too influenced by the outdoor conditions. The first showed an indoor increase of the average temperature of 16.8 °C with gradients over 30% for relative humidity when the climatic conditions changes from Summer to Winter, the second showed average seasonal gradients of 14.3 °C temperature and 29% relative humidity. Scenario A showed that windows F4, F5, F6 and F7 should not be opened at the same time as this causes an airflow that leads to important microclimatic gradients in the main nave and the lateral apses with both wind direction. Moreover, the critical condition for potassium nitrates (KNO_3) crystallization is reached in Winter. This compound is the most diffused salt on the Crypt's masonry and it has equilibrium RH between 95.4% and 93.6% and T between 15 °C and 25 °C (Arnold & Zender 1991).

Scenarios C and D gave lower gradients but simulations showed an important airflow in the area of the right apse of the Crypt where canvas and frescos are placed. Particularly, with South wind, when air went into the Crypt by the windows F1 and F2, airflow pattern appeared intense in correspondence of a damaged fresco, contributing to its decay.

Results showed how Scenario D gave more suitable temperature and relative humidity conditions with an average temperature of 22 °C (North wind) and 22.5 °C (South wind) in Summer and 14.2 °C (North wind) and 14.6 °C (South wind) in Winter. For relative humidity, conditions were: 64% (North wind) and 70% (South wind) in Summer and 72% (North wind) and 76% (South wind) in Winter.

Fluctuations were lower compared to the previous cases, being equal to 2.8 °C in Summer and 2.4 °C in Winter and for relative humidity 14% in Summer and 18% in Winter. However, also this scenario was not suitable for Crypt's canvas conservation as window F1 generates turbulence near the right apse. Therefore, F1 and F2 windows should always be kept close.

The scenarios giving most suitable microclimatic values were E and F as they assure suitable temperature and relative humidity values within and between the seasons Moreover, indoor conditions are not affected by wind changes, and a low airflow creates lower turbulence and small variations of temperature and relative humidity.

Scenario E showed temperature between 19.2 °C and 23.0 °C in Summer (average 21.4 °C) and between 15.9 °C and 18.9 °C in Winter (average 17.7 °C). Relative humidity was between 48% and 70% in Summer (average 60%) and between 53% and 75% in Winter (average 65%).

The Scenario E seems to be preferable when the Crypt is opened to the public as it provides a better air replacement, useful to avoid problems related to the presence of visitors (Fig. 2).

Table 1. Average, minimum and maximum temperature and relative humidity conditions for the simulated scenarios.

		T (°C)						RH (%)					
		Summer			Winter			Summer			Winter		
Scenario	Wind	Av	Min	Max	Av	Min	Max	Av	Min	Max	Av	Min	Max
A	N	27.3	24.5	30.1	10.7	9.0	12.5	66	53	79	88	81	94
	S	28.2	25.7	30.7	11.1	9.2	13.1	69	58	80	90	83	96
B	N	26.8	25.1	28.5	11.8	10.2	13.4	73	66	80	83	78	88
	S	25.0	22.7	27.3	11.4	10.6	12.2	71	64	78	86	82	90
C	N	23.4	19.6	27.2	13.9	12.1	15.7	73	67	79	78	72	84
	S	24.6	22.5	26.7	13.5	12.4	14.6	70	64	76	84	82	86
D	N	22.0	20.0	24.0	14.2	11.9	16.5	64	54	74	72	64	80
	S	22.5	20.2	24.8	14.6	12.2	16.6	70	63	77	76	70	82
E	N	21.3	19.8	22.8	17.4	15.9	18.9	58	48	68	63	53	73
	S	21.6	20.2	23.0	18.0	17.2	18.8	62	54	70	67	59	75
F	N	20.8	19.4	22.2	18.0	15.6	20.4	55	45	65	59	50	65
	S	21.5	20.5	22.5	17.8	16.5	19.1	54	50	58	61	55	67

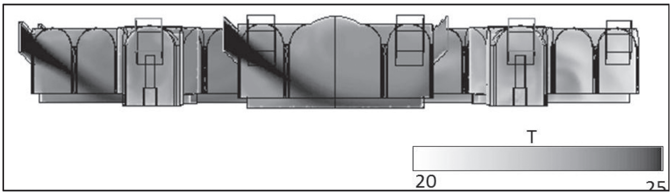

Figure 2. Scenario E: T (°C) distribution in summer conditions with South wind.

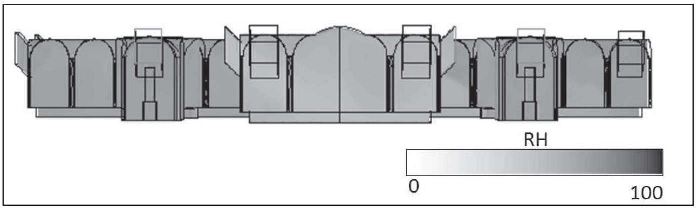

Figure 3. Scenario F: RH (%) distribution in winter conditions with North wind.

Considering that the Crypt is actually closed to the public and that people comfort is secondary in respect to conservation needs, the scenario ensuring the lowest microclimatic gradients and fluctuations is the scenario F that permits airflow only by the entrance of the Crypt.

This assessment ensures stable indoor relative humidity in the range between 45% and 67% with a gradient of 13% within Summer and 17% within Winter. Temperature range was between 15.6 °C and 22.5 °C in the whole period with a 3.1 °C gradient during Summer and 4.8 °C in Winter (Fig. 3). Temperature never falls under 15.6 °C in Winter and never rises up to 22.5 °C in Summer with a minimum relative humidity of 45% and a maximum of 67%. When season changes, simulations showed a variation of the average temperature of 3.2 °C and of relative humidity of 6% with a maximum difference of 6.9 °C temperature and 22% relative humidity. These values assure stability in the most delicate areas of the Crypt and are within the range suggested by conservation science (UNI 10969 2002).

4 CONCLUSIONS

The paper illustrated that CFD models supported by microclimatic monitoring can contribute to have a better control of the indoor environment in cultural buildings. Considering the CFD outputs, the following main actions for improving the Crypt's conservation can be synthesized:

- Crypt's windows should never be opened at the same time as outdoor variations would heavily influence the microclimate with a negative effect on conservation;
- to retain a temperature and consistent humidity throughout the Crypt, all the windows should be kept close. This also limits the airflow and the turbulence near the walls and columns;
- in case of people presence, the windows to be opened should be F3, F7, F9, while F1 and F2 should always be kept close for artworks conservation.

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

Microclimatic studies in Paranhos water galleries, Porto (Portugal)

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ABSTRACT: Paranhos constitutes one of the main water galleries excavated in the granite substratum of Porto City (Portugal) to gather the groundwater for public use during the past six centuries. The interest of this water gallery is double: a) Cultural Heritage and scientific value, b) Underground geotourism. A multidisciplinary research to study the microclimatology, geochemistry, mineralogy and geomicrobiology of the Paranhos catchwork galleries is currently in progress. The characterization of the main environmental parameters (air-rock temperature, relative humidity, CO_2, ^{222}Rn, etc.) in the internal atmosphere would allow the establishment of: a) Fluid-rock interactions and development of a physical-chemical model of air-water-rock, as a base to define their relations with unusual mineral formations and microbial communities b) Microclimatic parameters and determination of effective radioactive dose for visitors based on ^{222}Rn studies, as potential use as underground geotourism site under safe conditions.

1 INTRODUCTION

The regional framework of Porto area consists of a crystalline fissured basement complex composed of highly deformed and overthrusted Late Proterozoic/Paleozoic metasediments and granitic rocks (Chaminé et al. 2010). For more than six centuries, water was supplied to Porto City through fountains fed by numerous springs. Paranhos and Salgueiros Spring galleries catchworks (3.2 km long) were excavated in the granite substratum of the city to gather the groundwater for public use to Porto inhabitants (Fig. 1). Paranhos is one of the main water galleries excavated in the crystalline bedrock, moderately deformed granitic rocks, randomly crossed by aplitic/pegmatitic veins. Our study is focused in the sector between St. Dinis and Burgães street entrances reaching a total length of 910 m divided in three segments. St. Dinis is the shallower entrance (higher altitude), where overburden is minimum. Ventilation shafts are located in many sectors of the gallery. The tunnel has an internal diameter of 2,20 m and a maximum cover of 21 m and a minimum of 1 m.

Paranhos spring supplies shallow groundwater that responds quickly to precipitation events, being particularly vulnerable to contamination, especially nitrates and sulphates

(Afonso et al. 2006). However, the aquifer presents a low natural recharge due to the low permeability of the overlying urban area. Although groundwater is not more used for human consumption, other potential interests of the Paranhos gallery are currently evaluated:

a. Cultural Heritage and scientific value; aquifer vulnerability, urban speleological mapping and geo-engineering studies have been developed in the Paranhos galleries, but other scientific values can be remarked as the presence of unusual mineral formations (Sanchez-Moral et al. 2011) (e.g. Evansite) and microbial communities. Evansite comprise microlayers of amorphous hydrous aluminum-phosphate phases $Al_2(PO_4)_3$-5 · nH_2O) together with hydrolyzed uranyl groups and hydroxide $UO_2(OH)_2$ precipitates. The microbiological study of these environments represents an approach to the discovery of the large bacterial diversity, the understanding of the role and functioning of these microorganisms and their implications on the conservation of the geo-sites or their affinity to particular hydrological processes or supply of contaminants from the external soil. Recent scientific assessment revealed that biological activity played a major role in the development of these manganese oxides, specifically birnessite and todorokite (Miller et al. 2012). Additional interest is related to the conservation issues of geo-sites.
b. Underground geotourism; as economical resource to attract tourists and investment. Artificial and stable underground spaces such as aqueducts or water galleries can be suitable for underground geotourism, previous establishment of the safe conditions for visitors.

The aim of the current study is the characterization of the geochemical and microclimatic dynamics of the Paranhos water gallery with special emphasis on the study of exchange cycles of atmospheric CO_2. Concerning the establishment of safe conditions for potential visitors, the study also deals about characterization of ^{222}Rn gas emanation from host rock granite and radioactive minerals.

2 MATERIAL AND METHODS

Three fixed microenvironmental sampling stations were established in the Paranhos gallery (Porto 1, 2 and 3, Figure 1B) allowing the continuous monitoring of next parameters of air: 1) Air temperature and relative humidity with HOBO Pro v2 and Tinytag Plus 2 data loggers; 2) CO_2 concentration measured using a ELG-33 datalogger (CO_2 meter). This sensor is located in a permanent station (Porto 2). All parameters are registered every 1 hour and the records are downloaded every 3 months. Radon 3) Gas ^{222}Rn measured by passive integration method (3 months period) with Kodalpha Radon dosimeter (GT Analytic).

In order to characterize cave levels of CO_2, $\delta^{13}CO_2$ and CH_4 several air samples are taken every six months in an established points network along the gallery. Samples were obtained by filling Tedlar air sampling bags with capacity of 1 L and analyzed afterwards in laboratory by using an optic spectrometer Picarro G2101-i. Isotopic relationship $\delta^{13}CO_2$ is measured as

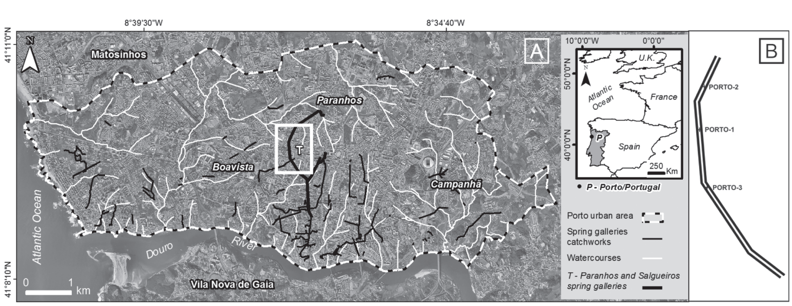

Figure 1. A) Geographical location of the Paranhos and Salgueiros Spring galleries. Modified from Chaminé et al. (2010). B) Sketch of the studied section of the tunnel that corresponds to white square in Figure 1A, showing three microclimatic stations.

a calculation from $^{12}CO_2$ and $^{13}CO_2$ concentrations analyzed by the spectral system. During the same campaign, a 24–48 hours test for radon gas is performed at Porto 2 station using a Radon gas detector Durridge, RAD7.

3 RESULTS AND DISCUSSION

Monitoring period was initiated in February 2012. The 6 months period of microclimatic characterization in the Paranhos gallery is providing next data:

Air temperature and relative humidity: constant relative humidity values are near saturation (100%). Porto 1 and 3 stations present high response to daily changes, but a temperate response to seasonal cycles. Porto 2 is characterized by an accumulative effect of air temperature that could be related to the higher topographic location acting as hot air trap (Fig. 2A).

CO_2: the low CO_2 average concentration (around 700 ppm) of winter-spring period increased to 1,200 ppm during late Spring-Summer; this effect can be interpreted as an indication of the summer reduction of the ventilation in the Porto 2 section (Fig. 2B).

^{222}Rn: radon gas is used as a quantitative index of ventilation in subterranean environments, but also it is fundamental for calculation of occupational dose of potential visitors. Passive Kodalpha detectors are indicating a clear seasonal increase of radon concentrations in Porto 3 from the winter-spring to summer season, and opposite pattern for Porto 2 (Table 1). A 48 hours test of continuous monitoring (30 minute data) in Porto 2 has also allowed the identification of this seasonal behavior, but also daily oscillations of coupled ^{222}Rn and CO_2 (Fig. 3).

Microenvironmental mapping from two campaigns (February and September 2012) for CO_2, $\delta^{13}CO_2$ and CH_4 has allowed the observation of the spatial-seasonal variation of these parameters in the tunnel. This environment, as many caves, is characterized by relatively high levels of CO_2 with very low $\delta^{13}C$ isotopic signal values and low levels of CH_4 compared with the external

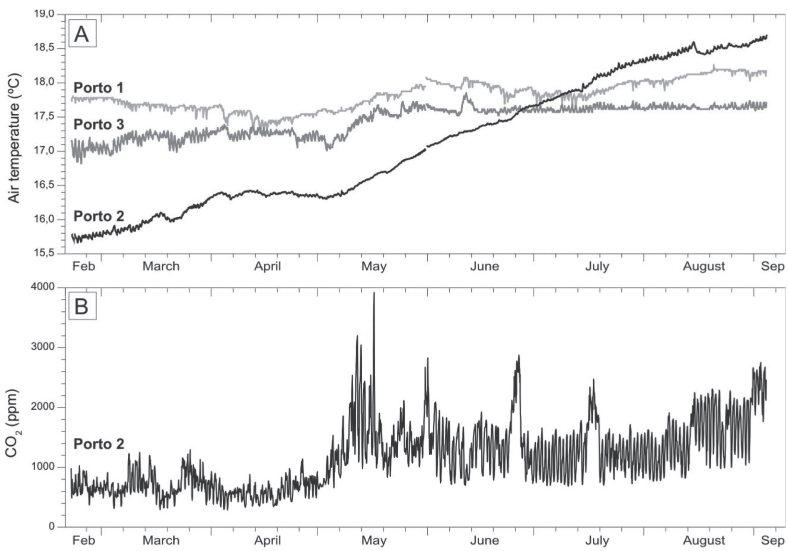

Figure 2. A) Temperature record in the three stations (Porto 1, 2 & 3). B) CO_2 record in Porto 2 station.

Table 1. Radon activity of air (^{222}Rn, $Bq \cdot m^{-3}$) in the three stations.

Period	Porto 1	Porto 2	Porto 3
21/02/2012–07/05/2012	15992 ± 1439	18819 ± 1506	7528 ± 678
07/05/2012–26/07/2012	12401 ± 1868	14049 ± 983	9131 ± 639
26/07/2012–06/09/2012	18784 ± 1315	12749 ± 892	12951 ± 907

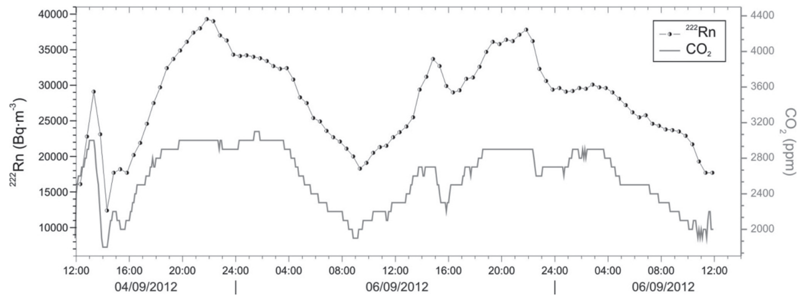

Figure 3. 48 hours continuous monitoring for ^{222}Rn and CO_2 (Porto 2, early September 2012).

atmosphere. CO_2 present in the internal atmosphere has a soil-derived origin. The highest CO_2 concentrations, minimum CH_4 and lighter isotopic values in both measured periods correspond to the Porto 2 section, although it is relatively close to the St. Dinis Entrance. This could be related to a relative isolation of the Porto 2 area respect the rest of the tunnel.

4 CONCLUSIONS

The six months period of environmental monitoring of the Paranhos gallery allowed the identification of the Porto 2 as the less ventilated sector of the tunnel by using microclimatic continuous monitoring (temperature, relative humidity and CO_2) and mapping-interpretation of tunnel levels of CO_2, $\delta^{13}CO_2$ and CH_4. Radon gas passive detectors also indicate the highest ^{222}Rn-activity of air in this area of the gallery, but an increase of ventilation rate towards the summer. The temperature records in Porto 2 indicate an accumulative effect probably due to the higher altitude, less forced ventilation via ventilation shafts and because the characteristics of the St. Dinis closure (hermetic door) and size of the tunnel. An opposite pattern is detected in the other extreme of gallery (Porto 3) and, to a lesser extent, in the middle of the gallery (Porto 1).

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Bio-susceptibility of thermal insulation systems used for historical buildings

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ABSTRACT: In historical buildings of Northern countries high levels of energy are necessary for reaching comfortable temperatures. For this reason several indoor insulation systems based on historical and ecological materials are on the market that should improve the thermic performance. However, using organic materials bears the risk of fungal growth. Therefore, five ecological indoor insulations systems were tested for their bio-susceptibility against various fungi both under natural- and under laboratory conditions. Fungal growth was evaluated by cultivation as well as by molecular methods. The materials turned out to have a different susceptibility towards fungal contamination. Whereas insulations made of bloated Perlite (plaster and board) did not show any fungal growth under natural exposition, loam and weed had high cell counts. In laboratory experiments, wooden soft-board represented the best environment for fungal growth. As a result, bloated Perlite is the most appropriate material for thermal insulation from the microbiological point of view.

1 INTRODUCTION

The ongoing climate change calls for necessary changes of human behavior and -living. In colder European climate zones, thermal insulation of houses is self-evident to reduce the amount of energy for heating. Exterior insulations systems are frequently applied on modern, newly built houses and Styrofoam is the most common exterior insulation system. However, a high percentage of our living houses are historical buildings under preservation order. These buildings are now included in country specific regulations and ordinances to enhance the "energy efficiency". Since an exterior insulation is incompatible with monument protection, alternative insulation techniques have to be applied Historical, organically and ecological insulation materials, such as bloated Perlite, cellulose, loam, reed, weed or wood are on the market but the risk of these materials is a possible microbial contamination through bacteria and fungi. Microbial growth on building materials is a problem that has been known for a long time, but floods, wet years, thermal modernization, air-conditioning systems, construction or material faults, poor and improper ventilation are major reasons for an increase of the relative air humidity and dampness of surfaces (Samson et al., 2010). These climatic conditions foster microbial growth (Sterflinger 2010). The properties and the common occurrence of microorganisms contribute to the fact that they represent the most frequent cause of bio-deterioration of building materials (Piñar & Sterflinger 2009). Furthermore, a worldwide phenomenon called sick building syndrome—SBS—(Sykes 1988) has been confirmed as a recognizable disease by the World Health Organization (Akimenko et al., 1986). All these properties and effects of microbial growth call for the need to gain more insight into the micro-biota inhabiting the different construction materials.

Nowadays, the isolation and identification of microorganisms still sticks to classical culture-based methods to estimate microbial contamination in buildings. Cultivation allows a quantitative and qualitative assessment of the environment. Nevertheless, the dramatically changes in microbiology over the past 20 years have developed fast and sensitive technologies that can be applied for studying microbial communities without the need for cultivation (Hill et al., 2000). The first crucial step for a successful and complete analysis of the micro-biota is the choice of an appropriate DNA isolation method (Martin-Laurent et al., 2001).

In this study 5 ecological indoor insulation materials were tested for their bio-susceptibility. The materials were investigated both under natural conditions—after 2 years of installation in an historical building—and under laboratory conditions. Therefore, samples items of all materials were inoculated with 3 commonly indoors occurring fungi and treated in a climate chamber for half a year. After this incubation time small samples were taken for cultivation- and molecular analyses. The colony forming units of each material were determined as well as DNA was extracted and evaluated by Nano Drop measurements. The same procedure was performed with samples taken from the historical house. In order to apply an appropriate DNA extraction method for the insulation materials we evaluated up to 13 direct—*in situ* DNA extraction methods with 3 typically used building materials. Attention at the evaluation of these protocols was focused on the parameters: 1) the quantity and 2) the quality of the DNA; 3) visualization of the extracted DNA; and 4) the ability of the DNA to be amplified in different PCR reactions. Additionally, the amplified PCR products were analysed by Denaturing Gradient Gel Electrophoresis (DGGE) in order to compare the community fingerprints obtained from the different isolation methods and sample amounts.

2 METHODOLOGY

2.1 *Classical cultivation studies*

Five indoor insulation materials—bloated Perlite (plaster and board), loam and reed, wooden softboard and sprayed cellulose—were evaluated. Therefore, small areas (5 × 5 cm) of the test items were inoculated with each 1 ml of 4 spore solutions from 3 commonly indoors occurring fungi (ACBR-Culture Collection, www.acbr-database.at: *Cladosporium cladosporioides*, *Aspergillus niger* and *Penicillium chrysogenum*, and a mixture of all 3). For 6 months, the samples were incubated in a climate chamber at 28°C and 90% relative humidity. Afterwards, samples from the surface were removed for cultivation and molecular analysis. Similar, 2 years after installation of the insulation systems in the historical building, samples were taken and 1 g of each material was shaken in 100 ml Erlenmeyer flasks, filled with 50 ml Tween 80 for 1 hour at room temperature on a rotary shaker (170 rpm). Hundred Microliter of each solution of a dilution series (10^0–10^{-3}) were plated on each two Malt-extract-agar plates (MEA) supplemented with 20 µl Streptomycin (Stock: 25 mg/ml) to inhibit bacterial growth. The plates were incubated at room temperature and fungal growth was checked every day. Colonies on the plates were counted to finally calculate the colony forming units (CFU) for each material.

2.2 *Molecular analyses*

In order to extract DNA from the insulation material an appropriate isolation method had to be found to overcome the biases commonly occurring during DNA extraction from building materials. Therefore, 3 commercial DNA extraction kits for soils and four standard DNA extraction protocols were tested with common plaster, red brick and gypsum cardboard (Ettenauer et al., 2012). Each material was ground, homogenized and 3 different samples amounts (50, 100 and 250 mg; each in triplicate) were weighed for each extraction protocol. After DNA extraction, the DNA yield and -purity (A260/A280 ratio) were assessed using the Nano Drop spectrophotometer. Therefore, from all triplicates the DNA concentration and -purity was measured thrice and mean values and standard deviations were calculated. Afterwards, the triplicates were pooled and electrophoresed on 1.5% agarose gels. Further, the pooled DNA was used for PCR reactions with 3 fungal ITS primer pairs (ITS1/ITS4, ITS1/ITS2 and ITS3/ITS4) and 1 bacterial 16S rRNA primer set (341f/907r). Amplification products were assessed by visualization on 2% agarose gels. Genetic fingerprinting using DGGE analysis was performed with fungal and bacterial PCR fragments. According to the results obtained from these criteria (DNA-quantity, -quality, agarose gel electrophoresis, PCR- and DGGE results) the methods that worked better were identified and continually eliminated others that did not work as well.

According to the results from the comparative extraction study the most suitable method was used for the isolation of DNA from all samples of this study. Hundred milligram of each insulation material were used for the DNA extraction.

3 RESULTS AND DISCUSSION

3.1 *Classical cultivation studies*

Fungal colonies growing on MEA plates derived from the insulation materials were counted and the CFU values were calculated. Figure 1a shows the calculated CFU-values.

After 6 months incubation under optimal growing conditions, fungal colonies were detected on all test items. The CFU values ranged from 5.0×10^2 to 1.97×10^6. The distinct strongest fungal growth was found on the wooden cardboard samples (CFU: 9.83×10^5 to 1.97×10^6). On reed boards with loam, bloated Perlite boards and sprayed cellulose, germination numbers of about 2 orders of magnitude lower were calculated. The best results, with the lowest CFU values (2.5×10^3 to 2.1×10^4) were found on the bloated Perlite plaster.

From the *in-situ* samples only on the wooden soft-board and reed board with loam a few fungal colonies germinated. The CFU values ranged from 1.5×10^3 to 1.63×10^4. No fungal growth was observed on the other materials. The control samples of all materials, taken before the inoculation with fungal spores did not show any fungal growth at all.

3.2 *Molecular analyses*

All 13 extraction methods allowed the isolation of DNA from all sample amounts of all 3 building materials. However, Nano Drop measurement for the DNA concentration showed very divergent values. All 3 kits delivered the lowest DNA yields (Fig. 2a). Protocols including a purification step using columns or spin filters yielded drastically lower DNA amounts than standard methods using phenol/chloroform precipitation. A lot of DNA is lost, whereas purity measurements, visualization and PCR analysis showed that many contaminants could be eliminated. The standard protocols showed the highest DNA yields. Up to 3 orders of magnitude more DNA could be isolated from the same sample amounts. However, they also had lowered A260/A280 ratios revealing impurities that co-precipitated with the nucleic acid (Fig. 2c). These findings were confirmed by negative results obtained from electrophoresis and PCR analysis.

The DNA yield did not correlate to the sample amounts. All methods gained more DNA from the 50 mg samples than from the 100 or 250 mg samples (Fig. 2b). This is due to the

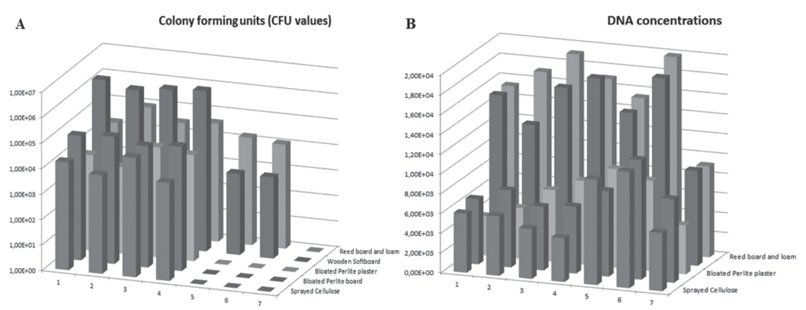

Figure 1. 3D diagrams showing (a) the CFU values on a logarithmic scale and (b) the DNA yields. Sample items incubated with *Cladosporium cladosporioides* (1), with *Aspergillus niger* (2), with *Penicillium chrysogenum* (3), with a mixture spores (4), samples from the 1st floor (5), and the 2nd floor of the building (6); not incubated control items (7).

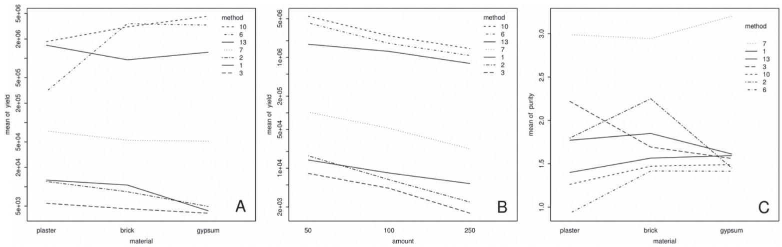

Figure 2. Interaction plots of the mean values for measurement variables yield and purity of corresponding factor combinations are displayed and linked by profile lines for each method. (a) Mean values for yield of the factor combination material and method. (b) Mean values for yield of the factor combination sample amount and method. (c) Mean values for purity of the factor combination material and method.

ratio: used sample amount versus added buffer volume for the extraction. Small buffer volumes are not enough to reach the whole sample material, when the sample material exceeds >100 mg. As a consequence the enclosed DNA in the material cannot be extracted completely. The DGGE results clearly demonstrated that the fingerprints were not influenced by the extraction methods, provided that the extraction allowed successful PCR amplification. The results further showed that fingerprints obtained from the 50 mg subsamples of homogenized sampling material represented the whole inhabiting microbial community.

The FastDNA Spin kit was the only method that revealed positive results for all parameters of all 3 building materials. Therefore, this method was applied for the samples and allowed the isolation of DNA from all tested insulation materials (Fig. 1b).

4 CONCLUSIONS

From the microbiological and hygienically point of view, plaster and board made of bloated Perlite are presented as being the most appropriate materials for thermal indoor insulation. The FastDNA Spin kit for soil (MP Biomedicals) is the method of choice for DNA extraction from construction materials. We recommend the standard application of this kit for molecular ecology analysis of building materials in order to set standards in the assessment of microbial community analysis and to allow comparisons of results between different laboratories.

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Biological crusts contribute to the protection of Neolithic Heritage in the Mediterranean region

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ABSTRACT: The presence of biological crusts on stone walls of Neolithic temples in the Mediterranean region determines a protective role against physical-chemical weathering, such as rain, wind or thermoclastism, despite their long consideration as a biodeteriorating agent. The bioprotection of biological crusts lasts after the death of organisms, as crusts of deposited substances remain. The role of biological crusts on soils has a different view, as their main role is binding soil particles. The disappearance of those crusts increases the release of dust, water run-off and reduces rain infiltration. Their loss can drive into a dismantlement of walls, as soils disaggregate. Any change in environmental conditions will modify growth conditions (light, water, temperature) and would determine the loss of biological crusts. Their disappearance would increase the risk of deterioration of the heritage and lead to aesthetical changes.

1 INTRODUCTION

Neolithic sites in the Mediterranean region have been largely identified; most of them refer to paintings in rock shelters and caves, while built structures are not so common. However, Maltese islands host a number of temples dated from 7000 years from present. Those sites are made in native limestone, composed of several chambers with grounds made on slabs or bare soil.

Stone heritage is subjected to weathering by atmospheric elements (rain, solar radiation, wind); additionally, organisms use those stones as substratum for their development. The colonization depends on several factors related to climatic parameters and also to the bioreceptivity of the substratum (Guillitte 1995, Prieto et al. 2006, Miller et al. 2012). The role of organisms growing on stone heritage has been controversial, most of the times considered a deteriorating agent (Seaward et al. 1989, Warscheid & Braams 2000, Lisci et al. 2003, St. Clair & Seaward 2004, Motti & Stinca 2011). However, recent studies have focused on the protective role that organisms, mainly biological crusts, have on stone heritage (Ariño et al. 1995, Souza-Egipsy et al. 2004, Concha-Lozano et al. 2012). Biological crusts are mainly composed by lichenized fungi, cyanobacteria, mosses and not lichenized fungi. The diversity and composition of those crusts are linked to the colonizing stage, which also conditions the deteriorating or protecting role of crusts.

Biological crusts growing on soils are an important element to bind soil particles (Belnap & Lange 2001), which reduce the release of dust and maintain the structure of walls and also affect the hydrology of the area. In addition, these communities enhance evapotranspiration.

Our aim was to study the biological crust growing on stones and soils and establish the bases for assessing changes due to alterations on environmental conditions, mainly by building shelters on Maltese temples to reduce weathering by atmospheric agents, such as rain, wind and solar radiation.

2 METHODS/APPROACH

The Neolithic temples studied are Ħaġar Qim and Mnajdra temples, located at the south coast of the island, and Tarxien temples, located within the city of Tarxien.

Biological crusts on stones were surveyed for all sorts of surfaces, horizontal and vertical. The main saxicolous communities were identified and three points for each community were selected to characterize the community and to use them as monitoring points for assessing future changes. The protocol to survey saxicolous communities followed Llop & Gómez-Bolea (2008).

Biological crusts on soils were examined in all the chambers and outer spaces of temples and the diversity of present species was annotated. The number of species belonging to main taxonomic groups (cyanobacteria, non lichenized fungi, lichenized fungi, hornworts, liverworts and mosses) was considered.

Data were analysed statistically by means of ordination for confirming the classification of inventories into the communities defined previously. The ordination was based in non-metric multidimensional scaling (NMS). Comparisons of main features characterizing the communities were carried on using non parametric methods (Kruskall-Wallis and Mann-Whitney tests).

3 RESULTS AND DISCUSSION

The biological crusts growing on native stones from the Maltese Neolithic temples can be differentiated into five communities. Two of them develop on horizontal surfaces and three are present on vertical surfaces. One of the communities from horizontal surfaces is characterized by the presence of species of *Caloplaca*, which lends a yellow to orange coloration to stones. The other community is defined by the blackish colour of *Verrucaria nigrescens*. The most common community in vertical surfaces is dominated by *Dirina massiliensis*, which gives a greyish tinge to stone surfaces. Less common are the communities of *Opegrapha calcarea* and the community of *Lecania spadicea*. The former is mainly composed by endolithic species, while the latter is dominated by the reddish brown thick thalli of *Lecania*.

The species richness is greater on horizontal surfaces than on vertical surfaces. Horizontal surfaces also gather a higher diversity, as showed by the Shannon index. However, there are no differences in terms of cover. When comparing communities, there are relevant differences between the community of *Opegrapha calcarea* and the other communities. The former holds the lower species richness and cover, with a greater percentage of endolithic species. This implies that the community of *Opegrapha calcarea* has a potential biodeteriorating role due to the pitting produced by endolithic thalli and reproductive structures (Warscheid & Braams 2000, Lombardozzi et al. 2012); despite the percentage of endolithic taxa is not negligible in all the communities. The remnant identified communities of biological crusts cover stone surfaces almost completely; additionally, thalli of these communities use to be thicker, yielding an important protection against weathering by physical agents. The protective role is obvious when comparing stones devoid of biological crusts with adjacent colonized stones (Fig. 1A, 1B). The protection yielded by biological crusts in Mediterranean heritage made on limestone has been highlighted by Concha-Lozano et al. (2012). Moreover, quite all the species integrating those biological crusts excrete calcium oxalate, which deposits below the thallus and in the uppermost layer of stone. This biogenic layer has a lower solubility than carbonate calcium and protects the stone even after the death of thalli (Ariño et al. 1995) (Fig. 1C).

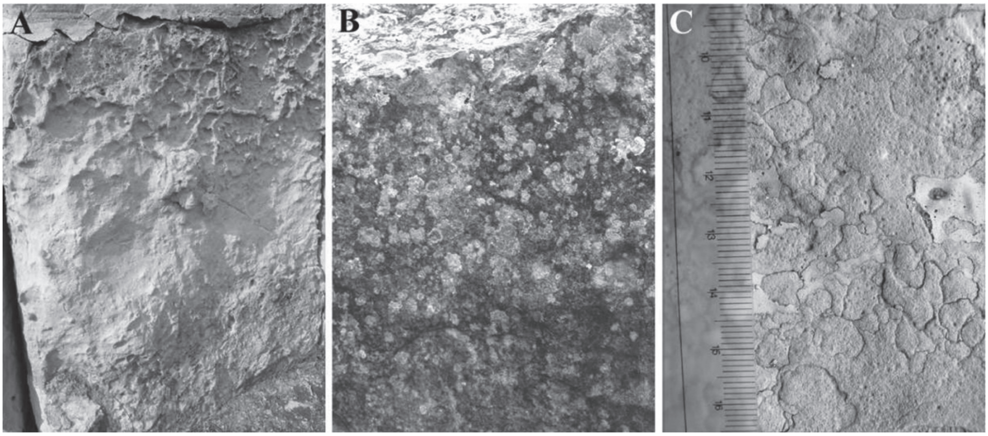

Figure 1. The protective role of biological crusts is important in Mediterranean limestone heritage. A) Vertical stones devoid of biological crusts are greatly affected by physical weathering. B) The presence of biological crusts protects stone surface, despite the changes in colour. C) The remains of dead thalli and the deposits of calcium oxalate prevent for weathering.

Biological crusts on soils are mainly composed by bryophytes, which includes hornworts, liverworts and mosses. There are also cyanobacteria and lichens and, occasionally, some fungi. They can be defined as rough crusts with no frost heaving; their surface roughness has a thickness of 1–3 cm (Belnap & Lange 2001). They occupy areas with low cover of vascular plants. We have focused on bryophytes, as main component of those biological crusts. The identified species of bryophytes have been distinguished into four main life strategies: perennial, colonists, annual shuttles and fugitives (During 1979, 1992). Colonists and annual shuttles are the most common life strategies. Annual shuttles correspond to hornworts, liverworts and mosses with a very short lifespan, less than one year. They appear predictably after seasonal rains and cover grounds and small cracks between stone slabs. Colonists are mainly mosses with a short lifespan, being annuals or pauciannuals, and most of them desiccation tolerant. They remain all over the year but they thrive more vigorously when water is abundantly available, then they sprout new shoots or develop reproductive structures. They provide water surface detention, increase net infiltration and reduce net runoff.

Changes on environmental conditions, such the building of shelters to protect the temples from physical weathering, greatly affect those biological crusts; consequently, severe alterations of crusts will take place driving to affectation in heritage. Several vital parameters will be affected, namely water and light. The reduction of those parameters will determine changes on biological crusts leading to the weakness of components and the growth of parasitic and saprotrophic organisms, which will use the available organic matter for their growth. Most of them are dematiaceous fungi and bacteria, and the main consequence will be the blackening of stone surfaces. Despite biological soil crusts can develop in low light intensity, the lack of rain will determine the complete disappearance of them with dramatic consequences on the sites. The life cycle of these communities require being completely flooded temporarily year after year. The disappearance of these crusts will lead to an unbinding of soil constituents; consequently, soils will be eroded and the mineral particles will move and lose. The release of mineral particles into an altered atmosphere, with a slowing of internal currents, could induce an increase in the deposition of dust on the walls of the temples.

Additionally to aesthetical alterations, the release of soil particles can affect the structure of temples. Most of the walls were built compacting stones and sand, the disaggregation of soil will lead to the loss of the binding agent and rock stability. In addition, there will be a gravimetric process where the soil particles will fall through the gaps of the wall stones.

4 CONCLUSIONS

Biological crusts on stones and soil have a protective role on Mediterranean heritage, which overpasses the deterioration produced by early stages of colonization. The disappearance of biological crusts would increase the risk of deterioration of the heritage and lead to aesthetical changes.

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The influence of substrate texture on early biological colonization

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ABSTRACT: Biological colonization of stone is a major concern in the preservation and presentation of cultural heritage. Colonization is typically associated with unpleasant soiling, and varying degrees of biodeterioration. A better understanding of why organisms grow where they do, will aid in developing preventative, and treatment methods for biosoiling of cultural heritage.

Sandstone exposure trials were set up at nine different locations across Northern Ireland to investigate the influences of local climate, local environmental, and micro-climatic factors on the early stages (up to 21 months) of biological colonization.

Results showed that, green and yellow soiling occurred on tooled stone surfaces, whereas darkening occurred preferentially on smooth surfaces.

It is likely that different populations of organisms occur on these surfaces with green algae occurring on tooled surfaces due to slower drying rates (i.e. prolonged moisture retention), and cyanobacteria and fungi thriving on smooth surfaces due to their ability to withstand moisture fluctuation.

1 INTRODUCTION

The bioreceptivity of a specific substrate will depend on a number of physical and structural variables, stone porosity, texture and capillarity will affect the ability of a group of micro-organisms to colonize it for several reasons. Primarily, texture or roughness gives pioneering organisms or their spores' cavities to settle in, making it less likely for them to be removed from the surface by wind or rain. Guillitte & Dreesen (1995) stated that bioreceptivity was controlled mainly by surface roughness, initial porosity and the mineralogical nature of the substrate. Tiano et al. (1995) determined the optimal growth conditions of a strain of green algae (*Pleurococcus*) and a strain of cyanobacteria (*Lyngbya*) under laboratory conditions, varying the substrate properties and pH, light intensity and temperature. They found that both types of microorganism had a positive correlation (>0.6) between growth and roughness and porosity values. Warscheid & Braams (2000) also note that uneven, porous surfaces are best for growth since they provide large surface areas and retain moisture. Again Viles (1988) and Pentecost (1992) in studies of Aldabra Atoll and Yorkshire, respectively, also found that substrate differences influenced colonization rates, with more porous substrates being colonized more rapidly. A more porous substrate will retain more water, further enhancing microbial growth and enabling a wider range of different organisms to inhabit it. "The porosity of the substrate is related to the penetration and retention of water, which, in turn, affects microbial colonization" (Crispim et al. 2003: 81). Surface texture is also an important factor in lichen colonization. Viles (1995: 28) commented that: "too hard and smooth a surface discourages lichen establishment; whereas on the other hand very friable surfaces do not provide any steady surface for colonization". McCabe (2007) observed that out of three different sandstone types used on Bonamargy Friary in Northern Ireland, the sandstones most negatively affected by the presence of lichens were more porous with a weaker bonding of matrix and quartz grains.

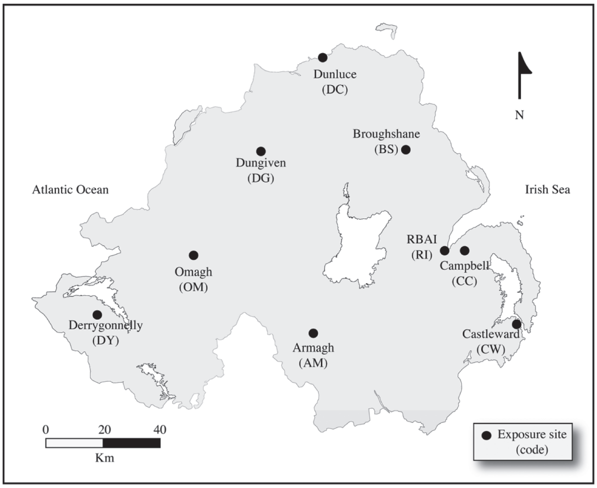

Figure 1. Map showing locations of the nine exposure trial sites within Northern Ireland.

2 MATERIALS AND METHODS

Nine identical exposure trial experiments were set up at sites with varying environmental conditions across Northern Ireland (Fig. 1). Four Peakmoor Sandstone blocks (15 cm wide) were cut at a 45° angle to represent buttress capstones on an historic building and were placed on the north-facing side of the exposure rack at each site. The left-hand side of each block was smooth (as cut); the right-hand side was tooled by hand.

The exposure trial ran for a total of 21-months, during which the four angled blocks were brought in at four main time periods: 9, 13, 17 and 21-months. After collection, the blocks were allowed to dry for 2–3 weeks before colorimetry measurements were taken (using a Konica-Minolta Chroma meter CR-410) on both the smooth and tooled sides of each block. Prieto et al. (2004) tested several methods and found that colorimetry provided a reliable estimate of biomass, with changes in color correlating closely with cyanobacterial cell aggregate numbers.

Testing of control blocks found that statistically there was no difference between L* measurements of the smooth and tooled sides of a fresh block. Texture did affect a* and b* readings, causing a significant shift toward the positive end of the axes in both cases. The average difference of 20 measurements was deducted from the textured readings to account for this discrepancy.

A brief on-site investigation of two exposed blocks (one a lower, and one a higher rainfall site) was carried out using a Surveymaster Protimeter to analyze difference in moisture content between the tooled and smooth sides of blocks, 28 readings were taken per block (14 each side).

3 RESULTS

3.1 *L* (dark to light)*

Table 1 shows considerable differences between darkening rates on the smooth versus tooled sides of blocks. The smooth sides of blocks are consistently darker than tooled. Paired t-tests found that for individual sites all but two were darker on the smooth sides, the other two sites showed no significant difference, and no sites had significant darkening on the tooled sides. When comparing time periods (9, 13, 17 and 21 months) all were statistically darker on the smooth side, as was the case for overall i.e. all sites and all time periods.

Table 1. Paired two-tailed t-test statistical results for L*a*b* colorimeter values.

	Analysis	L*	a*	b*
a)*	Total	0.E+0	5.57E-13	5.12E-10
b)*	Site BS	NS	0.001	2.99E-07
	Site DC	0.E+0	0.045	9.98E-09
	Site DG	4.77E-06	NS	NS
	Site OM	0.018	0.0096	0.004
	Site RI	0.021	0.00002	NS
	Site CC	0.00064	4.86E-06	NS
	Site DY	0.00001	NS	0.00002
	Site AM	0.047	NS	0.0082
	Site CW	NS	0.0001	0.00002
c)*	9 months	2.66454E-15	0.031	3.5E-06
	13 months	0.00427	1.01E-10	0.00009
	17 months	0.0056	0.00056	0.0008
	21 months	0.00039	0.0014	NS

* a) total (i.e. all sites and all time periods are compared df = 178) b) individual site comparisons (for all time periods, df = 18) and c) by time period (i.e. all sites for that time period df = 43). NS = no significant difference. For site codes see Fig. 1.

3.2 *a* (green to red)*

In the case of individual sites; six showed more significant greening on the tooled side and three showed no significant difference. There was a significant shift towards the negative (green) end of the a* axis when all sites were combined, and when compared by time period.

3.3 *b* (blue to yellow)*

In total there was a significant difference between b* values of smooth and tooled block sides, with a greater shift towards the yellow end of the scale on the tooled halves. This was also the case for six out of nine sites, and all but the 21-month time period.

3.4 *Moisture levels*

Protimeter results showed that for the two sites combined (df = 52), and at the wetter site (df = 24) there was no significant difference (paired two-tailed t-test) in moisture levels between sides. However at the drier site moisture levels were significantly higher on the tooled side (df = 24).

4 DISCUSSION

The fact that the comparable surfaces i.e. tooled or smooth were not only adjacent blocks of the same stone type, but were two halves of the same block essentially excluded any environmental differences and inter-block mineralogical variations. Therefore the sole difference between the two surfaces was texture.

The a* and b* results observed in this experiment coincided with the biological soiling patterns commonly reported in the literature i.e. that soiling occurs preferentially on textured surfaces. In contrast to this, the L* (i.e. dark to light) results showed lower (i.e. darker) readings on the smooth sides of blocks.

The shifts towards the green and yellow ends of the a* and b* axes (respectively) observed are likely to be attributed almost entirely to biological growth i.e. primarily green algae, the yellow and green representing the presence of chlorophyll a (green), and b (yellow).

The 'darkening' of blocks may be attributable to both biological and non-biological soiling. However non-biological particulate matter would still be expected to gather preferentially on the textured surface from which it would be more difficult to dislodge with precipitation run-off.

In terms of moisture, the wettest exposure site in Northern Ireland (BS) received a total of 2826 mm over the 21-month period; the driest (AM) received 1522 mm (data from MET weather stations near exposure sites). The wetter exposure sites may rarely get a chance to fully dry out before the next rainfall event, this persistent wetting may explain there being no significant difference in moisture readings at the 'wet' site. At the drier site however the smooth surface will dry much more rapidly than the tooled, effectively making the smooth side a more 'exposed' and challenging environment more suited to cyanobacteria and fungi.

The shift towards the dark end of the L* axis on the smooth side of blocks may therefore be due to preferential cyanobacterial and fungal growth on the smooth sides of blocks. The cyanobacteria are a diverse group, with many aeroterrestrial species possessing UV-protectant pigments (such as phycocyanin) and protective sheaths, allowing them to survive high UV levels and repeated wetting-drying cycles. It is for these reasons that Crispim & Gaylarde (2005: 2) stated that cyanobacteria were "particularly important on exposed surfaces". Many fungi are also equipped for these conditions, producing melanin (often responsible for the black staining related to fungi) to combat excess UV radiation (Saiz-Jimenez 1995). The slower drying rate on the tooled surface may also result in reduced temperatures on tooled surfaces. Caneva et al. (2008) state that the thermal optimum for cyanobacteria is 25–35 °C, rather than 20–30 °C for algae.

5 CONCLUSIONS

This study represents only the earliest stages of biological colonization and these patterns may well change over time, once pioneering organisms have become more established, stabilizing the environment. It appears that during this initial colonization phase (at least in a temperate climate); a textured surface may be a more suitable ecological niche for green algae, whereas an exposed, smooth surface may be a more appropriate habitat for cyanobacteria and fungi.

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Science and Technology for the Conservation of Cultural Heritage –
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A methodological approach to evaluate shelter effectiveness for the conservation of archaeological sites

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ABSTRACT: Shelters are structures built over archaeological sites in order to retard deterioration; however, some shelters negatively affect the remains they were meant to preserve. A method to evaluate shelter effectiveness has been developed based on monitoring decay and soiling processes on limestone sensors situated both inside and outside a case study shelter. This approach provides important benefits, including: 1) these samples can be analysed with both destructive and non-destructive testing methods, 2) they can be placed in different environments and sites to obtain information about common weathering processes, and 3) easily weathered materials can provide information within a short exposure period. This methodology could be applied extensively at different exposed archaeological sites by heritage professionals in order to support their decisions regarding shelters over limestone remains.

1 INTRODUCTION

Shelters, or covers for archaeological sites, might be a suitable preservation strategy which could provide effective protection for stone remains. Open shelters made of light-weight membranes are increasingly being proposed as medium-term preventive conservation methods due to advantages such as their minimal impact on the archaeological substrates (Rosina et al., 2011). While enclosed shelters have been more popular in Britain, open shelters have been used extensively in the Mediterranean region. One of the main reasons for this was the belief that open shelters were only suitable for drier climates (Ferroni & Laurenti 2006). However, some shelters negatively affect the remains they were meant to preserve (Stewart et al., 2006). Therefore, research is needed in order to establish scientific evidences on their impact on archaeological sites. In addition, bioclastic limestone has been widely used in built heritage. It is a heterogeneous limestone, less crystalline and dense than others and also prone to salt weathering (Smith et al., 2010). This study is part of a wider doctoral project which aims to provide a scientific assessment of the effect of lightweight, open shelters on bioclastic limestone deterioration rates and processes at archaeological sites in the Mediterranean basin and the United Kingdom.

2 THE BISHOP OF WINCHESTER'S PALACE IN WITNEY, UK

2.1 *Introduction to the case study*

Shortly after the excavation of the medieval palace in Witney (Oxfordshire) in 1984, the oolitic Cotswold limestone began to erode and salt efflorescences appeared on the stone surfaces (Historic Buildings and Monuments Commission for England 1988). The majority of the remains were then buried but the most significant elements, including the solar tower, were sheltered in 1991 with a polytetrafluoroethylene (PTFE) and glassfibre fabric open shelter (Fig. 1).

Figure 1. View of the Bishop's Palace archaeological site from the West.

The main reason was to reduce frost and extreme temperatures and minimize water ingress while providing display for visitors.

2.2 *Preservation state surveys*

As part of this project, an initial survey was carried out in the site in order to identify decay mechanisms. This included a visual assessment of the condition state of the remains, analysis of some decay products such as salt efflorescences and crusts, and a more in-depth study of some blocks in the site. In addition, a qualitative survey of the shelter condition was undertaken to understand how the shelter could contribute to the site deterioration (Stewart 2008).

3 PROPOSED METHODOLOGY

A reliable method to obtain information on the effects of a shelter is to monitor in a quantitative way both the environmental parameters and the change in chemical and physical properties in stone sensors inside and outside the shelter.

In order to understand how shelters reduce environmental events causing stone decay such as temperature extremes, freeze-thaw cycles, relative humidity fluctuations, and wetting events, environmental parameters are being monitored both inside and outside the Bishop's Palace shelter in this study (Fig. 2). Temperature and relative humidity are being recorded through hygrochron iButton® loggers (DS1923, Maxim Integrated Products, range = –20°C to +85°C and 0 to 100% RH, accuracy = ±0.5 °C and ±5% RH). These sensors have been placed over the surface of stone samples, in the shelter itself and outside. The surface wetness is measured with electrical impedance grids (TGP-0903, Tinytag leaf wetness logger, reading range = 0 to 100%, accuracy = ±2%). These loggers have been placed inside and outside the shelter in a horizontal position to simulate time of wetness on horizontal stone surfaces. In addition, data regarding the amount of rainfall and wind speed and direction is obtained through a nearby meteorological station in Minster Lovell, located less than 3 miles from the site.

Limestone blocks of different expected durability have been used as soiling and decay sensors. Cotswold cream limestone is a heterogeneous local oolitic limestone very similar to the one used for the construction of the Bishop's Palace. Portland limestone is a widely researched bioclastic limestone more dense than the Cotswold limestone. In addition, a particularly vulnerable chalk

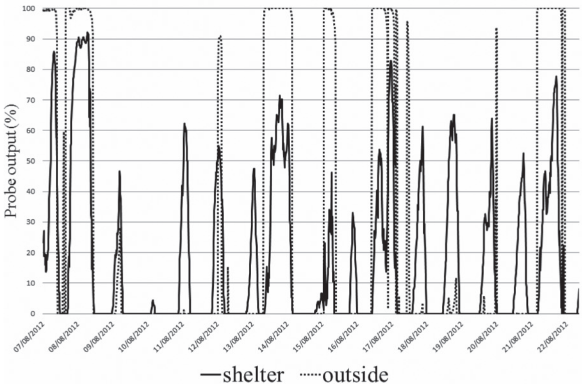

Figure 2. Surface wetness beneath and outside the shelter from the 07/08/2012 to the 22/08/12 (left) and soiling and decay stone sensors placed beneath the Bishop's Palace shelter (right).

Table 1. Physical properties of the stone used as soiling and decay sensors.

Standard test*	Property	Portland limestone	Cotswold limestone	Chalk
BS EN 3755:2008	Water absorption (A_b)	6.96%	12.52%	18.51%
BS EN 1936:2006	Open porosity (P_o)	14.46%	22.02%	31.17%
BS EN 1936:2006	Apparent density (ρ_b)	2100 Kg/m^3	2375 Kg/m^3	1773 Kg/m^3

* Tests were carried out at the Oxford University Rock Breakdown Laboratory.

has also been used in this study (Table 1). Four replicas of each stone type have been placed at four positions, selected after the preservation state survey of the remains: on the periphery of the site just under the shelter; over the walls (South-East and North-West side) where wind driven rain and shelter coverage could affect the conservation of the remains; beneath the centre of the shelter; and outside the shelter.

The extent to which the lightweight open shelter affects soiling and decay rates of the sensors is quantified through changes in flexural strength (Grindosonic MK5), dry weight changes, changes in hardness (Proceq Equotip 3), surface changes at a microscopic level (optical microscope), increase in the size of cracks and pores (Proceq Pundit Lab) and colour changes (Minolta CM-700d spectrophotometer).

This field-based study will be complemented with weathering experiments in the laboratory, a case study in the Mediterranean region and a modeling of deterioration rates based on the International Co-operative Programme on the effects of long-range transboundary air pollution on cultural heritage materials.

4 PRELIMINARY RESULTS FROM THE BISHOP'S PALACE CASE STUDY

The microclimate beneath the open shelter follows the external patterns. The temperature fluctuations are less extreme inside than outside the shelter. However, there is some unpredictability in the time that the stone remains wet under the shelter (Fig. 2). The lower levels of ventilation or the effect of condensation could be the main reasons. These could then be considered as effects of the shelter performance.

In addition, some changes in the surface colour of the Cotswold and Portland limestone samples have been recorded after just 20 days of exposure. On average, the samples placed underneath the shelter became darker, more saturated and yellower and the ones placed outside the shelter, slightly lighter, less saturated and less yellow. This can be seen as being due to the effects of air quality and deposition rate. The samples that are outside are exposed to direct rain and thus the washing of the surface.

5 OUTCOMES OF THE RESEARCH

Carefully chosen and monitored stone samples used as sensors of decay and soiling can provide a cost-effective and efficient methodology that can be applied at different sites covered with lightweight open shelters.

This approach provides important benefits. Comparisons are allowed because the same materials for the soiling and decay sensors could be used in both inside/outside environments and at different sites. These small samples will also provide an "early warning" method in relation to more intensive monitoring of the ruins. Although similar type of limestone could also be used in order to compare the results with the original stone at the site, easily weathered materials such as chalk can provide more information within a short exposure period. In contrast to the stones that make up the site, these samples could be analysed with both destructive and non-destructive testing techniques which could indicate decay before any visible signs become apparent through changes in parameters such as strength and hardness.

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Science and Technology for the Conservation of Cultural Heritage –
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Risks of atmospheric aerosol for cultural heritage assets in Granada (Spain)

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ABSTRACT: Assessment of atmospheric environmental risks related to tangible cultural heritage assets (CHas), in the context of their preventive conservation, is a key strategy to safeguard them. Here we summarize the results of atmospheric aerosol composition and its impact on Granada CHas. Investigations performed were: i) indoor and outdoor air pollutants identification and their effects on artworks used in closed and semi-open monuments, ii) field exposure tests to determine black soiling of limestones, and iii) *ad hoc* laboratory sea-salt ageing tests to learn about interactions between marine aerosols and carbonate stones with different surface finishes. Valuable information is provided and discussed about levels of atmospheric gaseous pollutants as well as chemical and mineralogical composition, size, and morphology of particulate matter, their concentration, trends, major sources and threats to artwork.

1 INTRODUCTION

Preventive conservation is a popular approach in terms of safeguarding our CHas and reducing the cost of future conservation actions (Brimblecombe 2005). It involves typifying historical assets, monitoring their microclimatic exposure conditions, and analyzing the interactions at the object-air (gases and particulate matter) interface. The major causes of damage on CHas in European cities are urban air pollution, climate change and socio-economic pressures. Thus, it is essential to identify atmospheric pollutants to ensure sustainable conservation of CHas in urban contexts, which requires a cross-cutting approach combining environmental research, restorers/conservators and local policies, to predict environmental damage risks to CHas.

Most monuments are placed in urban areas where pollution represents risk for outdoor/indoor constructions/decorative materials. Black crusts, material de-cohesion and dust deposition often occur on building exteriors causing aesthetic effects. Inside monuments, soiling and physi-chemical weathering of CHas can occur due to indoor/outdoor phenomena. The literature mainly deals with well protected, closed buildings, rather than semi-open monuments. Stone decay in polluted urban atmospheres is still a major problem even though acidic pollutant levels have decreased since the early 1990s. Currently black crust development and black soiling processes are tackled combining observations of weathered construction materials with *ad hoc* experiments under controlled laboratory conditions. However, extrapolation to natural conditions is not straightforward and leads to uncertainties in the estimation of decay rates, which are an important issue in CHas sustainability. Thus, much research has focused on field tests to address long-term sustainability of architectural materials. Further research has been performed to develop robust fitting parameters for larger datasets to improve dose–response functions which are appropriate for long-term predictions of soiling. Although essential for designing conservation policies of vulnerable CHas, these kinds of studies are still limited to few places around Europe.

In this context we performed two types of field measurements: a) indoor and outdoor air quality was assessed in the Alhambra and San Jerónimo monastery to identify atmospheric pollutant risks to their conservation, and b) an ageing test was performed on limestone under different urban conditions to assess its cultural heritage sustainability with respect to the black soiling process. Additionally, an *ad hoc* laboratory sea-salt ageing test was performed to study interactions between marine aerosols and carbonate stones with different surface finishes. In this work we present a short overview of these on-going investigations.

2 ENVIRONMENT AND ANALYTICAL TECHNIQUES

Granada (S Spain) is a non-industrialized medium-sized city situated in a natural basin surrounded by mountains (up to 3450 m). Due to this topography and frequent low wind speeds, in combination with traffic emissions, pollution-derived particulate matter often accumulates in its urban air. It is ~50 km of the Mediterranean Sea and ~200 km of the African continent. The region has a near-continental climate with cool/wet winters, hot summers and high diurnal temperature variability. Most rainfall occurs during winter and spring seasons leading to re-suspension of dust particles (dry seasons). When the wind direction is S and SW (prevailing wind directions) marine particles can be expected. Additionally meteorological conditions in spring and summer favor the arrival of Saharan and Sahel air masses.

Complementary analytical techniques were applied on atmospheric pollutants to determine their chemical and mineralogical composition, size and morphology (particulate matter), concentrations, trends, sources and threats to artwork: ion chromatography (IC) and UV-Vis spectrophotometry for analyzing gases (NO_2, SO_2, NH_3, O_3), and electron probe microanalysis (EPMA), scanning electron microscopy with energy-dispersive X-ray analyzer (SEM-EDX), transmission electron microscopy (TEM), X-ray Fluorescence (XRF), X-ray diffraction (XRD), Raman microscopy (RM) and the tandem technique EPMA-RM for characterizing bulk and single particles and black carbon (BC). Lightness and chroma changes using spectrophotometry was used to establish the soiling process on tested limestones under urban conditions and chromatic alterations of travertines and limestones subjected to a sea-salt ageing test. Salt weathering of stones was checked using Fourier transform-infrared spectroscopy (T-FTIR), optical microscopy (OM), environmental scanning microscope (ESEM), mercury intrusion porosimetry (MIP) and gas sorption isotherms (BET). During sampling campaigns in monuments, microclimatic parameters (T and RH) and daily meteorological conditions were registered.

3 INDOOR/OUTDOOR POLLUTANTS IMPACTING SAN JERÓNIMO MONASTERY

The monastery of San Jerónimo (MSJ) is located in the city of Granada, surrounded by busy streets. The interior of its church is covered with polychromes. Some of the stained glass windows are broken and the main entrance remains open during visiting hours, facilitating indoor/outdoor air exchange. The nature and origin of indoor/outdoor atmospheric aerosols (winter 2008) and the damage caused to artworks inside MSJ were assessed, as well as PM_{10} samples taken from the Andalusian Centre for Environmental Studies (CEAMA, Granada) (Kontozova-Deutsch et al., 2010). Results revealed that outdoor aerosols are related to the geographical characteristics and climate of the city. Severe day/night temperature fluctuations contribute to soil dust generation. Moreover, the basin-like shape of Granada surrounded by high mountains, in combination with heavy traffic, enhances soot particles accumulation, and marine particles can be expected with S and SW wind direction. Abundant soil dust particles and BC particles (~9%) were detected outside MSJ. Other particles such as $(NH_4)_2SO_4$ clustered with C, and Fe/Mn oxides plus S–Cl rich particles, and minor amounts of Br and Fe-rich rounded particles (related to traffic) were found. Salt aerosols (chloride, sulfate and ammonium-rich salts) and aggregates of both amorphous C and SiO_2 particles were also identified. Inside the church, NO_2 and SO_2 levels were high, implying indoor/outdoor air exchange. SO_2 concentration was higher than in other churches and NO_2 values surpasses the European Community limits suggested for museums (~30 μg m^{-3})(Watt et al., 2009). High levels of S, Pb, and chloride- and sulfate-rich aerosols inside MSJ indicated that the source of these particles was related to the intense decay of the construction/decorative materials, and to the copious salts found inside the church. Chemical reactions between Fe-rich pigments from paintings and chloride-rich salts were identified via the recognition of Fe-chloride particles. All of these particles promote a feedback process that triggers further weathering of the indoor materials. Moreover, although stable indoor microclimatic conditions were registered, inappropriate cleaning habits foster the re-suspension of particles which play a key role in the darkening of distant and isolated places inside the church.

4 AIRBORNE PARTICLES AT THE ALHAMBRA MONUMENT

Traditional access to the Alhambra from the city center of Granada was via Cuesta Gomérez passing through the Pomegranates Gate and the Alhambra park. Due to the decay of this Gate, a restoration program was launched (2007–2010) and this access was closed to traffic. During this time-span, air-quality research was solicited by the Alhambra Patronage. Atmospheric aerosols were analyzed in Cuesta Gomérez and the Alhambra and compared with those measured in Cuesta del Chapiz, a busy traffic access to the Albayzín also on a steep slope. Sampling campaigns (summer 2009–winter 2010) were conducted in the Alhambra at three locations based on their architectural characteristics, plus an outdoor reference (Horemans et al., 2011). The rooms of the Alhambra palaces consist of high, arch-like entries and many opened windows. Thus, indoor PM_1 and PM_{10-1} particles levels were fairly high and followed the variations in the outdoor air quality. The main PM_1 components were BC and secondary inorganic aerosols (ammonium sulfates and nitrates), mainly from vehicular traffic. Heavy metals originate from diesel exhaust (V and Ni) and tire tread emissions (Cu, Cr, Pb and Zn). PM_{10-1} particles were mostly made of soil dust, rich in calcite, dolomite and silicates (from surrounding geological materials) and with large amounts of NaCl, and Na-sulfates and nitrates (aged sea salts), mainly $NaNO_3$ (Potgieter-Vermaak et al., 2012). Ratios of typical mineral elements (Ti/Fe and Si/Fe) showed that North Saharan dust events contributed to the mineral aerosol content in summer. Summer cultural events are responsible for the re-suspension of local soil dust, increasing PM_{10-1} levels around the palaces. The high summer O_3 levels (up to 229 ± 7 μg m^{-3}) indicated dense smog conditions. BC levels at Cuesta Gomérez were comparable to those found inside the Alhambra palaces (0–15 μg m^{-3}). At the Albayzín, BC levels were extremely high, ranging from 2 to 35 μg m^{-3} (average ~8 μg m^{-3}). Although traffic is minimized in the Alhambra vicinity, BC levels are only slightly lower compared to other urban environments, e.g. Antwerp (Belgium). Opening the Pomegranates Gate for traffic could have serious implications for the BC levels and other traffic-related pollutants (blackening and decay of historic materials) inside the Alhambra monument and threaten their future conservation.

5 BLACK SOILING OF AN ARCHITECTURAL LIMESTONE DURING TWO-YEAR TERM EXPOSURE TO URBAN AIR IN GRANADA

The *Escúzar* limestone quarried near Granada city was selected for this study. The final goal was to evaluate its Cultural Heritage suitability to replace similar historic limestones in Andalusia, and its durability in present civil buildings (Urosevic et al., 2011a). It is texturally very heterogeneous, highly porous (29 ± 8%) and scarcely cemented (sparitic and micritic calcitic cement, i.e. crystal sizes >10 μm and <4 μm respectively). Stone tablets were placed vertically at four urban sites in Granada with contrasting local pollution micro-environments and exposure conditions. The back (rain-sheltered) and the front (exposed) faces of the stone tablets were studied for each site. Atmospheric particles deposited on the stone surfaces and on PM_{10}

filters were studied. Results revealed that BC and soil dust particles were the most abundant particles in the Granada air, intensifying the stone darkening. After the first year of exposure, gypsum crusts developed on all stone faces in all test sites except the least polluted one. Calculated total soiling showed stone black soiling in all sites, though mainly at the most polluted areas and on exposed stone faces. Indeed, surface roughness on the front faces was higher (due to the more intense rain wash-out), fostering more intense differential erosion between micritic and sparitic calcite areas, which in turn promotes a feedback process that triggers further black soiling. The soiling coefficient based on estimated BC values (SC_t) for the front stone faces ranged from 8.0 to 9.9×10^{-3} days$^{-1/2}$ μg$^{-1/2}$ m$^{3/2}$. After two years, almost all stones surpassed the 2% EAC value (effective area coverage or stone area percentage covered by black particles) considered to be the limit perceptible for the human eye (1.7 to 20.4%).

6 ROUGH AND POLISHED TRAVERTINE AND COMPACT DOLOMITE-RICH LIMESTONE DECAY EVALUATED BY A MARINE AEROSOL AGEING TEST

This work explores the potentially contrasting stone decay behavior due to different commercial surface finishings. Rough and polished stone surfaces behave differently according to salt-spray absorption, newly formed pore networks, composition and habits of salts, and chromatic changes. The polished travertine (*Olivillo*, quarried in Almería, Andalusia) surface, combined with a gypsum-rich plaster and an epoxy silicone resin infilling, helps to protect it against salt decay since this finish blocks the pore system in the near-surface stone. On rough surfaces, salt crystallization is more abundant and induces larger open porosity than in polished stones, which in turn makes it more vulnerable to further salt spray attack (Urosevic et al., 2010).

In the compact and homogeneous dolomite-rich limestone (*Sierra Elvira*, quarried in Granada, Andalusia) no stone detachments occurred, irrespective of their surface finish (Urosevic 2011). This is attributed to its interlocking crystalline texture that prevents intensive salt weathering. However a binding effect and coeval micro -fissure opening were found in the smallest pores. Salts precipitated as crusts in both rough and polished limestones, but with different compositions and morphologies. Thus, the stone surface finish strongly controls salt-spray absorption and salt crystallization onto the stone surfaces. At the microscopic level dissolution patterns (micropitting) were found in calcite crystals unlike dolomite crystals, largely in polished stones, revealing that dolomite-rich carbonate stones are less prone to salt decay. Moreover, results clearly indicate that dissolution processes are modified by polishing treatments of limestone surfaces. In both works polished stones become brighter and lose their valued warm tonality, since chromatic parameters displaced toward more blue and green values. Thus, salt cleaning interventions based on mechanical removal of efflorescences are not advisable.

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Microclimatic and Ground-Penetrating Radar surveys for damage diagnosis. The case of the Crypt of the Duomo of Lecce (Italy)

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ABSTRACT: The presence of particular environmental conditions inside monumental buildings is responsible for deterioration processes. The Crypt (1114) of the Duomo in the city centre of Lecce (South-Italy) is a valuable monument with many artworks in the interior, affected by salt damage on the masonry and columns. In order to provide a diagnosis of the damages, a microclimatic assessment and documentation were performed using various techniques. Here we focus on the results of a microclimatic monitoring combined with a decay mapping and Ground-Penetrating Radar (GPR) observations. The aim is to highlight the conditions that allow crystal growth and the presence of moisture sources in the subsoil, involved in the salt damage. In such a manner an explanation for crystallization and its variation over time is given.

1 THE CRYPT OF THE DUOMO OF LECCE

The Crypt (Fig. 1) of the Duomo of Lecce (South Italy) is a monument significant not only for its early date (1114), but also for the valuable frescos, oil paintings and sculptures in the interior. Deterioration in the Crypt mainly consists of salt efflorescences, stone pulverization, flaking paint layers of canvas, plaster crumbling and detachment. In particular, *in situ* observations highlighted two important periods for salt crystallization on the masonry. Then various surveys were performed in order to get a diagnosis. Here we focus on the microclimatic monitoring combined with a decay mapping and GPR observations. In such a manner the conditions for crystal growth are identified and an explanation for the salt damage over time is given.

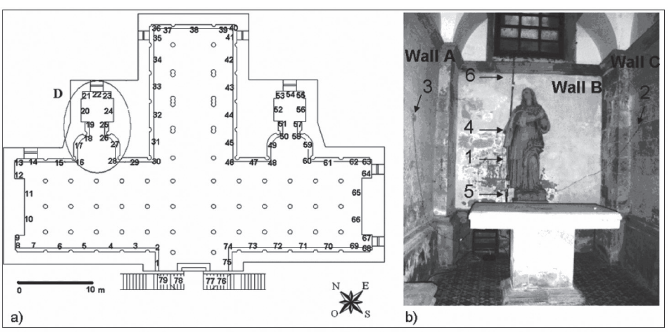

Figure 1. a) The map of the Crypt with the measurement points, b) the instrumentation in the D area.

2 MATERIALS AND METHODS

From November 2008 to December 2009 the main indoor and outdoor climatic parameters were measured both in continuous mode and on a grid of 54 points inside the Crypt by a TECNOEL psychrometer (accuracy 0.1 °C), as well as other measurements of indoor air temperature/relative humidity on 79 points, along the perimeter (Fig. 1a). The apse on the left North side of the Crypt (label D in Fig. 1a) was chosen to measure the presence of salt efflorescences and the related conditions. We observed here the most significant daily/seasonal variations. Surface temperature (Ts) probes were installed on the walls (1, 2 and 3 in Fig. 1b). Air temperature (T), relative humidity (RH) and dew point were also measured along a vertical line at 1, 2 and 3 m from the floor (4, 5 and 6 in Fig. 1b).

In the period November 2008–March 2010, the principal salt-affected areas were periodically documented by photos, then processed, by using image analysis tools such as Gimp and AutoCad.

The GPR surveys were carried out with a Sir-3000 georadar using a 270 MHz (centre frequency) antenna, by using acquisition parameters given in Cataldo et al. (2012). The centre antenna frequency was chosen in relation to the features of the investigated area (i.e. penetration depth and resolution ratio), with the aims of localizing potential sources of moisture, involved in the damage.

3 RESULTS

Figure 2 shows the indoor and outdoor T and RH values in the period November 2008–December 2009. In general the indoor Crypt microclimate seems affected by the outdoor conditions, especially regarding the thermal variations. Air temperatures were between 8 °C and 25 °C during that period, with the most significant variations in the period May–August. Relative humidity was between 66–81%, with the most significant variation between February and April. A typical spatial distribution of indoor T and RH shows that the north apse and the main nave of the Crypt the most significant T and RH variations occurred.

Focusing on salt efflorescences on the D area (Fig. 1a), diffusion was greater than 20% between November 2008–January 2009 (Fig. 3a) and between November 2009–March 2010 (Fig. 3d). A decrease was observed between February 2009–May 2009 (Fig. 3b) while the period characterized by the lowest diffusion was from June 2009–October 2009 (until 15%, Fig. 3c).

During the monitoring period surface condensation events were not recorded. Between June and October efflorescence appears to diminish, as surface temperature increases (about 21 °C and RH 77% in average).

Salts crystallization was more evident instead between November 2008–January 2009 (about 16 °C T and RH 73% in average) and November 2009–December 2009 (about 14 °C T and RH

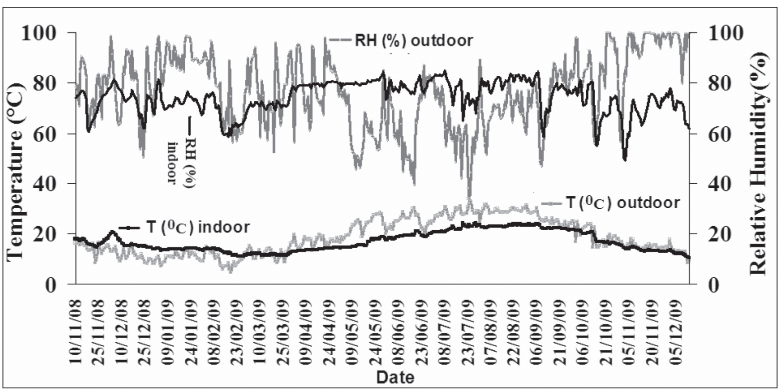

Figure 2. Indoor and outdoor temperature and relative humidity during the monitoring period.

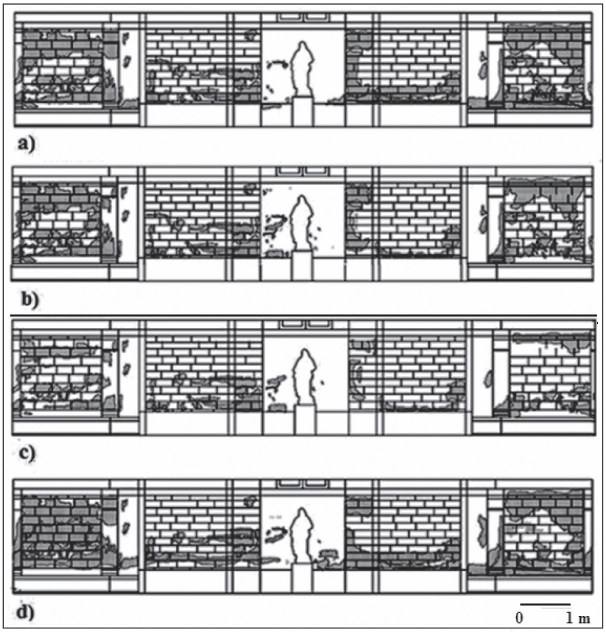

Figure 3. Salt efflorescences recorded in the period November 2008–March 2010.

70% in average). We observed that over 10 °C of T and 7% of RH variations occurred during November 2008–March 2010.

We assessed also that the relative abundance of salt efflorescence was closely associated with the salt content of the underlying plaster. Moreover water content measurements on the collected salt samples highlighted almost homogeneous values, independently on the depth and the sampling period.

In order to evaluate volumetric water content (VWC), resorting the empirical Topp formula (Topp et al. 1980), an estimation of Electro Magnetic (EM)-wave velocity of GPR data was needed. For this purpose, we used a very common method based on phenomenon that a small object (in comparison to dominant wavelength) reflects EM-waves in almost every direction.

In the data set, several diffractions hyperbola caused by stones and small objects are present (Cataldo et al. 2012), so the EM-wave velocity was determined from the point-source reflections. VWC determined from velocity obtained by this method has not often been used, because it provides only average soil water content to the depth of the point-source reflector and, therefore, user has no control over depth resolution. But in all radar sections acquired in the Crypt, any interface with changes in EM-wave velocities between the surface and the target depth level is recorded, as well as the errors involved.

We assessed that the differences in the values obtained estimating EM-wave velocity by using this method, instead of the interval velocity method, is less than 1%. So we obtained an almost accurate estimation of the subsoil volumetric water content in the Crypt: it varies from about 13% to 32% (Fig. 4b).

The amplitude spectrum analysis, done on the GPR signal windowed around 1 m depth, has shown that the meaningful spectrum was confined between 100 and 400 MHz band with a peak frequency of about 200 MHz. Comparing the map on the volumetric water content with the slice corresponding to the frequency 200 MHz (Fig. 4a), in areas with high EM energy attenuation volumetric water content is higher, i.e. along the lateral apses and the main nave. This situation is almost similar to that observed for the spatial RH distribution.

This scenario describes a situation in which salt efflorescences are due both to rain water absorbed on the walls, and from rising damp which is fed by the subsoil, especially on the columns. When rain water is absorbed, it dissolves the $CaCO_3$ of the limestone, a local soft

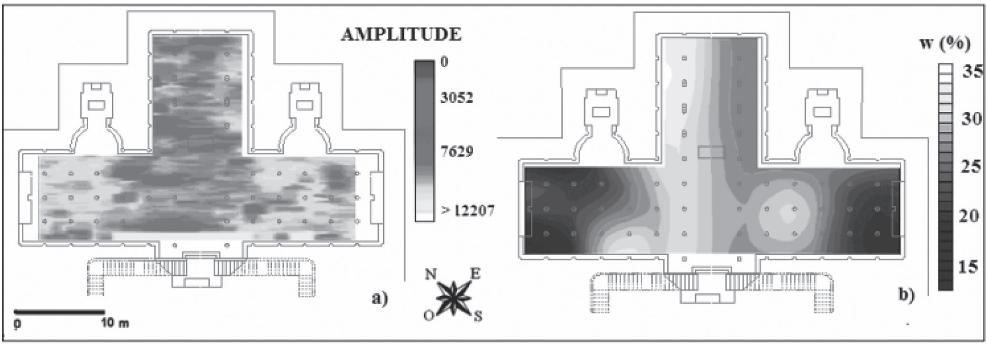

Figure 4. a) The slice corresponding to 200 MHz, b) the map of the volumetric water content (w).

bioclastic limestone ("pietra leccese") with high porosity, and salts deposit on its surface over time. During late spring, summer and autumn salt solution migrates within the pore system, but does not precipitate. The solution reaches saturation and begins to crystallize visibly when surface temperature is about 12 °C, or below. As water percolates through stones, it accumulates niter that originated from the subsoil, as assessed by chemical analysis not discussed in this paper. This origin could be attributed to organic matter on which the Crypt was built, it was used in fact as a burial place since the 1st until 19th century AD (Cataldo et al. 2012). Also probably farmland was not completely cleared prior to the construction.

4 CONCLUSIONS

The microclimatic conditions and the presence of sources of moisture in the subsoil of the Crypt of the Duomo of Lecce enhance salt crystallization. We observe crystallization for RH about 70%, in agreement with theoretical and experimental data for salt mixtures in the literature. However, many study cases show an increase/decrease of crystallization when temperature increases/decreases (Arnold & Zehnder 1991, Laue 2005, Sawdy & Price 2005). In our case, instead, it seems that a cyclic increase/decrease of salt efflorescence (Fig. 3) happens when temperature decreases/increases. This suggests that the relationship is more complicated to relate than expected. We aim to use more robust statistical tools and to study the spatial distribution of the moisture content in the masonry (Cataldo et al. 2009) to assess more precisely the entity of phenomenon, especially in short periods.

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

Entry and dispersion of microorganisms inside Altamira Cave: New evidences from aerobiological and atmospheric gases surveys

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ABSTRACT: Altamira Cave, a UNESCO World Heritage Site, houses one of the world's most prominent Palaeolithic rock art. The conservation of the rock art is threatened by microorganisms (bacteria and recently fungi). Previous studies revealed that the entry and dispersion of microorganisms and nutrients to the interior of the cave depends on the exchange rates between the cave atmosphere and the exterior through the entrance. Nevertheless, the data obtained in an aerobiological study combined with a multiparametric survey of atmospheric gases have shown that there is another possible entry and spread of microorganisms in the innermost area of the cave (the Well Hall), far from the single and most elevated entrance.

1 INTRODUCTION

Altamira (Cantabria, northern Spain) is a well-studied cave that houses one of the world's most prominent Palaeolithic rock art (Saiz-Jimenez et al., 2011). The cavity (270 m in length) is situated on a topographical hill (152 m a.s.l.) and has a depth of 3–22 m (average 8 m) below the surface. The cavity has a single entrance in topographically higher position, and includes a number of main halls having a downward trend from the outside access to the deepest part of the cave (Fig. 1). At present, the cave is permanently closed to visitors. The main entrance is closed by a metal gate (slotted surface <4%; thermally insulated) acting as the initial barrier to stop the exchange of matter with the outside. In addition a second door isolates the Kitchen Hall of the Crossing and the rest of the cavity (mainly the Polychrome Hall and Walls Hall).

Previous studies revealed that entry and dispersion of microbes (and nutrients) to the interior of the Altamira Cave depends on the exchange rates between the cave atmosphere and the exterior through the entrance (Cuezva et al. 2009, Saiz-Jimenez et al., 2011). These exchange rates are higher during the summer season (Cuezva et al., 2011). However, knowledge of other possible entries of microorganisms (and nutrients) is essential in order to ensure the conservation of rock art.

Here, we use a double analytical approach. First, a multiparametric survey of atmospheric gases developed for determining the spatial distribution of carrier (CO_2) and trace (CH_4) gases and the isotopic signal of CO_2 ($\delta^{13}C$). Secondly, an aerobiological study conducted to quantify the concentration and diversity of airborne microorganisms and their spatial distribution.

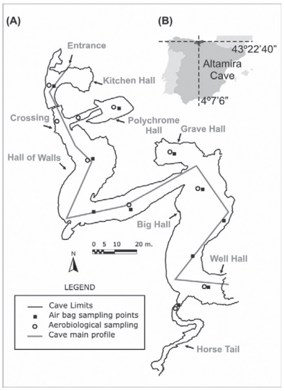

Figure 1. (A) Altamira Cave map with location of the aerobiological and atmospheric gases sampling points inside the cavity. (B) Geographic location of the cave.

2 MATERIAL AND METHODS

Cave air conditions are influenced by interaction processes with the outer atmosphere. In order to characterize cave levels of CO_2, $\delta^{13}CO_2$ and CH_4 certain number of air samples were taken along the cave covering the whole inner space in July 2012 (Fig. 1).

Samples were obtained by filling Tedlar air sampling bags with capacity of 1 L. Air is introduced inside the bag by using a hand air pump. Special seal system ensures the sample during transport and temporal storage. Samples were analyzed afterwards in laboratory by using an optic spectrometer Picarro G2101-i. The device identifies and quantifies different compounds in the optical spectrum obtained. Isotopic relationship $\delta^{13}CO_2$ is measured as a calculation from $^{12}CO_2$ and $^{13}CO_2$ concentrations analyzed by the spectral system. Precisions of 200 ppb, 10 ppb and 0.3% are guaranteed for $^{12}CO_2$, $^{13}CO_2$ and $\delta^{13}CO_2$ respectively. Precision of 0.1 ppm has been obtained for CH_4 compound in the concentration range studied (0–2 ppm).

An extensive aerobiological sampling all over the cave was conducted in June 2009 to quantify the level of airborne bacteria and fungi. The methodology used was published elsewhere (Fernandez-Cortes et al., 2011).

3 RESULTS AND DISCUSSION

A cave environment is characterized by high levels of CO_2 with very low $\delta^{13}C$ isotopic signal values and low levels of CH_4 compared with the external atmosphere. Average values recorded in Altamira Cave and its surroundings in the samplings carried out in July 2012 are shown in Table 1.

Data analysis using Keeling's Plot (Keeling 1958) indicated that the CO_2 present in the ecosystem has a soil-derived origin. Figure 2 shows that inside the cave the lowest CO_2 concentration correspond to the Entrance Hall due to the connection with the external atmosphere. This external influence is progressively reduced from the entrance inwards reaching the lower isotope signal values, maximum CO_2 and minimum CH_4 concentrations in the innermost areas (between the Great Hall and the Well Hall). However, in the last hall (Well Hall) is noticed a change of trend despite being the farthest hall from the only known accessible entrance. The slight increase of CH_4 and a lower concentration of CO_2 with heavier isotope values indicate the presence of an unknown connecting track to the outside near or in the Well Hall area.

Regarding the level of airborne microorganisms (bacteria and fungi), a distinct behavior along the cave has been observed. The concentration of fungal spores outdoor the cave is higher than inside the cave. Throughout the cave, the concentration of fungal spores is higher in the halls and galleries close to the entrance (Kitchen Hall, Crossing, Polychrome

Table 1. Environmental parameters in Altamira Cave.

Air	CO_2 (ppm)	$\delta^{13}C$ (CO_2) ‰	CH_4 (ppm)
Cave	1257	–19.9	0.62
Top soil	2887	–20.5	1.38
Exterior	420	–8.5	1.70

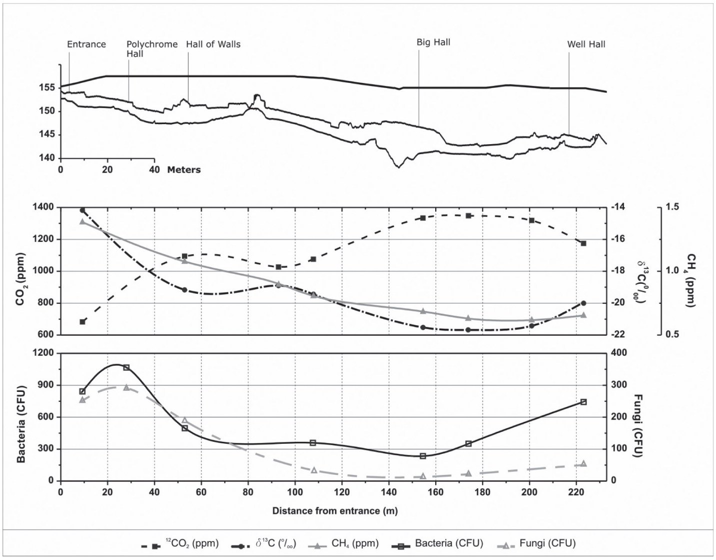

Figure 2. In profile, spatial distribution of airborne bacteria and fungal spores in Altamira Cave (June 2009) and CO_2, $\delta^{13}CO_2$ and CH_4 (July 2012) in the air of Altamira Cave.

Hall) and is reduced towards the interior (Walls Hall). The concentration of fungal spores reaches its minimum in the Grave Hall and Great Hall, ranging between 10 and 21 colony forming units (CFU)/m^3. However, the Well Hall reached 50 CFU/m^3. This can be attributed to a direct connection of the Well Hall with the exterior. Interestingly, a major abundance of *Cladosporium* spores was observed in Altamira, which is not common in other caves studied (Fernandez-Cortes et al. 2011, Porca et al. 2011). In the halls near the entrance, considering Walls Hall, Crossing, and Polychrome Hall all together, *Cladosporium* attained 79.6%, followed by *Epicoccum* (18.0%), *Penicillium* (1.0%), and *Aspergillus* (0.5%). Because *Cladosporium* and *Epicoccum* are considered common outdoor fungi, it is suggested that the abundance of *Cladosporium* all over the cave can be a consequence of the existence of a connection with the exterior not only at the entrance but also at the end of the cave, in the Well Hall. In fact, 84% of the fungal spores present in the Well Hall belong to *Cladosporium*.

The airborne concentration of bacteria inside the cave is higher than that recorded outside and also much higher than of the fungi. This can be understood taking into account that the ceiling and walls of Altamira Cave (Kitchen Hall, Crossing, Polychrome Hall and Walls Hall) are widely colonized by bacteria (Cuezva et al., 2009, Saiz-Jimenez et al. 2011). Thereby, the higher concentrations of airborne bacteria were found in the Crossing and entrance to Polychrome Hall. Considering all samplings together, the most abundant bacteria in Altamira Cave air was *Micrococcus luteus* (83.2%), followed by different species of *Pseudomonas* (7.8%) and *Bacillus* (2.1%). In the halls near the entrance (Walls Hall, Crossing, and Polychrome Hall), *M. luteus* concentrations ranged between 77.3 and 88.9%, while in some other halls (Wells Hall, Grave Hall) was absent.

Again the influence of a possible connection exterior-interior in the Well Hall is confirmed by the increasing number of bacteria in this hall (740 CFU/m^3, from which 89.2% belonged to *Bacillus weihenstephanensis*, a soil-dwelling bacterium) in comparison with the samplings obtained in the nearby halls (Great Hall: 360 CFU/m^3 and Horse Tail Gallery: 280 CFU/m^3). The Grave Hall that is an inferior hall, isolated in some way from the rest of the cave, shows the lower bacteria concentration in the cave (150 CFU/m^3).

The caves are considered oligotrophic environments, and areas with direct communication with the outside favor the entry of microorganisms and the development and dissemination of microbial colonizations. In Altamira Cave the area near the entrance has a higher level of airborne microorganisms in relation to nearby halls. However, an anomaly in the Well Hall in relation to nearby halls reveals a connection with the outer atmosphere at this site.

4 CONCLUSIONS

Gaseous phase exchange processes are the main natural factor for the entry and dispersion of microorganisms into Altamira Cave. Thus the main problem is the opening of the door, which reinforces the role of the atmosphere as a vehicle for the transport and dispersion of airborne microorganisms and nutrients inside the cave. The data obtained have shown that there is another possible entry of microorganisms in the innermost area of the cave (the Well Hall), far from the single and most elevated entrance. In fact, in the Well Hall the high level of airborne microorganisms in relation to nearby halls and galleries reveals a connection with the outer atmosphere at this site, which is also supported by the spatial distribution of carrier (CO_2) and trace (CH_4) gases and isotopic signal of CO_2 ($\delta^{13}C$). The presence of other cavities in a topographically lower position than Altamira and with direct connection to the outside could be the origin of the observed anomaly. This fact reinforces the importance of the second door, which separates the Kitchen Hall from the Crossing to prevent air flows between the old entrance and the Well Hall external connection. The data reported should be taken into account in future cave managements and conservation measures.

ACKNOWLEDGEMENTS

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Science and Technology for the Conservation of Cultural Heritage –
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Canonical Biplot as tool to detect microclimates in the inner and outer parts of Salamanca Cathedrals

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ABSTRACT: We analyzed values of temperature and relative humidity every two hours as month-year-localization, to detect the different microclimates present in the Cathedrals of Salamanca. To avoid the effect of seasonal time series have been carried out 8 different analysis (4 of temperature and 4 of relative humidity) in spring, summer, autumn and winter. The sensors were placed on the outside (environmental station) and inside (different heights inside of the two cathedrals and north and south positions in the Cloister). Canonical biplot was applied to different matrices, where the rows of the tested were divided into 21 groups (populations). When comparing the data from external sensor of the old cathedral (dome), with respect to the data of internal sensors of the building, the fluctuations in relative humidity and temperature were found. There are microenvironments in Cathedrals and the Cloister at some hours and months. There are not differences in the Cloister in spring and the both Cathedrals in winter and autumn.

1 INTRODUCTION

Analysis of different microclimates on monuments is very important for the determination of the pathologies present and the approach of its conservation (Iñigo et al. 2000, 2001, Rives & García-Talegón 2006). Salamanca is a city located on the Central Meseta of Spain, its climate can be defined as Mediterranean with a continental trend and strong daily fluctuations in temperature (as large as 30ºC), that produce stresses in exposed materials owing to processes of dilation/contraction (thermoclasty and freezing-thawing), specially in heterogeneous materials such as Villamayor sandstones (skeleton of the quartz and feldspar into a palygorskite, smectite and illite/mica). These decay processes lead to microfissures, plates, flakes and surface arenization. The different degrees and types of decay observed in exposed and protected materials in the Salamanca Cathedrals (New and Old Cathedrals) microenvironments are largely due to the above phenomena (Rives & García-Talegón 2006).

In the present work, the data of relative humidity and temperature from different sensors in the inner and outer parts of the Salamanca Cathedrals are analyzed to characterize different microenvironments in it from January 2010 to December 2010.

2 MATERIALS AND METHODS

The data of exterior relative humidity and temperature were obtained by the SKH 2013 model Skye home sensor. The data collection was done by the GEONICA home station. The autonomous sensors installed inside the Cathedrals of Salamanca were 175 model

Figure 1. Sensor location in the Cathedrals Salamanca's cross section.

TESTO home. The location of all the sensors in the Cathedrals of Salamanca (New and Old Cathedral and Cloister) is shown in Figure 1.

The sensor location was considering different heights on central naves of Cathedrals and different orientations in the Cloister (Iñigo et al. 2001). The period of analysis to characterize different microenvironments includes from January 2010 to December 2010. We analyzed values of the sensors every two hours as month-year-localization. To avoid the effect of different seasonal time series have been carried out 8 different analysis (4 of temperature and 4 of relative humidity) in winter, spring, summer and autumn, and within them have split by months.

2.1 *Statistical method*

The Canonical Biplot is equivalent to MANOVA analysis (Multivariate Analysis of Variance), but it includes all the characteristics of the Biplot method (Gabriel 1971, 1995). Results and graphic interpretation is described in Iñigo et al. (2004).

The results are summarized on several factor planes, where the variables are represented as vectors that start out from a hypothetical origin and the means of the different groups as stars surrounded by confidence circles in the same reference system. If two confidence circles are projected perpendicularly on one of the variables and the intervals of both projections do not overlap, this is tantamount to saying that there are differences between both means (Students' t test); the amplitudes of the circles will depend on the significance, α, determined (MSD, Bonferroni corrections, etc.). The rows of the different matrices tested were divided into 21 groups (populations) with specific characteristics:

- Varieties of analysis: temperature (T) and Relative Humidity (H).
- Localization: exterior weather station (Ext.), lower part New Cathedral (7), upper part New Cathedral (3), lower part Old Cathedral (9), upper part Old Cathedral (20) and Southern and Northern orientation cloister (18 and 19), Figure 1.
- Stations months: Winter [January (J), February (F) and March (M)], Spring [April (A), May (M) and June (J)], Summer [July (J), August (A) and September (S)] and Autumn [October (O), November (N) and December (D)].

The denomination of the populations shown in the figures is of the XYZ type, where: X = Temperature (T) and relative humidity (H), Y = Sensor location (Figures 1A and 1B) and Z = Months. Thus, for example, a population of temperature that is located in upper part Old Cathedral in April would be known as T20A.

3 RESULTS

The 8 analyzes give a Wilks lambda ($p < 0.01$). The inertia adsorption of the first main planes in all analyzes (>78%) to detect differences between the sensors (microclimates).

Winter: Differences were detected between the external and internal positions of the Cathedrals. Also, there are differences in the Cloister. Differences in relative humidity exist in all hours and months. These same differences are only during the last 12 hours in temperature, Figure 2.

Spring: Differences were detected between the external and internal positions of the Cathedrals. There are differences at different heights in both Cathedrals. Differences in relative humidity exist during the first 10 hours in every month in the Old Cathedral. These differences are detected at all hours in May and June in the New Cathedral. Moreover, there are only temperature differences in the New Cathedral in May and June. These same differences are only in June in the Old Cathedral, Figure 3.

Summer: Differences in temperature and relative humidity were detected between the external and internal positions of the Cathedrals. Also there are differences at different heights in July and August in both Cathedrals. There are differences in relative humidity between north and south positions in the Cloister during the first 12 hours in July and September. These same differences are detected during all months in temperature, Figure 4.

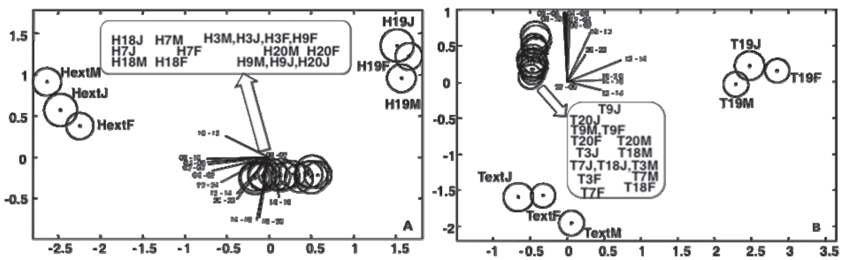

Figure 2. Plot of the 1–2 plane obtained after application of the Canonical Biplot method: A) Relative humidity and B) Temperature.

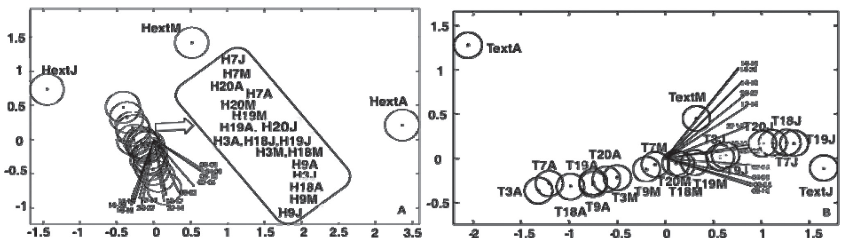

Figure 3. Plot of the 1–2 plane obtained after application of the Canonical Biplot method: A) Relative humidity and B) Temperature.

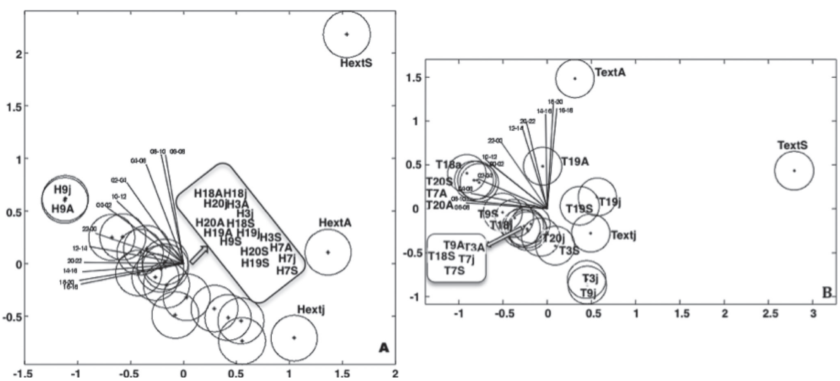

Figure 4. Plot of the 1–2 plane obtained after application of the Canonical Biplot method: A) Relative humidity and B) Temperature.

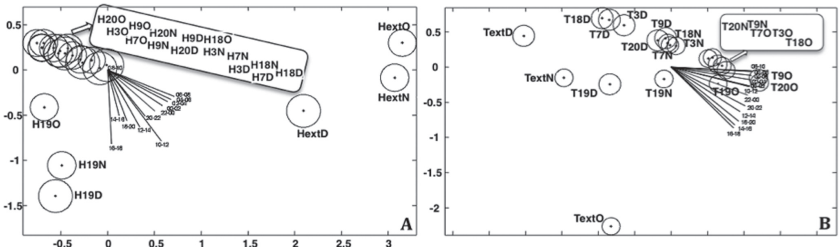

Figure 5. Plot of the 1–2 plane obtained after application of the Canonical Biplot method: A) Relative humidity and B) Temperature.

Autumn: Differences in temperature and relative humidity were detected between the external and internal positions of the Cathedrals. There are differences in relative humidity between north and south positions in the Cloister in November and December and the last 14 hours in October. Moreover differences of temperature exist in November and December during the last 12 hours, Figure 5.

4 CONCLUSIONS

Following application of the Canonical Biplot statistical method to the data obtained, which are as follows the following conclusions may be drawn: a) Canonical Biplot method is a useful tool for the detection of microclimates in Cultural Heritage, b) Clear differences were detected between inner and outer positions in all analyzes in the Cathedrals, c) There are differences at different heights in both Cathedrals (New and Old) in temperature and relative humidity at some hours and spring and summer months. There are not differences in winter and autumn and d) There are differences in temperature (last 12 hours) and relative humidity (all hours) between north and south positions in the Cloister in winter. These differences exist at some hours and in summer and autumn months. There are not differences in spring.

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Polar compounds in diesel soot and historic monument surfaces

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ABSTRACT: Diesel soot, an important contributor to atmospheric aerosols, consists of a complex mixture of compounds. However, a very limited knowledge on the organic composition of aerosol and the water soluble fraction exists. A considerable portion of polar (oxygenated) organic compounds remained unanalysed, and additional analyses are needed to identify the polar compounds. Column fractionation of a diesel soot results in the obtaining of a methanol-soluble polar fraction enriched in aromatic polycarboxylic acids. This analysis provides a comprehensive dataset and important clues for solving the chemical nature of the polar (oxygenated) aerosol fraction and for identifying the polar compounds deposited on the surfaces of historic monuments.

1 INTRODUCTION

Research on the chemical composition of atmospheric aerosols is essential for understanding aspects related to global climate, cloud formation, effect on human health, etc. A large part of the organic compounds from aerosols and particulate matter can be recovered in a water soluble fraction, which may represent up to 75% of the total organics. However, a very limited knowledge on the organic composition of aerosol and the water soluble fraction exists and this derives mainly from the fact that organic compound speciation has traditionally been carried out based on gas chromatography-mass spectroscopy (GC-MS) analysis. With this approach, a considerable portion of polar (oxygenated) organic compounds remained unanalysed, and the resolution of the complex mixture containing a wide range of different organic molecules is poor (Fuzzi et al., 2002).

Diesel exhaust, an important contributor to atmospheric aerosols, consists of a complex mixture of compounds. After emission, these compounds undergo chemical and physical transformations, or aging, in the atmosphere or in the deposition sites. Zielinska et al. (2010) stated that there are myriad of unknown organic species and its associated transformation products in diesel exhaust, and that additional analyses are needed to further elucidate the composition of the polar fraction, which is a significant gap in the knowledge of the atmospheric science community.

Black crusts are repositories of urban aerosols, as the monument surfaces passively entrap particulates in a gypsum matrix and, to some extend, the compounds were preserved (Saiz-Jimenez 1997). In this work we propose a fractionation protocol that provided a high degree of molecular resolution and clues for understanding the nature of the polar fraction of diesel soot and their components. The same fractionation scheme was adopted from black crusts from a monument. Both polar fractions were compared and their molecular features discussed.

2 MATERIAL AND METHODS

A fractionation protocol was applied to a sample of diesel soot obtained from the exhaust pipe of a community bus with seven years of service. The sample was obtained by scrubbing the exhaust pipe, and although this sample may not be representative of a real (fresh) diesel exhaust, since the soot material that accumulated over time in the exhaust pipe of the bus experienced modifications, the sample is representative of an aged diesel soot that undergo chemical and physical transformations, thus providing a range of primary and secondary reaction products, which is well suited for the evaluation of our analytical protocol and for the study of the large amount of unknown organic species present in diesel soot.

Twenty g of diesel soot was extracted in a Soxhlet apparatus with dichloromethane-methanol (2:1) during 70 h. The extracts were evaporated under vacuum at low temperature (below 40°C) and redissolved in dichloromethane-methanol (2:1). The resulting extract was chromatographed using a silica column, eluting with hexane (fraction I), hexane-dichloromethane (1:1) (fraction II), dichloromethane (fraction III), and finally with methanol (fraction IV). Details of the fractionation protocol and analyses were reported elsewhere (Gaviño et al. 2004). Briefly, fraction I contained mainly a homologous series of *n*-alkanes in the range C_{14}–C_{37}, *n*-alkenes (C_{15}–C_{27}), alkylcyclohexanes (C_9–C_{22}), and alkylbenzenes (C_{11}–C_{24}). Pristane and phytane, diagenetic products of phytol and molecular markers of petroleum including α,β-hopane biomarkers were also identified. Fraction II contained a complex mixture of polycyclic aromatic hydrocarbons (PAH), including some of their alkylated derivatives. This PAH mixture included sulphur-, oxygen-, and nitrogen-containing polycyclic aromatic species. Fraction III was dominated by the series of *n*-fatty acids (C_8–C_{30}). In addition, polycyclic aromatic quinones and some other compounds coeluted with the *n*-fatty acids. Fraction IV contained the polar compounds. Fractions I-III will be not discussed in detail in this paper. In addition, no attempts to quantify the different fractions were made because the primary purpose of this work was to find a protocol providing a good separation and identification of polar compounds in complex matrices.

Fraction IV was methylated with tetramethyl ammonium hydroxide (Sigma-Aldrich) (TMAH) and injected directly into a GC-MS Fisons GC 8000/MD 800. Alternatively, TMAH thermochemolysis of fraction IV was accomplished as described by Saiz-Jimenez (1994). In the analytical procedure used in this work, the carboxylic acids were recovered as the corresponding methyl esters and the hydroxyls as methoxyls. Throughout this paper they are referred to as acid and hydroxyls, their original forms, rather than as derivatised methyl esters and methoxyls. The compounds were identified by comparison of their mass spectra with a self-compiled data bank of compounds from a variety of macromolecules containing polar compounds (Martin et al., 1979, Saiz-Jimenez 1994). In addition, identification was achieved by computer analysis using the National Bureau of Standards and Wiley libraries, with the computer matching being checked against standards whenever possible.

3 RESULTS AND DISCUSSION

To ascertain the nature and presence of polycarboxylic acids, fraction IV from the diesel soot was subjected to thermochemolysis at 300°C. Thermochemolysis has been used for the characterization of humic substances and the polar functional groups of their building blocks, as well as for the analysis of complex macromolecular materials (e.g. lignins) containing carboxyl and hydroxyl groups (Saiz-Jimenez 1994). Using this approach, the oxygenated functional groups can be protected from further degradation during GC-MS analysis due to the use of TMAH.

Fraction IV upon TMAH thermochemolysis yielded a high number of compounds. No attempt was made to identify all compounds but the most abundant or representatives. The tentative identification of the most characteristic compounds is shown in Figure 1.

The number of resolved peaks in the thermochemolysis chromatogram was much higher than those obtained by room temperature TMAH methylation and direct injection of fraction IV in the CG-MS (data not shown), which suggests that a number of the polar compounds were not amenable to the study by this method. It may be hypothesized that fraction IV actually consists of a very complex and unresolved mixture of relatively small molecules and were released only when subjected to thermochemolysis, denoting that this method was more effective than room temperature TMAH methylation and direct injection on the gas chromatograph.

In the complex chromatogram of fraction IV from diesel soot, polycarboxylic acids represented the majority of compounds. In fact, benzenepolycarboxylic acids (including methyl and

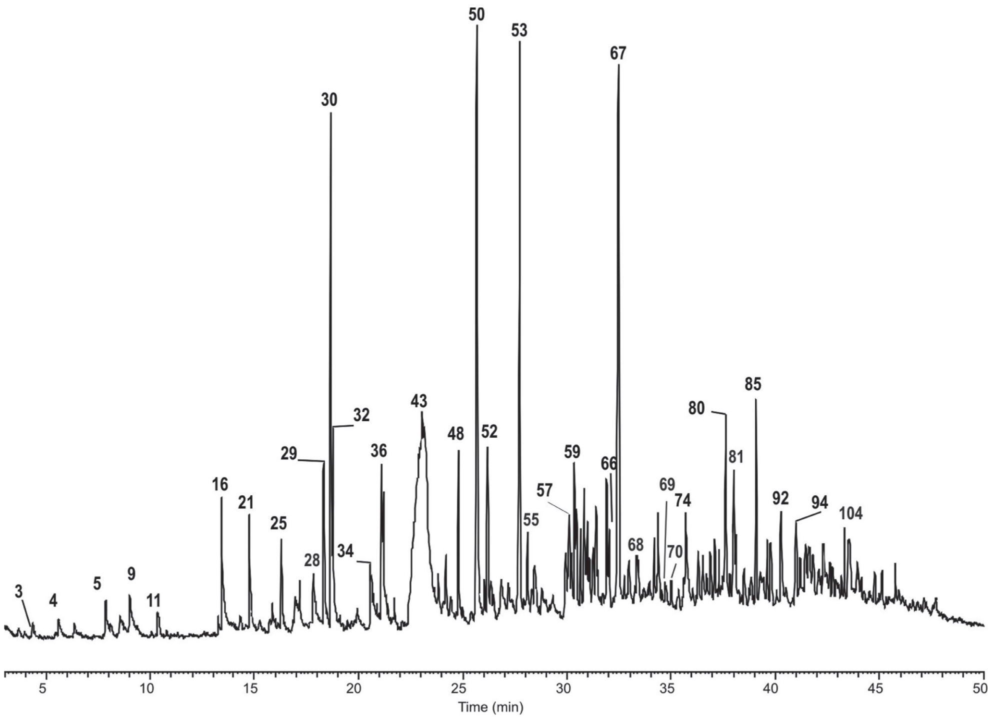

Figure 1. TIC chromatogram of fraction IV from diesel soot as analysed by thermochemolysis. Peak identification: 3 Hydroxybenzene, 4 Phenol, 5 Benzoic acid, 9 Pyridinecarboxylic acid, 11 Hydroxybenzoic acid, 16 Isobenzofurandione, 21 Furandicarboxylic acid, 25 Methylisoindoledione, 28 Thiophenedicarboxylic acid, 29 Benzenedicarboxylic acid, 30 Benzenedicarboxylic acid, 32 Pyridinedicarboxylic acid, 34 Methylbenzenedicarboxylic acid, 36 Unknown, 43 Unknown, 48 Cyanobenzenedicarboxylic acid, 50 Cyanobenzenedicarboxylic acid, 52 Benzenetricarboxylic acid, 53 Benzenetricarboxylic acid, 55 Hexadecanoic acid, 57 Hexadecanoic acid, 59 Naphthalenedicarboxylic acid, 66 Octadecanoic acid, 67 Unknown, 69 Acenaphthenedicarboxylic acid, 74 Dihydroxybenzenedicarboxylic acid, 80 Unknown, 81 Unknown, 85 Benzenedicarboxylic acid dioctyl ester, 92 Fluorenonedicarboxylic acid, 94 Anthracene/phenanthrenedicarboxylic acid, 104 Squalene. All acids were identified as methyl esters and hydroxyls as methoxyls, except for peak 57, which was identified as free acid of hexadecanoic acid.

hydroxyl derivatives) represented a 36% of the total identified products. Also carboxylic acid derivatives from polycyclic aromatic hydrocarbons (PAH) were present (naphthalene-, fluorene-, acenaphthene-, anthracene/phenanthrene-, etc.) representing a 23% of identified products. If fatty acids and oxygen-, nitrogen- and sulphur-heterocyclic carboxylic acids were also considered, all carboxylic acid derivatives amounted for 88% of the total identified products.

The identification of an important amount of carboxylic acid derivatives, including benzenepolycarboxylic acids, in the polar fraction of diesel soot is of interest since as far as we know no previous reports shed light on a complete or cuasi-complete individual characterization of their components. The low number of benzenecarboxylic acids identified by other authors is no satisfactory and does not correspond with the amount of benzenecarboxylic acids expected in aerosols and/or diesel soot (e.g. Gelencser et al. 2000, Subbalakshmi et al. 2000, Kubátová et al. 2009). In this work over 100 compounds have been identified, from which polycarboxylic acids constitute a considerable portion of the polar fraction of diesel particulate matter directly extracted from a bus exhaust. The information obtained on diesel soot composition, and particularly on the polar fraction, is more complete than that reported earlier. This also applies to the composition of the black crusts of Saint Denis basilica in France (Gaviño et al. 2004), where an important number of benzenepolycarboxylic acids were identified as major components of a polar, yellow fraction IV.

We show that diesel soot components, and by extension aerosol organic compounds and black crusts components, can be individualized after a fractionation in column, according to the polarity of their components. This fractionation results in obtaining fractions enriched in selected classes of compounds (hydrocarbons, PAH and aliphatic acids) and in a polar fraction enriched in aromatic polycarboxylic acids, which components can be analysed and chromatographed after protection of their functional groups with TMAH. This analysis could provide important clues for solving the chemical nature of the polar (water- and/or methanol-soluble) aerosol fraction and black crusts from monuments.

In the aerosols the compounds bearing carboxyls and hydroxyls can react to form esters for which it is needed an inorganic acid as catalyst. This reaction is possible in diesel soot, due to its H_2SO_4 content. The identification of a high amount of aromatic polycarboxylic acids upon thermochemolysis that were not evidenced by direct injection of the methanolic fraction in a GC-MS indicated that saponification of ester linkages might be a possible mechanism releasing a part of these aromatic polycarboxylic acids. If this hypothesis is confirmed, it will provide a new understanding of the chemical nature and origin of polymeric compounds in aerosols and black crusts. In fact, a number of important scientific issues are critical in air quality and climate change, such as to ascertain the role of carboxylic acids in cloud formation, the interaction of aerosols and volatile organic compounds with other molecules, the polymeric nature of humic-like substances (HULIS), etc. (Graber & Rudich 2006). A better knowledge of the composition of polar fractions in aerosols and particulate matter, as it was shown here for the polar fraction of diesel soot, can help to answer some of these issues.

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

The Seville Cathedral altarpiece: A microbiological and chemical survey of the dust

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ABSTRACT: The altarpiece of the Seville Cathedral was built between 1481 and 1565 and has a total perimeter of 20.10 m and 23.41 m height, which makes this altarpiece the largest in the world. The last restoration was performed in 1977, centered on ensuring its structural stability and consolidation of wood structures and polychromy. A new intervention to appraise the state of conservation is currently in progress. Our study is centered on the assessment of the dust accumulated on the surface including a survey of significant alterations from biological origin. The approach carried out combined molecular biology methods and analytical procedures. The composition of the dust samples is very heterogeneous, comprising mineral particles resulting from the deterioration of the building materials, fragments of decorative elements particularly gold leaf from the gilded wood, products from air pollution (soot), as well as biological fragments of insects, arachnids and bird droppings, in addition to bacteria and fungal spores.

1 INTRODUCTION

The Seville Cathedral, constructed in the early 15th century on the site of the Alhama mosque, of which the Giralda minaret still subsists, is one of the world's largest and is considered one of the most important monuments of Christendom. As usual in Gothic cathedrals, the main building material was stone, from various local quarries, in the provinces of Cadiz and Seville, and Portugal (Falcón 1980). The most abundant lithotype used was a yellowish fossiliferous calcarenite of Miocene age, locally known as *San Cristóbal* stone, and extracted from El Puerto de Santa María quarry (Cádiz).

The altarpiece of the Seville Cathedral was built between 1481 and 1565 and depicts the life of Jesus Christ on carved wood decorated with gold leaf and polychromy. The huge scale of the work, which has a total perimeter of 20.10 m and 23.41 m height, makes this altarpiece the largest in the world (Fig. 1a). Several artists were involved in the execution of the altarpiece, such as Pyeter Dancart, Pedro Millán and Maestre Marco, as well as others of unknown identity. However, most of the altarpiece work seems to have been performed by Jorge and Alejo Fernández Alemán. Before the restoration intervention in 1977, serious concerns emerged about the structural condition of the altarpiece, including wood parts in danger of collapse, as well as accumulation of dust on the surface, flaking and lack of adherence of the polychromy and gilding. This restoration intervention was centered on ensuring its structural stability and comprised the consolidation of wood structures and polychromy, as well as the attenuation of losses of different materials.

An intervention to appraise the present state of conservation of the Seville Cathedral altarpiece is currently in progress. Our study is centered on a detailed characterization of the dust accumulated on the surface including a microbiological approach.

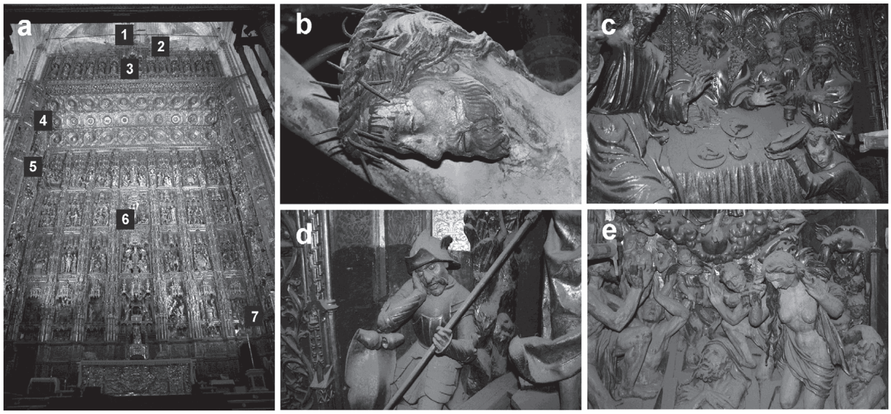

Figure 1. a. The altarpiece of the Seville Cathedral showing the areas where the dust samples (1–7) were collected. b. *Cristo del Millón*. c. Detail of the *María Magdalena unge los pies de Jesucristo* panel. d. Detail of the *Resurrección de Jesucristo* panel. e. *Pecado original y expulsión del Paraiso*.

2 MATERIAL AND METHODS

Seven dust samples were collected in March 2012 from the surface of the altarpiece (Fig. 1). The scientific approach carried out combined microbiological analyses: isolation of bacteria and fungi on culture media and molecular identification by sequencing of rDNA, and physicochemical analyses: observations by stereomicroscopy and field emission scanning electron microscopy (FESEM), X-ray diffraction (XRD), X-ray fluorescence (XRF) and Fourier-transform infrared spectroscopy (FTIR).

Before analysis, the samples were sieved and divided into five fractions depending on their particle size. Sieves were used with the following pore diameters: 475, 250, 150 and 75 µm. Stereomicroscopy observations were performed to characterize the physical and morphological properties of the different particles found within the samples. The finest fraction (<75 µm) was then analyzed by XRD and XRF. Additionally, other fractions were analyzed by XRD and FTIR.

Aerobiology methodology for identification of airborne bacteria and fungi was described elsewhere (Fernandez-Cortes et al., 2011).

3 RESULTS AND DISCUSSION

3.1 *Microbiological characterization*

All analyzed dust samples contain high amount of microorganisms. High concentrations of bacteria and fungi, between 10^3 and 10^5 colony forming units per gram (cfu/g), were detected (Fig. 2, Table 1). According to the molecular identification, the bacterial were dominated by species of *Bacillus*, followed by species of *Massilia*, and a small portion of *Staphylococcus*. The most abundant fungal species belonged to the genera *Cladosporium*, *Penicillium*, *Chaetomium*, *Aspergillus* and *Trichoderma*. These microorganisms have high sporulation rates which facilitate their dispersion. All detected microorganisms have a cosmopolitan distribution and are frequently isolated from any environmental sample.

3.2 *Physicochemical characterization*

Stereomicroscopy observations revealed that the composition of the dust samples was very heterogeneous, comprising different components of the building materials (Fig. 3a), fragments of decorative elements particularly gold leafs from the gilded wood and pigments from the

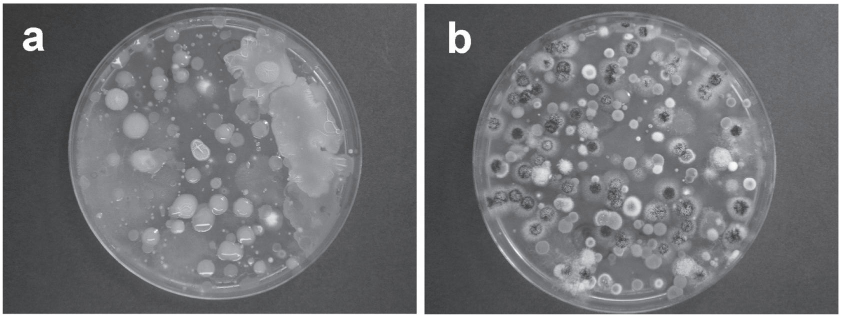

Figure 2. Isolations on culture media. a. Bacterial colonies on Trypticase Soja Agar + Cycloheximide. b. Fungal colonies on Dichloran Rose Bengal Chlortetracycline Agar.

Table 1. Counting of microbial colonies grown on culture media as colony forming units per gram.

Dust sample	Bacteria (cfu/g)*	Fungi (cfu/g)*
1	1.98×10^5	9.28×10^4
2	2.78×10^4	5.04×10^3
5	1.25×10^5	1.21×10^5

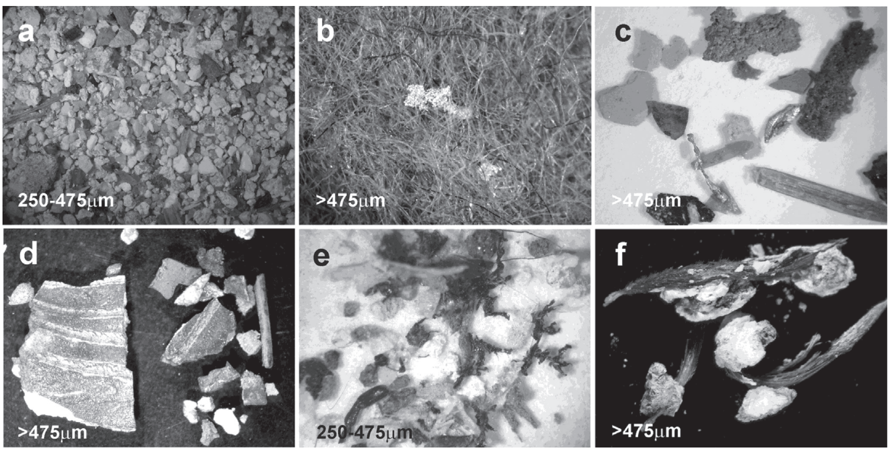

Figure 3. Stereomicroscopy images from different fractions of the dust samples. a. Grains of building materials. b. Fibers and gold leafs. c. Pigments. d. Fragments of gilded wood. e. Fragments of insects and arachnids. f. Bird droppings.

polychromy (Fig. 3b–d). Also, abundant fragments of insects, arachnids (Fig. 3e) and bird droppings enriched in uricite were detected (Fig. 3f). XRD analysis revealed the presence of calcite, quartz, dolomite, gypsum, halite, illite and anhidrite, which are mostly the mineral constituents of the building materials. A lead chromate, likely $PbCrO_4$, was detected by XRD, suggesting that a yellow pigment was used in the form of chrome yellow on the sculptures of the altarpiece. It must be mentioned that the chrome pigments were in use by 1816 (Douma 2008), which indicates that this pigment was used in conservation intervention performed in 1977 or before, but not at the time of the altarpiece construction. Barium sulfate, $BaSO_4$, was also identified by XRD, which sometimes is used in restoration works as a partial replacement for titanium dioxide in paintings, reducing pigment costs. Moreover, copper resinate was identified by FTIR. In the 15th and 17th centuries artists used copper resinate to add glaze on paintings laying a layer of copper resinate over verdigris to form a deep saturation of green color (Douma 2008).

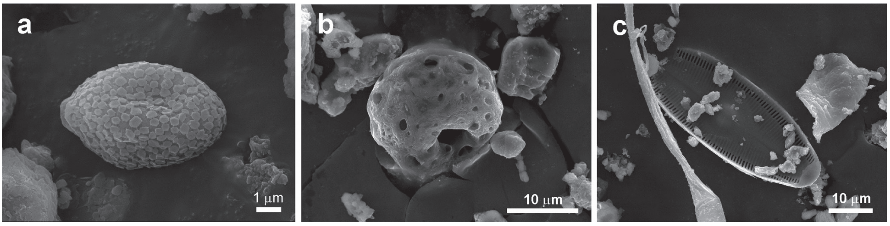

Figure 4. FESEM images of the dust samples depicting: a. Pollen grain, b. Soot particle, and c. Diatom.

According to FESEM analysis, abundant pollen grains (Fig. 4a) with different morphologies were observed within the dust samples, together with soot particles probably resulting from air pollution and frequent liturgical activities inside the cathedral. Note that the cathedral is in the centre of the city, an area that until 2006suffered from intense automotive traffic, which produced an atmosphere of carbon monoxide, sulfur dioxide, soot, hydrocarbons and other substances from vehicle exhausts (Saiz-Jimenez et al. 2004, Reyes et al. 2006). In addition, some diatoms were observed (Fig. 4c) probably derived from the building stones and/or water infiltrations in the roof of the cathedral.

4 CONCLUSIONS

The dust is mainly composed of stone minerals and decorative elements, denoting an important deterioration of the building materials from the vaults and the altarpiece.

The dust also contain a high microbial contamination specially enriched in bacterial and fungal species, which may cause biodeterioration in case of water availability (high relative humidity, leaks from the vault, etc.) on the different materials and would represent a risk for the conservation of the artworks. Insects and arachnids are also common in the dust.

It is recommended a cleaning of the altarpiece dirtiness. The opening of doors in the upper terraces should be avoided and a control of the opening time in the main gates to decrease dust concentration inside the Cathedral is needed. Furthermore, regular maintenance seems necessary due to the high concentration of dust accumulated over extended periods of time.

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Decay assessment through wireless sensor networks implementation for architectural heritage conservation

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ABSTRACT: Built heritage decay, a highly complex issue, involves a host of factors. The key agents of decay can be identified and related to both spatial and time-wise changes and trends in variables by monitoring microclimatic parameters with wireless sensor networks. Such a network was installed in St. John the Baptist Church at Talamanca de Jarama, Madrid, a sixteenth- and seventeenth-century structure, to determine the effects of outdoor agents and indoor factors, namely the presence of people and heating, on the inside walls of the church.

1 INTRODUCTION

Today, the focus in built heritage conservation is on prevention, with a view to minimising or eliminating asset exposure to decay and consequently the need for direct intervention. With those aims in mind, the strategy followed entails the identification, detection and control of the factors causing decay. Non- or only minimally destructive techniques play a crucial role in this endeavour, whereby the development of specific tools for diagnosing and preventing decay provides ideal support for the implementation of such strategies. Wireless sensor networks form part of this scenario, given their capacity to acquire and monitor a large number of variables indicative of damage to building materials, such as the presence of salt or moisture (Martínez-Garrido et al. 2012). This emerging technology features countless benefits for the prevention of cultural heritage decay, most prominently the ability to detect possible damage at a very early stage via continuous, long-term monitoring of variables and intelligent data processing. Such information facilitates decision-making on preventative action and the concomitant reduction in long-term costs. Moreover, the absence of cables in these networks makes them much less invasive than other types of sensors and readily reconfigurable and adaptable to the needs of each application and study.

2 OBJECT OF THE MONITORING ACTION: ST. JOHN THE BAPTIST CHURCH, TALAMANCA DE JARAMA, MADRID, SPAIN

A wireless sensor network was installed in St. John the Baptist Church at Talamanca de Jarama, Madrid, Spain. This sixteenth-century Renaissance church was rebuilt over a thirteenth and fourteenth-century Romanesque-Gothic temple. The apse is the only remaining part of the earlier structure. The original stone and the most characteristic building material on the church is an Upper Cretaceous dolostone. Its 36.50 × 12.50 × 10.50 m rectangular floor plan houses a main nave, two aisles, the apse and a tower. The plaster and paint surfacing on most of the inside walls conceal the stone and brick below. On the building exteriors, a dolostone ashlar dado clads a brick, dolostone and occasional flint stone rubble wall. The heterogeneity of the materials and the natural variations in the microclimate, along with the changes generated by the forced air heating system inside the church, accelerate decay. The main symptoms of decay detected were salt crystallisation and the formation of moisture fronts to a height of 1.50 m on the walls, which are approximately 0.50 m thick. The presence of this moisture, due to capillary water absorption, may have been intensified by walkways recently built outside the church.

3 METHODOLOGY

Six measuring points were chosen to fully monitor the church structure in general and its agents of decay in particular. MEMSIC MICA2 motes supplied by the manufacturer were used in interiors. These motes, which operate at frequencies of 868/916 MHz, were positioned along vertical lines on the walls selected to study areas with different building materials, different orientations and different exposure to the stream of heating system air. Three positions were selected on the south façade: opposite the north wing heating system (mote 7), on the south wing (mote 4) and on the apse (mote 1). Two of the three on the north side (motes 6 and 2) were established to monitor the north wing in the same manner as the south wing, while the third (mote 3) was defined by the heating vent to characterise the stream of outflowing air. The monitoring points are mapped in Figure 1. Temperature and relative humidity conditions were measured at different depths and heights. The heights, chosen on the grounds of the flow of air emitted by the heating system, the indoor ventilation and the moisture front detected by other hygrometric techniques, were 40, 140 and 240 cm. The sensors were set at a depth of 20 cm in all cases except in the apse (mote 1), where the depth was 10 cm. In addition, each line had a fourth sensor at a height of 240 cm to measure surface relative humidity and temperature. A two-minute sampling frequency was used throughout.

The outdoor climatic conditions were recorded on motes supplied by Libelium. Relative humidity, temperature, rainfall, and wind speed and direction were monitored by a wireless weather station. The data gathered were processed by the same unit as used in the MICA2

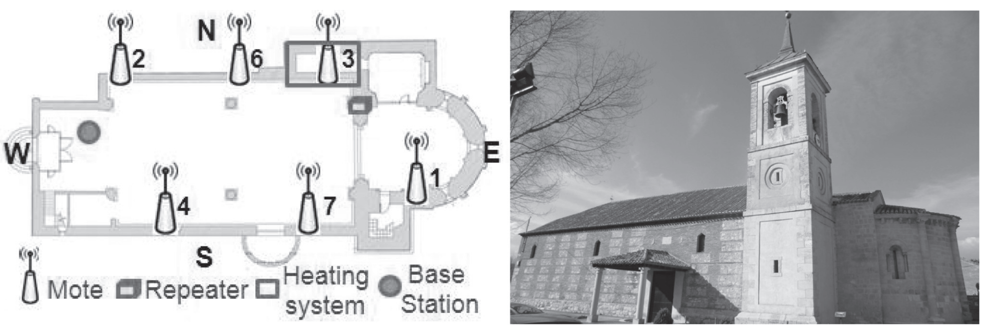

Figure 1. Location of measuring points (left) and photograph of the south façade and apse of the church (right).

network, whose base station exchanged data packages with the weather station. The communication protocol was ZigBee and the operating frequency 2.4 GHz.

4 RESULTS

According to the analyses, outdoor weather conditions, the heating system and activity inside the church affected the church to different degrees.

4.1 *Outdoor climatic conditions*

St. John the Baptist Church at Talamanca de Jarama is exposed to a continental climate, namely cold winters with frequent overnight frost (yearly means: temperature, 14 ºC; relative humidity, 60%; rainfall, 445 mm; wind speed, 4 m/s). By way of example, Figure 2 shows the orientation-induced differences in the effects of the weather conditions during the Christmas holidays (23 December 2011–1 January 2012). Insolation was observed to be an important climatic factor. While a mean temperature of 3.7 ºC and a mean relative humidity of 73.5% were recorded on both the north and south façades, with winds primarily from the north at a mean speed of 3 m/s, the south façade (mote 7), more exposed to insolation, exhibited daily heat-cold, day-night cycles not recorded on the north façade (mote 6). A height-dependent thermal gradient was also observed in the embedded sensors. On the south façade, temperature declined with rising monitoring height, while on the north, the temperature recorded by the highest sensor (240 cm) was in-between the readings taken by the sensors at 40 and 140 cm. The effect of insolation grew more intense with the change in season to longer daylight hours, even though solar radiation hit the façade at a smaller angle.

4.2 *Heating system*

At a given orientation, the effect of the heating system depended on the material studied and its proximity to the air flow. Figure 3 shows that the temperature recorded by the embedded sensors was higher on the south façade, made of mixed materials (dolostone, brick and plaster), than on the dolostone apse. Heat tended to concentrate at the foot of the church (motes 2 and 4, Fig. 1), with the widest variations observed in the sensor at 240 cm, which followed the same pattern as the surface sensor. On average, it took 9.81 hours to return from the peak to the average indoor temperature after the heating was turned off.

4.3 *Presence of people*

The presence of people in the church when the heating was off induced no material change in the data recorded, due to the light traffic and scant activity in the building. The greatest

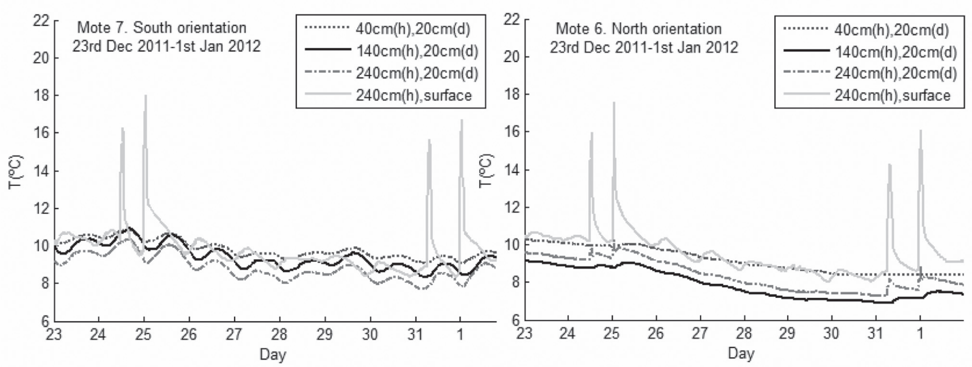

Figure 2. Comparison of the effect of insolation based on temperatures recorded at different north-south orientations (mote 6–mote 7), heights (h) and depths (d).

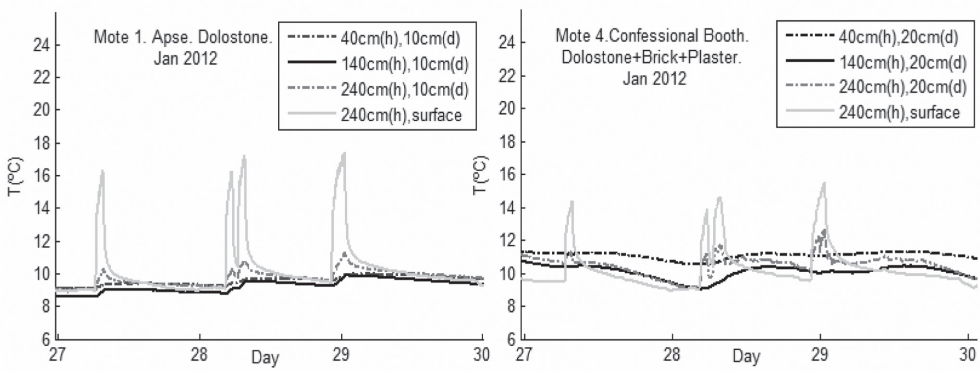

Figure 3. Comparison of the effect of the heating system based on the temperatures recorded for a given orientation at different heights (h) and depths (d) on different materials: mote 1 (dolostone), mote 4 (dolostone, plaster and brick).

increment with respect to the normal conditions was 0.81 ºC recorded on 1 April 2012 (Palm Sunday), which concurred with maximum church activity on the occasion of the holy week (1–9 April 2012). During that week, the mean outdoor temperature and relative humidity were 10.44 ºC and 74.5%, while the mean indoor values were 15.25 ºC and 52.32%.

5 CONCLUSIONS

Outdoor weather conditions were the cause of the greatest fluctuation in the data gathered, while human activity was only minimally relevant to decay. The heating system had an intermediate impact on the data distribution. Its cyclic pattern of use, i.e., intermittent over fairly short periods of time, may intensify decay. Other factors to be considered in this regard are the thermal stress generated in the materials and the temperature distribution by height and depth. The relative humidity data recorded at all monitoring points, irrespective of sensor orientation and the material studied, exhibited a clear trend toward saturation at under 1.5 m, the height of the moisture front on both façades.

ACKNOWLEDGMENTS

The cooperation received from the Diocese of Alcalá is gratefully acknowledged. The present study was funded under projects CGL2011-27902, GEOMATERIALES (S2009/MAT-1629), CONSOLIDER-TCP (CSD2007-0058) and BIA2009-14395-C04-01. Research by M.I. Martínez-Garrido has been supported by a PICATA predoctoral fellowship of the Moncloa Campus of International Excellence (UPM-UCM, CSIC). Dra. S. Aparicio was financed by the postdoctoral JAE-Doc program of the Spanish National Research Council (CSIC).

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Vivianite: A historic blue pigment and its degradation under scrutiny

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ABSTRACT: Vivianite is a mineral that was used as a blue painting pigment. However, in several artworks, vivianite has degraded to grey or yellowish colour. Our study confirmed the following degradation series caused by oxidation: vivianite—metavivianite—Fe^{3+} analogue of metavivianite—santabarbaraite. A procedure of identification of vivianite or its degradation products in microsamples of painted artworks was suggested (SEM-EDS followed by μ-ATR μ-FTIR). Vivianite was synthesized by an optimized method and model samples with water and linseed stand oil were created. These were subjected to artificial ageing in a climate chamber by intense UV light; these experiments are on-going.

1 INTRODUCTION

Vivianite is a monoclinic mineral with ideal chemical composition $Fe^{2+}_3(PO_4)_2 \cdot 8H_2O$. It is relatively common and occurs in various types of environments. It can be found in the form of minute to very large crystals (up to 1.3 m) (Guillemin 1964), or as several types of aggregates (Bernard & Hyršl 2006). The colour of commonly encountered earthy vivianite ranges from light greyish green to saturated blue, most frequently being light blue. Vivianite crystals are commonly dark coloured; nevertheless lightly-coloured specimens are also reported.

The documented span of vivianite use as a painting pigment stretches from 1050 till 1780. A comprehensive review of vivianite's usage in painted artworks was given by Richter (2007). Dominant countries of origin of these artworks are Germany and Austria, spreading throughout the indicated time interval. They encompass mostly the polychromies on wood and the wall paintings. However, the 17th century's artworks with identified vivianite are mostly of Dutch origin, with such famous names as Rembrandt van Rijn, Aelbert Cuyp or Jan Vermeer. These artworks are usually canvas (or panel) paintings (Richter 2007).

It is documented that in some of the artworks, vivianite has degraded and changed its colour to yellowish/brownish or grey (van Loon 2008, Howard 2003). Vivianite and its degradation process have been discussed in the mineralogical literature. Having iron in bivalent state, vivianite is prone to oxidation (Pratt 1997, McCammon & Burns 1980). According to Pratesi et al. (2003), the oxidation series proceeds from monoclinic vivianite through triclinic metavivianite to amorphous santabarbaraite. This was corrected by Chukanov et al. (2012), who state that between vivianite and santabarbaraite is one more degradation product, which was confirmed by our study. The processes of these changes have never been studied in relation to painted artworks and with respect to possible interaction with binders.

2 METHODS AND SAMPLES

This study comprised samples from painted artworks, namely from various works representing horses and scenes of hunt by Jean George de Hamilton (1672–1737), a painter of Belgian origin, who spent his life mainly in today's Austria and the Czech Republic. The presence of vivianite in his palette is presented for the first time to the international audience. One studied sample is from an altar by anonymous master from a church in Dupuş, a Romanian village.

For thorough study of vivianite degradation, a synthetic counterpart was needed. However, previously described processes using ammonium salts as one of the starting materials led to vivianite, but also to a by-product, which we were unable to separate (even though using recommended procedures). Therefore, an adapted process of the synthesis with green vitriol as a strating material was used; the resulting vivianite was checked for purity by X-ray diffraction (XRD) and used to create model samples with water and linseed stand oil (Kremer Pigmente, GmbH & Co. KG), because vivianite was used mainly in aquarelles and oil paintings, however changes in vivianite's colour in oil paints have been noted (Brewster 1832). These samples were subjected to artificial ageing in a climate chamber under UV-A light with maximum intensity at 365 nm, which was emitted by mercury discharge tubes Phillips Actinic TL 15 W. The temperature was set at 20 °C and the air humidity at 50%.

The following devices were used for the study of the samples: X-ray diffractometer (XRD) PANalytical X'PertPRO MPD, scanning electron microscope (SEM) JSM-6510 JEOL equipped with energy dispersive spectrometry (EDS) detector SSD INCA from Oxford Instruments, Thermo Scientific Nicolet Nexus 670 Fourier Transformation Infrared (FTIR) transmission spectrometer, UV-VIS spectrophotometer AstraNet equipped with fibre optics and an integration sphere LabSphere RSA-FO-150 with geometry 8°/d, Raman spectrometer inVia Reflex Renishaw (514 and 785 nm lasers), micro-attenuated total reflectance (μ-ATR) FTIR spectroscopy Thermo Scientific Nicolet iN10 with germanium crystal, reflection FTIR spectroscope—Continuum from Thermo Scientific Nicolet.

3 RESULTS AND DISCUSSION

A new research by Chukanov et al. (2012) revised previously accepted theory about vivianite's degradation: according to Chukanov et al. (2012), the oxidation degradation series is as follows: vivianite—partly oxidized vivianite—metavivianite—Fe^{3+} analogue of metavivianite—santa-barbaraite. The charge of the molecule during oxidation of iron is equalized by transfer of (H_2O) to (OH). This series was confirmed by the XRD measurements of Kremer Pigmente GmbH & Co. KG vivianite, a commercially available pigment, which was measured in our laboratory in 2009, then stored in dark and measured again in 2012. It is clearly visible (Fig. 1) that the amount of Fe^{3+} analogue of metavivianite has raised significantly.

Vivianite is a rare pigment and has been identified so far only in about 70 artworks (Richter 2007, Castro et al. 2009, Karl 2009, Sheldon 2007). However, it is possible that this number is so low, because when vivianite is degraded to grey it could be easily overlooked during routine analysis of the artworks. Therefore it is important to settle the correct procedure for vivianite (or its degradation products) identification. Vivianite colour layers are often so thin that it is not possible to analyse them by micro X-ray diffraction. The first analysis usually comprises SEM-EDS which proves the presence of iron and phosphorous in the grains, but for the structural analysis, vibrational spectroscopies are the methods of choice for their resolution and ability of identification of structural modifications. This has been proved on mineralogical samples of (meta)vivianites from various localities. Therefore, three types of vibrational spectroscopies were applied on microsamples of artworks: Raman spectroscopy (785 nm

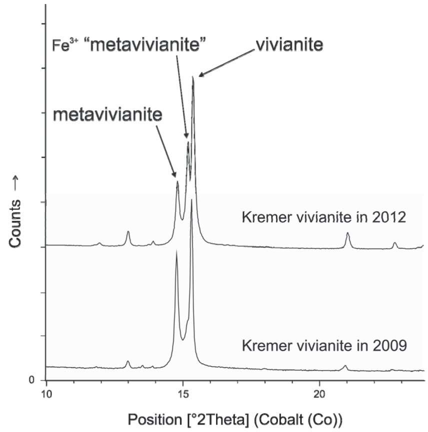

Figure 1. X-ray diffraction analysis of the same sample of Kremer Pigmente vivianite in 2009 and in 2012. The amount of Fe^{3+} analogue of metavivianite has raised significantly.

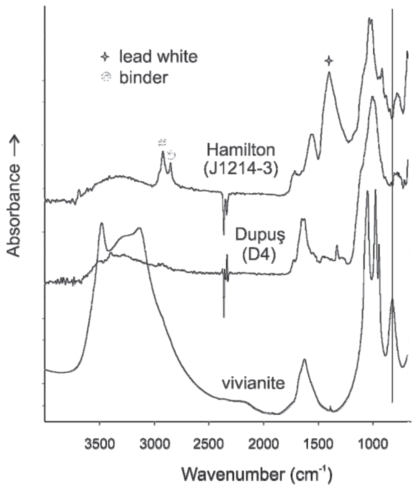

Figure 2. μ-ATR μ-FTIR measurements of two samples containing metavivianite from painted artworks, one from Jean George de Hamilton's The Bay Stallion Mignon and one from anonymous painter's altar painting placed in a church in Dupuş, Romania. A FTIR in transmission mode spectrum of vivianite is placed there for comparison. A shift of peak from approx. 820 to 780 cm^{-1} is marked by vertical line.

laser), μ-FTIR in reflexion mode and also μ-FTIR equipped with μ-ATR germanium crystal. The vivianite layers were too thin to get good quality spectra from the reflexion μ-FTIR; Raman spectra were hindered by fluorescence. The most suitable method proved to be μ-ATR μ-FTIR, where identification of (meta)vivianite was possible. The spectra recorded by μATR μ-FTIR are on Figure 2 together with the vivianite spectra recorded in transmission mode for comparison. As proved by the spectra of mineralogical samples, the crucial peak shift for the recognition of vivianite/metavivianite is from ~820 to ~780 cm^{-1} as indicated by the vertical line. Therefore, a suggested process of identification of vivianite in painted artworks is as follows: first identify grains containing both phosphorous and iron, then by the means of μATR μ-FTIR confirm the presence of vivianite or its degradation products.

To monitor the degradation process, measure the occurring colour change and to describe the changes of vivianite with oil binder, a synthetic vivianite was prepared and mixed with water and linseed stand oil. These samples were inserted into a climate chamber and subjected to artificial ageing by intense UV light. Half of the samples represented check samples and were shielded from the light. The experiments are on-going; the samples are being periodically measured by XRD, FTIR in transmission mode and UV-VIS spectrometry. Longer ageing experiments will clarify the colour changes in the artworks containing vivianite. It is possible that the colour changes of vivianite to yellowish-brown colours (as described in medieval English wall paintings (Howard 2003)) are due to photo-induced oxidation resulting in yellowish/brownish amorphous santabarbaraite, and the changes of vivianite to grey are in relation with its reaction with oil binders. Further research will follow to clarify this issue.

4 CONCLUSION

The study confirmed the degradation series of vivianite proposed by Chukanov et al. (2012). A suitable procedure of identification of vivianite (or its degradation products) in colour layers of painted artworks was suggested: elemental analysis by SEM-EDS followed by structural analysis by μ-ATR μ-FTIR. Such identification can help in reconstruction of original colouring of the artwork or the determination of its provenance (ascription to a certain author or region due to vivianite's rareness and specificity). A synthetic vivianite, produced by an optimized method, was mixed with water and linseed oil and these model samples were subjected to ageing experiments, which are still on-going.

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The authors are grateful to Dalibor Velebil from the National Museum in Prague and Andreas Massanek from the Technische Universität Bergakademie Freiberg for allowing us to sample vivianites from their archive, which were used for testing the suitability of various laboratory methods for identification of vivianite and its degradation products. This research was supported by a student grant GAUK (Grant Agency of Charles University) No. 632212 (2012–2014).

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Stabilization works at Olvés Church (Zaragoza-Spain)

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ABSTRACT: The Olvés Church is a three naves basilica. From its construction in 1767, it suffered important damages and successive reparations. The church is built on a clayey hillock on top of the village with very fort slopes. The retaining walls that surround the church have suffered movements. A soil study was done to know its properties and the reason of the movement. Also, the structural roof is broken and it is not fixed to the walls that can move. The first phase is done, with a paved square over an ancient cemetery. The next phase is a new roof structure to support the lean walls. After that done, the repair inside can start.

1 INTRODUCTION

Olvés (Zaragoza-Spain) is placed next the Ramblares gorge, in the Jiloca valley. The village has only 178 inhabitants. It is placed on the east slope of a clayey hillock with very fort slopes (Fig. 1).

The church is a three naves basilica. From its construction in 1767, only the ancient tower and a little chapel of the previous church remain. It has suffered important damages and successive reparations along its life (Fig. 2).

Twenty years after its construction an intervention was necessary and during the 19th century it was closed due to risk of failure. In 1910 the church was repaired as well as in 1980 and during November 1994 a part of the retaining walls was falling and some works were done to stop the damage. Some of the woks done were, for instance, a beam between the foundations, some buttress in the church headboard and some walls to help secure the arches.

The church is built on a clayey hillock on top of the village with very step slopes. An ancient cemetery exists on the west side of the church with some retaining walls surrounding it. This situation has facilitated rain water entering through which has produced pushing movements under the church.

Figure 1. Church actual state. It is sited on village top. The roof is broken. Some of the neighbouring houses are collapsing.

Figure 2. Actual church situation, over a retaining wall and very cracked, specially the apse.

Also, the village's population is decreasing and the mud or adobe walls of the church's neighbouring houses are collapsing. The traditional materials houses are mud or adobe wall, wood and brick. The roofs materials are wood and tiles. These materials are very sensitive to humidity. With their abandonment, the houses are rapidly degraded and they collapse, mainly those near the church, because they are more exposed. Then the church becomes more vulnerable, due to the environment minor impermeability, overall the west and north sides of the church, where the cemetery and the closer houses are sited.

The rain water comes in the cemetery, also the neighbouring fallen houses and passes under the church inducing the clayey hillock and the church to move.

Nearly thirty years ago, the last works to stop the church movement were made and from then the church is closed even though there are internal walls to hold it in place. The side walls of the church nearby the slope have a lean of roughly twenty seven centimetres. In 1992, the Architect M.A. Bordejé carried out a project to repair the church in two phases, but it was not done. Nevertheless the project was fit to obtain the information over the consolidation works made just now.

2 DIAGNOSTIC

In 2010, the Zaragoza Province Government (Diputación Provincial de Zaragoza) commissioned AIPA (UPM Research Group of Analysis and Intervention on Architectural Heritage) the study works for its consolidation. The current situation being:

a) Church in state of abandonment.
b) Walls and columns with severe deformations and cracks.
c) Some internal walls to support the arches in two directions.
d) A foundation reinforcement in concrete of the columns with a 70% increase of its surface, mainly sited at the east of the church.
e) Reinforced concrete tied beams between the columns foundations which are used as internal walls foundations.
f) Bricks and stone masonry buttress in the headboard.
g) A horizontal reinforced concrete beam in the headboard wall in the middle of its elevation.
h) A vertical retaining wall in the east and northeast side, missing in the southeast side. The existing wall is cracked.
i) A cracked and deformed pavement between the church and the retaining wall.
j) An abandoned ancient cemetery.
k) A little cave below the church. Its entrance, without door, is sited in the cemetery.
l) Three brick vaults were fallen and rebuilt with wood and a lightweight material, but two of them have fallen again.

3 STUDIES DONE

The following studies were done:

a) A building's damages study, realized by AIPA, where a revision of cracks in walls and vaults was made, as well as a visual analysis of the roof, walls and columns. The greater damages are located in the east side where the slope is more pronounced and where a leaning of around 27 cm was found in the wall.
b) A soil study, realized by ASG (Geotechnical and soil engineering), to know the geotechnical and geological characteristics. Four mechanical bore and three dynamic penetration test were made (Fig. 3). Also some samples were taken and some standard penetration test (SPT) were made, in order to analyze the soil properties.
   The church is sited over a 0.4 m to 2.6 m stratum of filling, which lies on a great thick of clayey Tertiary material. There are some insertions of materials of the same origin as clayey or loamy (Figure 4). These materials are of low plasticity, without swelling phenomena.

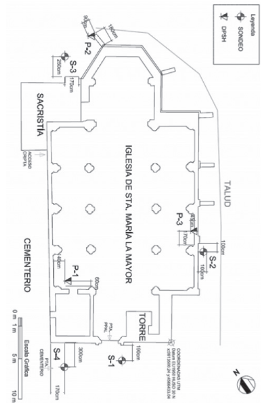

Figure 3. Church plan and soil study point situation.

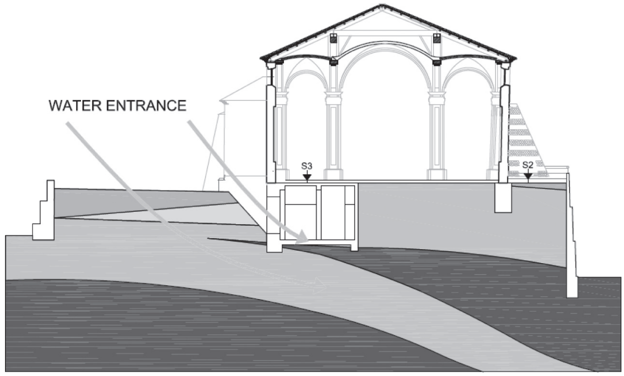

Figure 4. Soil description. Filling and different insertions of clayey materials. The rain water comes in bellow the church by the soil cemetery and the cave.

The soil bearing capacity is between medium and high, but there are zones with a lower bearing capacity. The soil moisture increases with the proof, and a great content of ion sulphate exists. The sulphate material is water soluble and can change the soil characteristics, specially the zones where the water goes through.

c) With the building's damages study and a soil study the reason of the soil and church movement was analyzed. Also, the efforts on the building walls and over the soil were calculated and compared with the soil bearing capacity and its water influence.
d) The principal causes of the church problem are the high clayey slope around the church, the retaining walls without water exit, the easy water entrance from the cemetery and the elevated content of gypsum in the soil. The water decreases the bearing soil capacity and increases the soil pushing behind the retaining walls. With the soil movement, the retaining walls move and as a consequence the pavement, the walls, the vaults and the roof crack.
m) The nearby houses contribute to the stability of the church and the impermeability of the soil. The houses collapsing nearby the church increase the problem; first their roofs broke which allow the rain water admission deteriorating the mud and adobe masonry walls until collapsing.

4 REPAIR PROPOSALS

4.1 *The works already realized*

The church is not a catalogued cultural heritage asset and the village is very small, consequently there is a short amount of money for the refurbishment. Therefore the reparation must be done in phases. Since the main problem was the water entrance through the soil, the first phase was to pave the cemetery, which was converted into an open square. In addition, the cave entrance was closed and the pavement around the church repaired. Some large pipes to collect the rain water were included and the water driven to the urban drainage. In addition, a reinforced concrete wall has been shooting out where the houses collapsed in order to avoid the water entrance. All this allows the control of the water entrance, the soil humidity, the bearing soil capacity and the pushing of the soil on the retaining walls.

4.2 *The following phases*

The second phase consists of building a new roof structure with a reinforcement to hold the lean walls. It will have, trusses made out of wood and steel as well as a leaning beam to reinforce

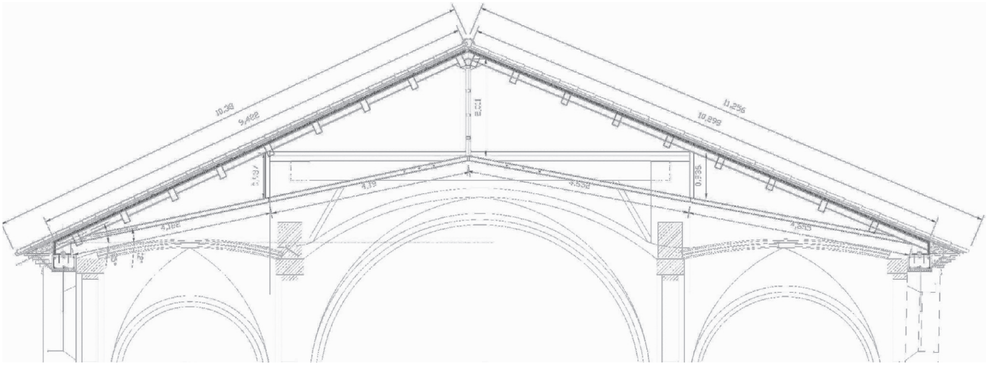

Figure 5. New roof structure, with a concrete tie-beam on the walls and the wood and steel trusses.

the walls, vaults and arches. At present the roof structure is broken with some elements lost. Also some tiles rubble was abandoned above and must be retired (Figure 4).

After that, the main restoration works will be made. The rehabilitation of the church interior may be done taking away the internal provisional walls that support the arches in two directions. At the same time it is possible to complete the foundation reinforcement, to repair the wall and vaults cracks to replace the vault fallen and finally to repair the decorative elements.

5 CONCLUSIONS

The church has had very important movements since the beginning of its construction. It has been repair and rebuild sometimes. Actually it has an important stability problem. The church is not a catalogued cultural heritage asset and there is a short amount of money to repair it. The reparation must be made in phases and with a short budget.

The main destabilization problem is the water entrance bellow the church. The first phase has consisted of to avoid that with the paving of the cemetery, a reinforced concrete shoot out wall to protect the collapsed houses zone, the close of the cave entrance and the inclusion of a pipe to drive the rain water to the urban drainage system. The second phase must rebuild the roof structure, the trusses and the support elements. The new trusses must be attached to a concrete tie-beam to stabilize the church walls. The following phases are, to take away the internal walls that support the arches, to complete the foundation reinforcement, to repair the wall and vaults cracks, to replace the vault fallen and finally to repair the decorative elements.

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Detrimental rock black fungi and biocides: A study on the Monumental Cemetery of Cagliari

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ABSTRACT: Black meristematic fungi are important and underestimated biodeteriogens of stone monuments in the Mediterranean area. They are difficult to remove in reason of their ability to grow inside the rock and to cope with several physical and chemical stresses such as high and low temperatures, low water and nutrients availability, high UV irradiance, osmotic and acidic stresses, and biocides.

Chemicals used in restoration treatments are detrimental for the operator and the environment and it is of high interest to find a customized and effective protocol to reduce their use. In this perspective this study focused on seven marble sculptures of the Monumental Cemetery of Cagliari, three of which treated eighteen months before with the biocide Biotin®R. Twenty-six black fungal isolates were obtained and identified by molecular methods. Agar diffusion test was applied to twelve different strains in order to evaluate their response to some biocides of common use: Preventol®RI 50, benzalkonium chloride, Lichenicide 264 and Biotin®.

In the last decade a big deal of interest has been paid on biological agents that, along with chemical and physical factors, contribute to the weathering of outdoor cultural heritage. The impact of biota on exposed rocks exerts in both aesthetical and structural damage. Pigments such as carotenoids and melanins, produced by microbes as protectants against UV radiations and other environmental stress factors, are responsible mainly of the aesthetic alterations (Diakumaku et al. 1995, Fong et al. 2001, Gorbushina et al. 1993, Moeller et al. 2005); structural damages are due to the metabolic activities of rock colonizers with the production of organic and inorganic acids, chelating agents, enzymes and extracellular polymeric substances (EPS). Microorganisms operate also mechanical alterations into the mineral structure due to the growth itself as well as shrinking and swelling cycles of the colloidal biogenic slimes inside the pore system (Warscheid & Braams 2000).

Humidity, solar radiation and temperature, as well as the deposition of inorganic and organic nutrients, and the stone type influence the settlement, growth and development of microorganisms on bare rock surfaces. Therefore, microbiota on monuments vary greatly with changes of atmospheric and microclimatic conditions and geographical zones. Frequently they form structurally and functionally complex communities, called subaerial biofilms (SAB) which survival and success depend from a collective growth habit. SAB may be composed of algae, cyanobacteria, chemolithotrophic and heterotrophic bacteria, fungi, but also lichens, mosses, protozoa and a variety of small animals (Gorbushina 2007). Fungi dominate in SAB from temperate climate to arid and warm environments (Mouchacca 1995) thanks to their mycelial growth habit along with the capacity of some species to grow dimorphically by changing from hyphal to yeast-like or meristematic growth (Gorbushina et al. 1993, Wollenzien et al. 1995). On monuments there are two major morphological and ecological groups of fungi that are adapted to different environmental conditions. In moderate or humid climates the fungal communities are dominated by hyphomycetes of soil and epiphytic origin including species of *Alternaria*, *Cladosporium*, *Epicoccum*, *Aureobasidium* and *Phoma* (de Leo et al. 1996, Sterflinger 2010). Instead in arid and semi-arid environments the fungal community shifts towards black yeasts and microcolonial fungi (MCF) because of their extraordinary extremotolerance and absence of competitors. The most frequent black fungal genera found are *Hortaea*, *Sarcinomyces*, *Coniosporium*, *Capnobotryella*, *Exophiala* and *Trimmatostroma* (Sterflinger 2010). MCF are perfectly adapted to the life on rocks, an extreme environment, being able to cope with rapid changes in the intensity of radiation, temperature, water and nutrient availability making them the most persistent inhabitants of perennially exposed rock surfaces. Different studies were carried out on black fungi concerning their limit of life that confirmed an extraordinary ability to tolerate chemical and physical stresses such as extreme temperatures, which on exposed rocks may span between –45 and 60 °C (Sterflinger et al. 2012) as well as high levels of UV radiation (Onofri et al. 2008, Selbmann et al. 2011), but also with halophilic (Sterflinger 1998, Zalar et al. 1999) and outer space conditions (Onofri et al. 2012), radioactivity (Wember & Zhdanova 2001) and not last biocides (Sterflinger 2010).

Conservation practice has to choose between many different techniques when planning the cleaning of historical stones. In particular it must be considered the nature of the "dirt", cleaning methods available for different materials, possible detrimental effects and damages that could be exerted from treatment, effectiveness of treatment and costs.

Commercial biocides and antimicrobially active compounds can be commonly classified as alcohols, aldehydes, organic acids, carbon acid esters, phenols and their relatives, halogenated compounds, and various synthetic products (Warscheid & Braams 2000). Regardless the efficiency of the biocides/chemicals, that are generally applied following standard procedures suggested by manufacturing houses, the most important objection to their use in the conservation of exposed and often highly frequented historical stoneworks is their ecotoxicological effect on workers, visitors and environment. In fact, even if toxic effect are known, allergenic and synergistic effects of biocides on human health are not completely understood (Warscheid & Braams 2000). It is therefore a priority to find new tools to preserve both cultural heritage and public health. In this perspective this study focused on 7 marble sculptures of the Monumental Cemetery of Cagliari (Fig. 1), 3 of which treated one year before with the biocide Biotin®R. The marble monuments were sampled using non-invasive techniques (Wollenzien et al. 1995). Twenty-six isolates of black meristematic fungi were obtained,and were preserved in the Culture Collection of Fungi from Extreme Environments (CCFEE) of the Department of Ecological and Biological Sciences, Università della Tuscia (Viterbo, I). Molecular studies revealed the presence of species already reported as associated with marble monuments such as *Aureobasidium pullulans* (De Bary) G. Arnaud ex Cif., Ribaldi & Corte and *Knufia chersonesos* Bogom. & Minter; in the meanwhile a number of strains where never found on stones and others belong to underscribed taxa.

In order to evaluate optimal growth conditions, temperature preferences were tested in triplicate, on a selection of strains (Tab. 1) inoculated on MEA in Petri dishes and incubated at 0, 5, 10, 15, 20, 25, 30 and 35 ± 1 °C. Cultural characteristics and growth rate were performed on PDA (potato dextrose agar), MEA (malt extract agar), CZA (Czapek dox agar) and OA (oatmeal agar); plates were incubated at 15 °C. Both temperature and cultural tests were performed in triplicate and diameters of colonies recorded weekly.

Agar diffusion test was applied to a selection of strains isolated and performed at 15 °C in order to evaluate their susceptibility against 4 biocides of common use such as Preventol® RI 50, benzalkonium choride, Lichenicide 264 and Biotin®R. The fungi tested showed different growth rate, thermal preference as well as sensitiveness to biocides. A number of factors may influence the effect of biocides as concentration, time of exposition, pH, temperature, presence of interfering materials, and the types, numbers, location, and not last the metabolic state of microorganisms. Metabolically active rock settlers are, in fact, more sensitive to biocides and their biological state is strictly dependent on physical conditions on the rocks, such as temperatures or water availability.

Therefore, all these factors must be taken into account to set an appropriate treatment. This procedure may avoid the spreading of more resistant microbial species that, changing the

Figure 1. Severe deterioration on one of the marble sculptures studied.

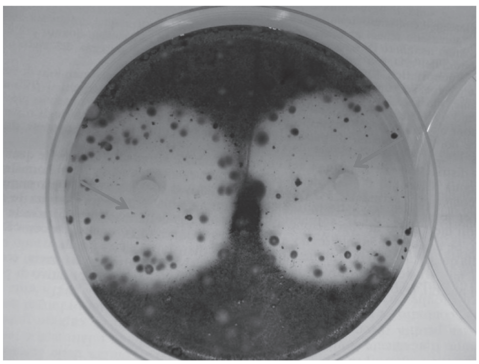

Figure 2. Biocide treatment on dual cultures. One of the strains is sensible to the biocide effect (inhibition halo); the other one (black spots) grows even close to the inoculum patch (red arrows).

Table 1. Thermal preferences of a selection of strains isolated from marble sculptures of the Monumental Cemetery of Cagliari. In bold the optimal growth temperatures.

CCFEE strain n.	Temperature (°C) 0	5	10	15	20	25	30	35
5703	0,23 ± 0,02	0,33 ± 0,03	0,38 ± 0,03	0,54 ± 0,14	0,95 ± 0,12	**1,08 ± 0,11**	0,30 ± 0,02	0,12 ± 0,02
5704	0,15 ± 0,04	0,20 ± 0,02	0,27 ± 0,03	0,62 ± 0,26	0,83 ± 0,05	**0,93 ± 0,06**	0,30 ± 0,03	0,18 ± 0,03
5707	0,23 ± 0,03	0,4 ± 0,03	0,45 ± 0,03	**1,34 ± 0,11**	0,93 ± 0,03	0,75 ± 0,03	0,17 ± 0,03	
5710	0,37 ± 0,09	0,28 ± 0,09	0,30 ± 0,06	0,54 ± 0,14	1,03 ± 0,12	**1,25 ± 0,30**	0,27 ± 0,05	0,30 ± 0,06
5723	0,28 ± 0,04	0,3 ± 0,06	0,35 ± 0,05	0,63 ± 0,15	**0,67 ± 0,11**	0,50 ± 0,14	0,30 ± 0,06	0,23 ± 0,07
5736	0,35 ± 0,05	0,25 ± 0,08	1,92 ± 0,09	3,97 ± 0,45	**4,82 ± 0,97**	4,70 ± 0,98	4,17 ± 0,69	
5769	0,20 ± 0,06	0,28 ± 0,04	0,22 ± 0,07	0,36 ± 0,1	0,37 ± 0,05	**0,45 ± 0,1**	0,23 ± 0,05	
5770	0,13 ± 0,05	0,22 ± 0,07	0,28 ± 0,07	0,40 ± 0,1	**0,43 ± 0,05**	0,38 ± 0,07	0,20 ± 0,06	0,18 ± 0,07
5776	0,22 ± 0,07	0,37 ± 0,07	0,37 ± 0,07	0,82 ± 0,11	0,87 ± 0,15	1,03 ± 0,16	**1,07 ± 0,19**	
5778	0,43 ± 0,07	0,70 ± 0,13	0,95 ± 0,08	3,18 ± 0,33	**3,70 ± 0,35**	3,13 ± 0,30	0,37 ± 0,09	0,20 ± 0,08
5792	0,25 ± 0,05	0,40 ± 0,06	0,42 ± 0,07	1,14 ± 0,1	1,62 ± 0,10	**2,02 ± 0,22**	0,35 ± 0,08	0,30 ± 0,06
5793	0,47 ± 0,06	0,75 ± 0,08	1,08 ± 0,17	2,84 ± 0,36	**3,38 ± 0,24**	2,95 ± 0,19	0,20 ± 0,06	0,25 ± 0,05

balance of the original community, could become predominant and more detrimental with visible detrimental effects even years after treatment. In the meanwhile, the different dose/effect responses to biocides recorded gave new insights on the possibility to obtain a more effective treatment against these organisms, using a synergistic combination or more targeted biocides.

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*Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)*

Microbiological and molecular investigation in the Capuchin Catacombs of Palermo, Italy: Microbial deterioration risk and contamination of the indoor air

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ABSTRACT: The Capuchin Catacombs of Palermo contain over 1800 preserved bodies, spanning the 16th–20th centuries AD, many of which show serious evidence of biodeterioration. In order to protect these remains, an extensive microbiological and molecular investigation was recently performed. Samples were taken from skin, muscle, bone, hair, clothes and stuffing materials, as well as from the surrounding wall materials, many displaying rosy discoloration. In addition, air samples were taken to investigate the impact of this microbial contamination on the indoor air quality.

Results showed that the mummies are heavily contaminated with moulds. In some areas of the crypt the fungal spores in the air reached more than 2000 spores/m^3, classified as being of potential health risk to visitors. Molecular analysis showed complex microbial communities colonizing the mummies and the surrounding walls, consisting of bacteria, archaea and fungi. Halophilic microorganisms were dominant, being responsible for the rosy discoloration observed. Fungal sequences revealed pathogenic fungi related to the deterioration of the mummies.

1 INTRODUCTION

Ancient mummies have already been investigated using molecular methods, contributing to the rise of a new field called molecular paleontology (Marota & Rollo 2002). A particular sector within mummy studies is the investigation of the DNA of ancient microorganisms, which improves the knowledge of issues such as the spread of diseases (Zink et al. 2002), the mummification mechanisms involved (Rollo et al. 2000), and the effect of diet on human paleopopulations (Cano et al. 2000). However, literature regarding the opportunistic microorganisms and their ability to colonize and deteriorate ancient bodies is scarce. There are few well-known examples demonstrating the colonization of mummified remains by opportunistic fungi, one such case being the restoration of Ramses II carried out in Paris during the years 1976–77. The mummy showed a dense fungal population with species belonging to the genera *Aspergillus* and *Penicillium* (Mouchacca 1985). The genus *Aspergillus* was also dominant amongst the microflora of the air and dust of the Egyptian mummy chamber at the Baroda Museum in India (Arya et al. 2001). In a recent study, molecular analysis enabled the detection of the *Clostridium* species related to the putrefaction of human remains (Jurado et al. 2010).

Figure 1. Mummies displayed along the sides of the corridors of the Catacombs of Palermo (a). Biodeterioration caused by moulds (b) and insects (c).

The Capuchin Catacombs of Palermo were founded at the end of the 16th century AD as a burial site for deceased friars. Mummified bodies were placed there between 1599 and the early 20th century AD (Piombino-Mascali et al. 2010). The Catacombs form an impressive site where over eighteen hundred bodies, many of which still retain soft tissue, are displayed along the sides of the corridors or stored inside coffins (Fig. 1a). These mummies are mainly the result of a spontaneous-enhanced preservation mechanism (Aufderheide 2003). Shortly after death, bodies were taken to special preparation rooms, and laid on terracotta pipes to allow draining of the corporeal fluids and to promote spontaneous desiccation of the cadavers. The rooms were then sealed for about a year, after which time the corpses were exposed to the air, washed with vinegar, and dressed. Some bodies were also preserved through anthropogenic methods, such as dipping into lime or arterial injections with special chemicals (Piombino-Mascali et al. 2010). Today, many of the mummies show signs of severe deterioration, mostly due to moulds and insects (Figs. 1b, c).

In order to assess the preservation and contamination of the human remains in the Capuchin Catacombs of Palermo, a complex sampling campaign was devised in which the air, the surrounding walls, and materials from the mummies themselves were investigated. Samples were analyzed by conventional cultivation techniques alongside molecular methods, including direct DNA extraction, PCR-based DGGE fingerprints, combined with clone libraries and sequencing analysis.

2 METHODOLOGY

2.1 *Sampling*

Samples from human remains, such as skin, muscle, bone, hair, clothes, stuffing materials and surrounding wall materials were obtained using forceps and scalpels. The samples appeared to be heavily damaged by moulds, insects and a massive rosy discoloration present on the walls. Air samples were taken and analyzed both quantitatively and qualitatively (air sampler MAS 100 eco, 2% MEA, DG18), in order to investigate the impact of microbial contamination on the indoor air quality.

2.2 *Cultivation*

Fungi collected from the air samples on filters (Sartorius, Germany) were isolated upon 2% MEA 2% and DG18 (Merck, Austria). Pure cultures were identified based on their morphology and sequencing of rDNA (ITSI-5.8S-ITSII). In addition, three different media containing 3%, 10% and 20% of NaCl respectively (Ettenauer et al. 2010) were used for the isolation of halophilic microorganisms. Flasks were incubated aerobically at room temperature (22 ± 3 °C) over a total period of four weeks. After three days and later, once per week, aliquots were serial diluted and plated onto the same solid media and under the same conditions to the isolation of pure cultures.

2.3 *Molecular analyses*

DNA was directly extracted from human remains and wall materials as described by Piñar et al. (2012). DNA crude extracts were further purified with the QIAamp Viral RNA mini kit (Qiagen, Hilden, Germany) following the manufacturer's instructions, and used for PCR-based DGGE fingerprint analysis of the archaeal and bacterial 16S rDNA (Piñar et al. 2001; Schabereiter-Gurtner et al. 2001) and Internal Transcribed Regions (ITS) (Michaelsen et al. 2006). Clone libraries from these amplified fragments were screened by DGGE and selected clones were sequenced (Schabereiter-Gurtner et al. 2001).

3 RESULTS AND DISCUSSION

Concerning the indoor air quality, in some areas of the crypt the amount of fungal spores present in the air exceeded 2000 spores/m^3. Medically, this amount must be classified as posing a potential health risk to visitors.

First observations showed a massive rosy discoloration of the Catacombs' walls (Fig. 2a), which are in direct contact with the surrounding soil. The water migrating horizontally into the walls carries a huge load of soluble salts, including chlorides. Due to changes in physical parameters, salts from the solution precipitate at the exposed surface, creating the so-called salt efflorescences (Fig. 2b). This phenomenon is causing material losses and destruction due to cracking and detachment of the walls, which are accumulating on the surface of the coffins and mummies, producing further contamination of these materials. Moreover, the salt creates an environment for the settlement of halophilic microorganisms (Piñar et al. 2009), which could be isolated from all wall samples, many of them showing red pigmentation (Fig. 2c), directly related to the color of the walls.

On the contrary, the surface of many mummies—including the heads and clothes—was heavily contaminated with moulds. There was superficial growth of fungi, but also a deep infection of skin, remains of muscle fibers and stuffing material. Thirty-three fungal species were found on and inside the mummy materials, some were common airborne fungi and some originating from the material used as stuffing in the clothing of the mummies.

Molecular techniques, including direct DNA extraction from all different materials, PCR amplification using specific primers for bacteria, archaea and fungi and further DGGE-fingerprinting enabled the detection of complex bacterial communities colonizing all types of samples. In contrast, fungi were only detected in the samples taken directly from the mummies, but were absent in the wall samples. This can be explained by the fact that the growth of hyphomycetes is generally suppressed by high salt stress. In addition, archaea were only detected on wall materials and on bone, most probably due to the contamination of the latter material by the salt detached from the wall.

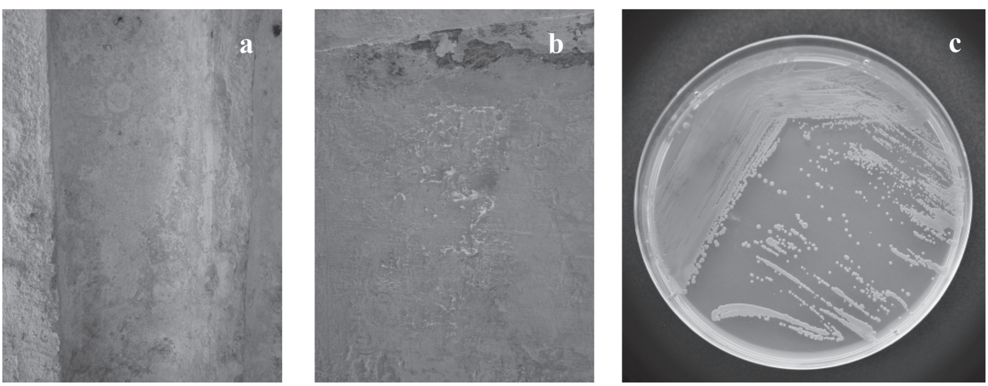

Figure 2. Rosy discoloration (a) and salt efflorescence (b) observed on the Catacombs' walls. Bacterial strain isolated from the walls showing red pigmentation (c).

Sequencing analyses showed coherent results with our previous observations. Among bacteria, halotolerant and halophilic species of the Gamma-proteobacteria dominated, as sequences related to the genera *Halomonas*, *Chromohalobacter* and *Salinisphaera*. In addition, sequences related to pathogenic bacteria belonging to the order *Clostridiales* were detected on samples derived from the mummies.

The detected archaeal sequences were closely related to different uncultured archaeons in addition to the cultured genera *Halococcus* and *Halobacterium,* already recorded from other salt-attacked monuments (Piñar et al. 2009).

Among fungi, pathogenic species of the genus *Phialosimplex* dominated on samples derived from the mummies. These species have been described as the causative agents of fungal keratitis (Hsieh et al. 2009).

4 CONCLUSIONS

This study provides an initial insight into the problems facing the human remains located in the Capuchin Catacombs of Palermo. The complex sampling campaign performed at the Catacombs and the strategy used for the analysis of samples, combining conventional cultivation and molecular techniques, contributed to the success of this investigation. Firstly, the indoor air quality showed a very high concentration of fungal spores/m^3 with levels significant to pose a potential health risk to visitors. Secondly, the environmental conditions at the Catacombs have allowed the formation of salt deposits on the walls, which offer a special habitat for very specialized halophilic microorganisms. Salt cracks are detaching and contaminating the surfaces of other mummy materials, as clothes, hairs and bones, allowing the settlement of halophilic microorganisms also on these materials. On the other hand, pathogenic bacteria and fungi, well-known for their keratinolythic activities, were detected on and inside the mummy materials. These microorganisms can be directly related with the deterioration suffered by the mummies. Finally, the presence of insects is worth mentioning, which are mainly contributing to the deterioration of the coffin wood and the clothes of the mummies.Simple measurements such as an optimal ventilation, the cleaning of dust and detached salt, and the installation of insect traps, will help achieve improved conservation of the mummies. The application of further disinfectant treatments to combat mould formation and growth will be decided by future restorers.

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Physical and aesthetical decay of built heritage from biological films developed on joint mortars

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ABSTRACT: Porous stone materials can be affected by lithobiontic communities' colonization responsible for physical-chemical processes that lead to their biodeterioration. In urban areas with high levels of atmospheric pollution, in the aesthetical decay of facades due to soiling by particulate matter deposition, the development of biological films must be considered. The biodeterioration processes affecting the joint mortar used on the limestone facades of the Formerly Workers Hospital of Maudes (Madrid, Spain) and its contribution to facades soiling are studied. Lichen thalli are directly involved in the material disruption and foster significantly the degree of darkening. While limestone darkening is very heterogeneous and mainly responds to its interaction with air pollutants, for the joint mortar it is much more homogeneous and, in areas of higher humidity and with no direct pollution exposure, is due to a biofilm development. In all other areas where joint mortar shows darkening, this is mainly because of its interaction with air pollutants.

1 INTRODUCTION

Porous stone materials can be affected by lithobiontic communities' colonization responsible for physical-chemical processes that give rise to their biodeterioration, also contributing to the loss in aesthetical value of built heritage (Viles & Gorbushina 2003). Thus, in urban areas with high levels of atmospheric pollution, in the aesthetical decay that occurs in facades due to soiling by particulate matter deposition (Grossi & Brimblecombe 2008), the development of biological films must be considered (de los Ríos & Ascaso 2005, Thornbush & Viles 2006). The texture and composition of building materials, its state of preservation, its location at constructions and/or the environmental agents determine its resistance to microbial colonization (Lisci et al., 2003). Mortars are very susceptible materials to biodeterioration processes, mainly due to its high porosity and because they are usually located in areas where moisture is retained (de los Rios et al., 2009). This study focuses on biodeterioration processes affecting the joint mortars used on the limestone facades of the Formerly Workers Hospital of Maudes (Madrid, Spain), built by architect Antonio Palacios between 1908 and 1916. The building layout consists of four naves arranged in a rotate cross around a courtyard and its façades design displays many set backed elements. The limestones used are classified as biomicrites, pelmicrites and biopelmicrites (Folk 1962), from the Southeast of the region. The stone blocks show a rough surface. Largely due to the urban environment that surrounds the building, the main decay forms observed are related to blackening processes, with the development of black crusts (Perez-Monserrat et al., 2011). Joint mortars also showed these black crusts, as well as cracking and disruption. Moreover, the joint mortar located in upper areas, a lime and cement one with silica aggregate with a total mercury accessible porosity value of 17%, mainly displayed the development of biofilms. Between 2006–2008, the facades were restored, the limestone was cleaned and the joint mortars were entirely removed, being repointed by a new lime mortar.

2 MATERIALS AND METHODS

The interaction of the former joint mortar with colonizing microorganisms has been analyzed by means of Scanning Electron Microscopy with backscattered electrons (SEM-BSE). This technique allows the study of organisms *in situ*, without removing them from the substratum where they have developed (Wierzchos & Ascaso 1994). The contribution of the joint mortar biological colonization to the facades darkening is quantified through the comparative analysis of the chromatic parameters of the surface limestone with respect to the mortar by means of Spectrophotometry. The CIELab (1986) chromatic parameter lightness (L*) and the white (WI) and yellow (YI) indices defined by ASTM standards have been considered. *In situ* surface color measurements have been performed, using a MINOLTA CM-2002 spectrophotometer with CIE Standard Illuminant D65 and a 10° observer angle. Four vertical levels have been set up in the facades: socle and bottom, medium and upper levels. When selecting the stone blocks to measure, factors such as the front plane of facings where they are located and their degree of protection were considered.

3 RESULTS AND DISCUSSION

3.1 *Interaction of joint mortar with colonizing microorganisms*

By means of the SEM-BSE technique, it is observed that mortar colonization mainly corresponds to crustose lichens that grow directly from the binder, and to chasmoendolithic lichens entering into the fissures and/or pores. Epilithic lichen thalli are arranged completely attached to the mortar (Fig. 1a, b). Towards the surface, an outermost zone (1) and an inner one (2) are observed. In the former, with an important degree of disruption, the mortar is embedded by thallus, while fungi begins to colonize it in the later, that displays a better conservation state. Mortar colonization by black yeasts takes place in favor of previous existing cracks. These fungi are entering in pores and/or fissures connected to the surface, continuing its colonization by the cracking of mortar (Fig. 1c).

SEM-BSE technique revealed how the lichen thallus anchoring fosters the mortar breakdown, as cracks formation is linked to its attached structures (de los Ríos et al., 2004). Wet-dry and/or freeze-thawing processes may also participate in the mechanical effects produced by microbial colonization, since they could change the lichen thallus volume (Saiz-Jimenez & Ariño 1995, Ascaso et al., 2002). The lichen hyphae growth produces significant stresses, because by penetrating into the mortar cracks hastens the gradual separation of aggregate and binder off. Wetness promotes this process significantly, allowing the lichen thallus hydration and, therefore, the widening of the cracks where they have penetrated. Besides, the moisture in the fissures encourages endolithic colonization (de los Rios & Ascaso 2005). On the other hand, the black yeasts are slow growing black microcolonial fungi typical of urban environments, which provide very dark shades to building materials and entail an important agent of decay (Gorbushina et al. 1993).

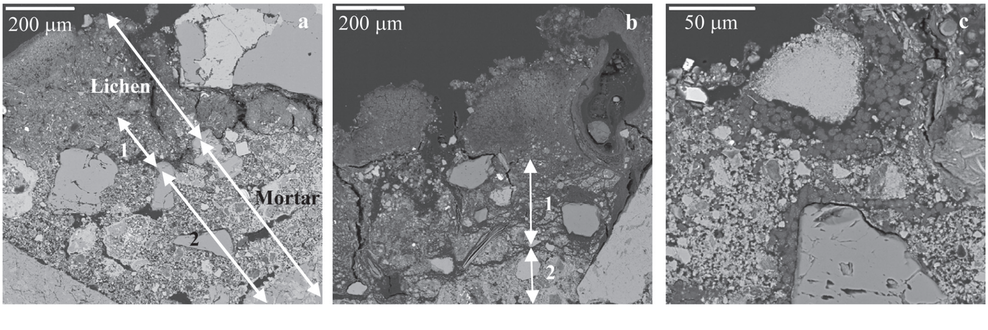

Figure 1. SEM-BSE images of the joint mortar colonization: a) Crustose lichen-mortar interface, b) Mortar disruption by the anchoring of epilithic lichen thallus, c) Mortar colonization by black yeasts.

3.2 *Contribution of biological colonization to the facades darkening*

Before the last restoration works on the facades (2006–2008), the main decay forms that limestone displayed were related to soiling and blackening processes. The building showed an important aesthetical decay and the joint mortars contributed significantly to the darkening degree of the facades. On joint mortars located in areas of higher humidity and with no direct pollution exposure, their blackening was due to a biofilm development. In all other areas where joint mortar showed darkening, this was mostly because of its interaction with air pollutants. This process involves black crust formation on joint mortar as well and, on site, it looks very similar to the biofilm studied (Arnold & Zehnder 1990).

Limestone darkening was very heterogeneous and mainly responded to its interaction with air pollutants, to the rusticated finishing blocks and to the own passage of time (Perez-Monserrat et al. 2012). Table 1 shows the values of lightness and white and yellow indices (before the cleaning operations) measured on the limestone blocks that shape the Northeast facade of the building, facing diagonally to the street with the highest intensity of traffic that borders the property. The high heterogeneity of the stone blackening is also conditioned by the parallel or diagonal exposure of the blocks to traffic (a), by the advancing plane of the facade (b), by its more or less protected position (c) and by the height where they are located in (d). In areas of higher humidity and with no direct pollution exposure, the biofilm developed on joint mortar conferred a homogeneous and intense blackening (Table 2), that darkened significantly the mortar and the area

Table 1. Color measurement of limestone blocks on Northeast façade of the building and some of the variables considered.

		L		WI		YI				
		Mean	Std	Mean	Std	Mean	Std	b	c*	d
Limestone without darkening		75.58	3.19	13.85	7.01	18.20	3.15			
Socle	1	68.00	4.44	8.92	4.86	19.40	2.49	4/5	0	0
	2	66.94	5.31	9.73	2.40	18.50	0.37	4/5	0	1
Bottom level	1	60.23	8.61	4.35	6.41	22.47	5.00	1/5	0	1
	2	65.00	8.31	6.73	9.18	20.93	5.93	4/5	0	1
	3	51.47	4.38	4.41	2.63	19.60	3.25	3/5	1	1
Medium level	1	63.77	9.80	7.34	6.76	20.18	4.27	4/5	0	2
	2	55.90	5.05	2.78	3.93	22.65	3.14	1/5	0	2
	3	52.63	2.46	–1.66	1.03	27.02	1.29	1/5	1	2
Upper level	1	54.17	10.03	–0.11	7.31	26.63	5.82	4/5	1	3
	2	49.62	9.51	3.41	3.49	21.06	3.04	5/5	0	3
	3	61.26	11.07	7.10	4.89	19.76	2.15	1/5	1	3

Variable "a" is 45º for all measurements, as this facade is oriented diagonally to traffic.
* 0 means no shelter limestone block and 1 shelter one.

Table 2. Color measurement of the joint mortar studied.

		L		WI		YI	
		Mean	Std	Mean	Std	Mean	Std
Mortar without biofilm		77.76	0.23	19.88	0.61	15.68	0.23
Mortar with biofilm	1	43.04	0.49	3.00	0.36	19.40	0.53
	2	45.85	1.34	2.91	0.62	20.22	1.32
	3	45.96	0.47	3.20	0.49	19.80	0.93
	4	44.90	1.77	2.61	0.37	20.50	1.03
	5	47.46	1.12	2.86	0.23	20.68	0.58

where it is located. Although these biofilms were developed in very specific areas, not particularly visible because of their location, their high dark hue entailed significant aesthetical decay.

4 CONCLUSIONS

This paper provides information on the effect of biological colonization in joint mortars, entailing the implementation of the SEM-BSE technique in such materials, widely used in built heritage. The technique allows confirming that the biofilm corresponds both to epilithic lichen as endolithic lichens and free-living fungal colonization. Lichen thalli are directly involved in the mortar disruption, leading to the decohesion of its components. The high porosity of the ancient mortars promoted the lithobiontic community colonization. These factors, along with the location of the mortar in the building, highly exposed to environmental decay agents, in an urban environment, and the passage of time have hastened their disruption. Besides, lichen thallus foster significantly the degree of darkening that facades showed before its cleaning. The biofilm conferred a very intense and homogeneous dark hue to the ancient joint mortar located in the upper level, with significant moisture. Its removal was considered necessary, mostly for improving the aesthetic appearance of the facades.

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Indoor pollution and metal corrosion by organic acids: Case study of the Oteiza Museum (Spain)

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ABSTRACT: Organic acids, mainly acetic and formic, are known to be significant pollutants in the museum environment. These acids are emitted from construction materials, such as wood, paints, varnishes, etc. and cause degradation and corrosion of several materials such as metals. This research presents a case study of the measurements of these acids and its corrosivity in the Oteiza museum in Navarra, Spain. Two display cases were selected where passive sampling was carried out for measuring the concentration of these acids while copper and lead coupons were exposed to evaluate the corrosivity of the atmosphere. Results showed that acids concentrations were elevated and significant corrosion products were found on the metals surfaces. Based on these results, the museum conservator has implemented corrective measures to reduce the concentration of these acids. This collaboration between conservator and conservation scientist is the base to take efficient preventive conservation measures for assuring the museum collections.

1 INTRODUCTION

1.1 *Indoor pollutants: Are we aware about them?*

The concern about the presence of indoor pollutants in museums has increased lately due to the use of new materials for the construction of showcases as well as the wide trend on changing them when a new exhibition will take place. Usually, these materials are not tested and, even if they are labeled as "low emission materials", they do emit and can cause degradation in the objects inside the showcases. All these side-effects could be avoided if simple emission tests would have been carried out but the lack of practice, time, sometimes consciousness and, obviously, money, play against us. Moreover, it is important to know what kind of pollutants we have for keeping them under control and to understand the interaction of the pollutants with our objects.

1.2 *Organic acids and their effect on metals*

The main pollutants that take part in the degradation and corrosion of metallic cultural heritage are organic acids (basically, acetic and formic acids), and other factors as O_3, reduced sulfur compounds (HS, SOC), VOCs, RH and temperature, can react synergistically with them (Raychaudhuri & Brimblecombe 2000, deFaria et al. 2010). These pollutants are emitted from the showcases construction materials and mainly affect lead and copper based metals.

Measurements of these acids and assessment of their effect on metallic heritage have been carried out in museums in northern Europe, UK and the USA, but as far as the authors' known, no studies have been made in museums in Spain or in the southern Europe in general.

2 CASE STUDY: OTEIZA MUSEUM (SPAIN)

Jorge Oteiza (1908–2003) is a basque artist who worked in different disciplines as Sculpture (that is the field by which he is more known), Paint, Architecture, Poetry, Aesthetic, Film, Anthropology, Education or Politics.

The Museum is located in one of the slopes of Alzuza (Navarra, Spain) and connects different spaces where his house-workshop and the museum galleries are the main ones. Above all, the museum has sculptures, some of them stored inside showcases, where we performed our tests:

(i) In one showcase—OT-I–, in the exhibition room called "laboratorio experimental", on the first floor, where the sculpture group "desocupación de la estatua", basically made of lead, tin and cork, is located. This showcase is made of MDF, painted with acrylic paint and the door frame is made of oak. It has three aeration grilles (Fig. 1, left side).

(ii) Inside the case number five in the storage—OT-II–, in the basement. The sculptures inside this case are made mainly of lead, tin, cork and chalk. The case is made of stainless steel painted with epoxy paint, shelves are made of stainless steel and the door is made of glass (Fig. 1, right side).

3 OBJECTIVES

The objectives of this study are: to measure the organic acids inside the two places that have been mentioned and to measure their corrosivity as well, in order to develop a preventive conservation plan to stop the deterioration of the objects and to avoid further conservation problems.

4 METHODOLOGY

In order to measure the concentrations of acetic and formic acid inside the two chosen spaces, a passive sampling technique using Palmes tubes, has been utilized (Palmes et al. 1976, Gibson et al. 1997). The exposure time was 14 days and two tests were carried out: first of all, Test I, for measuring initial pollutants concentration; second time, Test II, after implementing some corrective measures (periodic cases ventilation), for checking whether the pollutants concentration has been reduced and it can be considered under control.

During Test I, two Cu and two Pb coupons of high purity were displayed at the same time as the Palmes tubes inside the showcases for measuring the corrosivity. In this case, the exposure time was eight weeks.

They were displayed on a methacrylate base, leaving both sides exposed to the air, for comparing the influence of particle deposition in the corrosion. Corrosivity understood as the ability of one atmosphere to produce corrosion (ISO 2009) was determined by gravimetry,

Figure 1. Photograph of the exhibition room (on the left) and the storage (on the right).

weighing the coupons before and after the test using an analytical and digital balance. Color change was also measured with a colorimeter, using an observer angle of 10º and illuminant D65, and expressing the color changes in CIE L*a*b (where color is represented by three parameters from 0–100: L* which is luminosity, a* the position in the axis green-magenta, b* in the axis blue-yellow). Moreover, some lead coupons have enough corrosion products after the test for analyzing them by X-Ray Diffraction (XRD).

5 RESULTS AND DISCUSSION

Table 1 summarizes the organic acids concentrations before and after implementing some conservation measures in order to reduce the pollutants and, therefore, their consequents hazards: Results show high concentrations of organic acids, taking into account Tétreault's NOAEL guidelines (Non Observable Adverse Effect Level): at 54% RH for Pb below 0.1 ppm for both acetic and formic acids (Tétreault et al. 2004). In the literature, concentrations of acetic acid have been higher than formic ones but, in the case of OT-I, is the other way around (Grzywacz & Tennent 1994).

Regarding corrosivity, Figures 2 and 3 show gravimetric and colorimetric results for Cu and Pb coupons, respectively. Pb seems to increase its M more than Cu when organic acids are present. On one hand, colorimeter information is very valuable in both cases, above all in L* axis but, regarding Cu, the a* axis gave us information about the earlier stages of corrosion which is related with the formation of cuprite. On the other hand, in the case of Pb, the b* axis showed the beginning of the formation of the corrosion products. These corrosion products were identified by XRD as lead formate.

This high formic acid concentration can be related with the showcase paint emissions and, in both OT-I and OT-II, we presume that the sculptures inside, themselves, emit a significant amount of acetic acid. In OT-I, the showcase itself is another obvious source of acetic acid because is made of wood.

As far as we can see, the concentration of acids in the showcase where more degradation problems in the objects had been observed (OT-I) has been reduced on behalf of the

Table 1. Organic acids concentrations after the two tests performed.

	OT-I (ppm)*		OT-II (ppm)	
Test	Acetic	Formic	Acetic	Formic
I	1.1	1.3	0.1	ND
II	0.3	0.6	ND	ND

* At an atmospheric pressure of 1 atm and temperature of 20ºC.

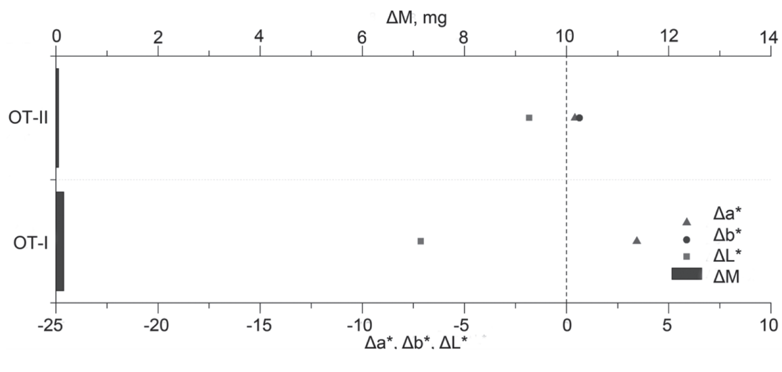

Figure 2. ΔM, Δa*, Δb*, ΔL* Cu coupons.

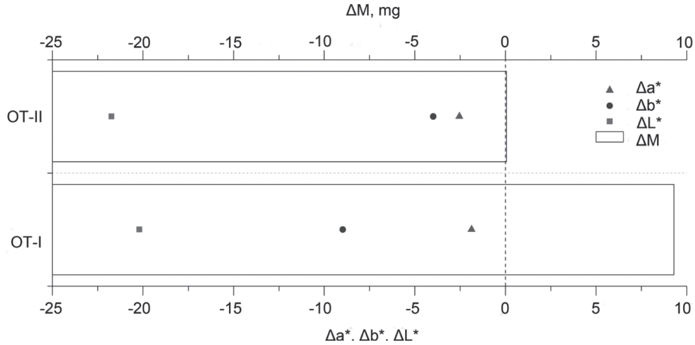

Figure 3. ΔM, Δa*, Δb*, ΔL* Pb coupons.

conservation measures as simple ventilation. Anyway, its concentration is still above the NOAEL. In the other hand, OT-II, has reduced the acetic acid concentration.

6 CONCLUSIONS

The causes of the corrosion problems in the Oteiza Museum are the organic acids, whose concentrations were rather high in comparison with some preventive conservation guidelines (NOAEL). Gravimetric and colorimetric techniques were useful to measure the corrosivity of the two showcases using Pb and Cu coupons. The main sources of these pollutants were the showcases themselves (wood and paints), as well as the sculptures inside them. Implementing simple, easy and economic preventive conservation measures as ventilating the showcases can reduce pollutants concentrations. Since organic acids concentrations after the ventilation were still above the NOAEL in the OT-I's showcase, new preventive conservation measures will be set up and its efficiency assessed performing new tests.

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The degradation of cellulose acetate: Advanced analytical tools for non-destructive study of design objects

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ABSTRACT: The preservation of design objects collections require an increase of knowledge regarding the constituent materials and innovative non-invasive imaging tools for a rapid, precise and not destructive assessment of the condition of historic objects. This study focused on the analysis of cellulose acetate: standard specimens have been studied and compared to a well-known Italian design lamp from '60s part of the *Triennale Design Museum* collection (Milano, Italy), the Nesso™ lamp produced by ARTEMIDE™. The aim of the work is to develop a protocol for material characterization and degradation patterns analysis and evaluate its efficacy for better understanding the cellulose acetate polymer support.

1 INTRODUCTION

Cellulose acetate (CA) has been widely used for a variety of consumer products including textiles, plastic films and disposable items. The degradation behaviour of CA was extensively studied, particularly in the context of the highly problematic preservation of photographic emulsions, while only few studies were conducted on moulded materials (Allen et al., 1987, Edge et al., 1990). A large number of design objects made of CA were produced during the last century and are now becoming part of design museums and collections. Their conservation is intimately linked to the knowledge about degradation mechanisms of polymers within museum environments.

In this work we present the results concerning an investigation on the degradability of reference CA under simulated conditions of ageing, with the final aim to understand the phenomena taking place on an industrial material produced in the '60s. Specifically, the analysed object, namely a Nesso lamp traded by ARTEMIDE™, is part of the *Triennale Design Museum* collection (Milano, Italy).

2 EXPERIMENTAL

Reference material and sampling. Reference CA (39.7 wt.% acetyl content, average M_n ~50000, determined by GPC) was supplied from Aldrich. Samples from the *Nesso* lampshade were collected from easily accessible but hidden areas.

Instrumentation. Fourier transform infra-red (FTIR) analyses were carried out with a Nicolet 6,700 spectrophotometer equipped with a DTGS detector or coupled with a Nicolet Continuum FTIR microscope equipped with an HgCdTe detector cooled with liquid nitrogen. Spectra of standard specimens were collected on films casted from 10% wt. polymer in dichloromethane solution on KBr windows in transmission mode, in the optical bench between 4000 and 400 cm^{-1}. Spectra of micro samples were recorded using a micro compression diamond cell accessory with the IR microscope, between 4000 and 700 cm^{-1}. All spectra were acquired with 128 acquisitions and 4 cm^{-1} resolution. Fluorescence excitation emission (EE) spectra were acquired using a quartz fibre-optic probe for both excitation and the collection of fluorescence emission. Spectra of CA thin films prepared by spin coating of 10% wt. polymer in chloromethane onto glass microscopic slides (76 × 26 mm) were acquired in Front Face geometry (23°) for both excitation and collection of emission on the optical bench. Excitation was provided by a Xenon arc lamp Fluorolog, Jobin-Yvon/Horiba; with variable excitation between 300 to 500 nm (resolution of 5 nm). EE spectra were generated using Matlab (Mathworks) (Nevin et al. 2009) and were plotted as contour plots with 20 different levels of intensity from the maximum (black) to 10% of the minimum intensity (white). Bands are reported in the text as (excitation wavelength/nm): (emission wavelength/nm).

Ageing treatments. Accelerated ageing was carried out under two different regimes: (1) thermal oxidative ageing at 60°C constant temperature in an air circulating oven, or (2) photo-oxidative ageing following the Italian Normative UNI 10925:2001 for artificial solar light testing.

3 RESULTS AND DISCUSSION

3.1 *Degradation behaviour of the reference CA*

Accelerated thermal-oxidative ageing of the CA films for times up to 2000 h led to moderate modifications of the FTIR spectra of the polymer (not reported), mainly due to the elimination of absorbed residual water molecules (decrease of the signals at 1640 and 3460 cm^{-1}), a moderate depolymerisation (slight decrease of the signal at 1050 cm^{-1}, related to the ν C–O–C glycosidic linkage) and a limited deacetylation of the cellulose rings (slight decrease of the signal at 1235 cm^{-1}, due to ν C–O–C acetate side chain). At the same time, the fluorescence properties of CA do not change during the thermal-oxidative treatment, thus confirming the good stability of the polymer under mild accelerated ageing through temperature increase.

On the other hand, the FTIR spectra of standard CA showed significant structural changes as a consequence of photo-ageing, and particularly, a general decrease of the signals of the entire spectrum possibly due to the elimination of volatile compounds. The spectra were normalized over the peak at 1370 cm^{-1} (δ C–H), assumed as constant during the first steps of ageing, in order to assess other spectral modifications (Fig. 1). More in detail, after 500 h irradiation the following modifications are visible: the intensity of the broad peak at about 3460 cm^{-1} (ν_a O–H) and the signal at 1050 cm^{-1} (ν C–O glycosidic linkage) decrease, whereas the signal at 1745 cm^{-1} (ν_s C = O) increases and broadens. These modifications suggest that the hydroxyl groups of CA are undergoing oxidation, with the consequent formation of new carboxyl groups; at the same time the depolymerisation of CA started by scission of the glycosidic bonds. For longer time of ageing the spectra show a slight depletion of the signal at 1230 cm^{-1}, suggesting that the deacetylation of the polymer is in progress; moreover the signal at 3460 cm^{-1} increases, indicating the formation of new OH groups possibly by hydrolysis.

The EE spectra of the photo-aged films show some variations of the emission signals with respect to the initially visible emission band at 318:374 nm and the fluorescence emission around 250:470 nm (Fig. 1b, c, and d) The band at 318:372 nm is bathochromically shifted towards longer wavelength and broadens during ageing. The progressive modification of the fluorescence behaviour of the CA polymer can be related to the increasing concentration of degradation products, which were documented by FTIR spectroscopy. The oxidation of the hydroxyl groups leads to the formation of new carboxyl groups, which are tentatively ascribed to the appearance of a new fluorescence maximum around 440 nm (Plitt & Toner 1961).

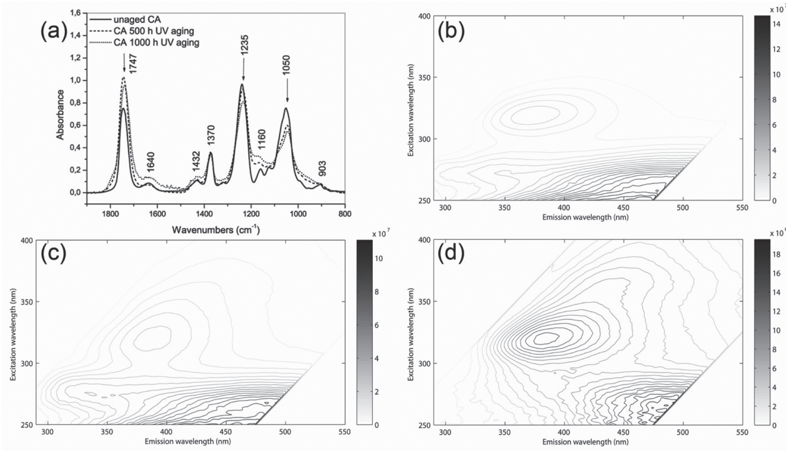

Figure 1. FTIR spectra of the reference CA before and after 500 h and 1000 h of photo-oxidative treatment in the range 2000–800 cm^{-1} (d); EE spectrum of the standard CA before (b), and after 100 h (c) and 2000 h (d) photo-ageing treatment, respectively.

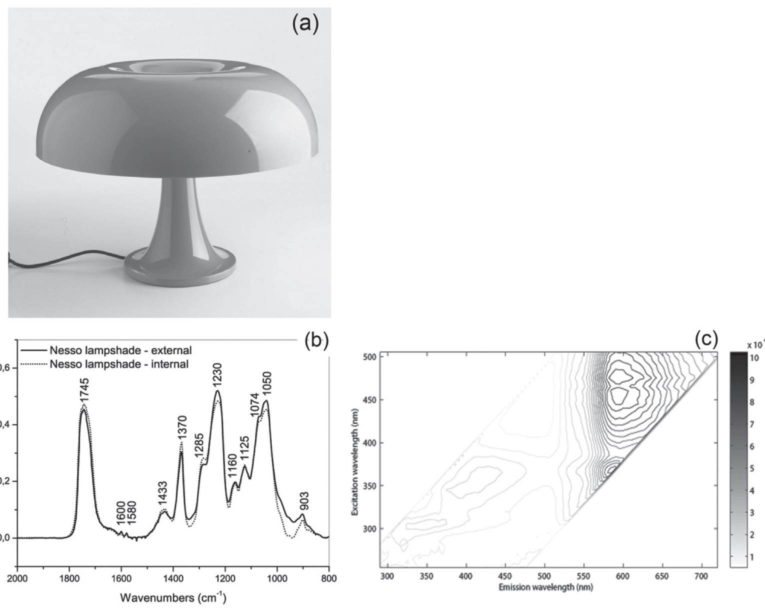

Figure 2. The *Nesso* lamp (a), FTIR spectra of samples from both sides of the lampshade, in the range 2000–800 cm^{-1} (b), and EE spectrum of the external side (c).

Moreover, after 500 h treatment the following modifications may be observed: a new fluorescence peak is observed at 365:480 nm and that centred at about 250:470 nm is bathochromically shifted towards 275:490 nm. This behaviour suggests that the ongoing oxidation of the hydroxyl groups, detected by FTIR spectroscopy, leads to the formation of new fluorophores which are highly unstable and are lost with further light exposure.

3.2 *Analysis of the* Nesso *lampshade*

Spectra collected from internal and external side of the lampshade (Fig. 2a) were compared in order to assess the difference in the polymer deterioration, due to the different exposure conditions. The micro-FTIR spectra of both samples are similar to each other, and only few additional signals were visible with respect to the reference CA. (Fig. 2b). Such new features include the presence of absorption bands at 1580 and 1600 cm^{-1} (aromatic ring skeletal vibration), 2983 cm^{-1} (ν C–H), 1444 cm^{-1} (δ C–H) and the two shoulders at 1283 (νa C–OC) and 1074 cm^{-1} (νs CH–O), all of theme suggesting the presence of a phthalate plasticizer. The degradation phenomenon is slightly more pronounced in the internal side of the lamp, and may be due to its exposure to artificial lightening, with moderate signs of deacetylation (depletion of the signal at 1230 cm^{-1} and increase of the OH stretching peak at 3460 cm^{-1}) and depolymerisation of the cellulose (depletion of the signal at 1050 cm^{-1} due to the glycosidic linkage).

The EE spectra collected from the internal and external surfaces of the Nesso light diffuser are similar, confirming the homogeneity of the analysed polymer suggested by FTIR data. In particular, the spectra are dominated by the strong fluorescence emission at 590 nm, due to an orange colorant, perhaps the perylene red discussed in a previous work (Toja et al. 2010). Another weak signal, centred at 305:345 nm, was ascribed to the presence of the phthalate plasticiser. Finally, a very weak peak centred at 345:395 nm was attributed to the presence of unknown additives or to fluorescent species which accumulate with the onset of oxidation, as also observed in the evolution of the fluorescent properties of standard polymer (Fig. 2c).

4 CONCLUSIONS

The study of behaviour on simulated ageing of standard samples allowed highlighting the main degradation processes involved in the oxidation of CA. Additionally, the analysis of micro-samples from the *Nesso* lampshade allowed to identify the constituent material, i.e. plasticized CA, and evaluates its actual state of conservation.

Standard CA specimens proved to be stable under mild thermo-oxidative treatment during the entire investigated temporal range. By contrast, photo-oxidative treatment leads to significant molecular modifications which include the depolymerisation of cellulose, the deacetylation and finally the oxidation of OH groups. As a result of deacetylation, a temporary yellowing of the material and the development of a new fluorophore at 365:480 nm was observed. The oxidation of the polymer proceeds during the ageing treatment and can be correlated with the development of the signal at 318:372 nm and its gradual bathocromical shift.

The analyses of the Nesso lamp suggest that the CA collected from the internal side of the lamp is slightly degraded, due to initial deacetylation and depolymerisation. The molecular characterization and the degradation processes taking place in the lamp were observed by both FTIR and fluorescence spectroscopy and the results were in good agreement.

The results obtained in the analysis of CA encourage the use of fluorescence spectroscopy in combination with FTIR spectroscopy as reliable methods for the assessment of the condition and the early evaluation of degradation phenomena in the analysis of polymeric design objects. The combined use of imaging techniques and micro-invasive spectroscopy allow the assessment of degradation process since the early stage and permit a continue monitoring of the conservation condition reducing or even avoiding sample collection. Data from the controlled ageing of standard materials is essential for supporting the interpretation of the phenomenon on the real cases. In order to improve the effectiveness of the proposed methodology, future work will focus on the creation of a data-base of polymers and additives.

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Rogerio-Candelera, Lazzari & Cano (eds)

Characterization of decay products and building materials on the ancient wall of Vitoria-Gasteiz using micro analytical instrumental techniques

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ABSTRACT: A complete analysis of the ancient walls of Vitoria-Gasteiz was achieved in order to study the state of conservation. In situ Raman and EDXRF analyses in combination with laboratory techniques (SEM-EDS, FTIR) revealed that this monument is suffering sulphation processes due to the proximity of a road. The presence of lead sulphate in the back crust is also noticeable.

1 INTRODUCTION

1.1 *The medieval city walls of Vitoria-Gasteiz*

If we have to talk about environmental care and Cultural Heritage, the city of Vitoria-Gasteiz (Spain) should be mentioned as an European model in Cultural Heritage protection and sustainable environmental policies. In fact, the city has been awarded as "The European Green Capital 2012". The city is immersed in a complete urban transformation and the mentioned environmental policies have been linked to the Cultural Heritage protection. That is the case of the well known old cathedral (Santa María) and, more recently, the city walls, both placed in the medieval downtown, preserving the architectural structure and design of the antique city. The case of the medieval city walls is a good example of how the protection of the Cultural Heritage can be used in everyone's benefit because a green area has been set in the middle of the medieval downtown around the walls.

Vitoria-Gasteiz was developed from the very begging as a fortified settlement. At the end of eleventh century the city walls started to be built and were completely finished during the twelfth century. By thirteenth century, the population had to go beyond the city walls and the city grew around them with the streets devoted to each guild, acquiring its characteristic almond-shape that still preserves. Even though they were "forgotten" for many years, the city walls have been the mainstay around which the modern city has been growing. Due to their social and urban importance, at the end of the twentieth century they were "rediscovered" and completely restored. All along the history of the walls, they have suffered many transformations (see Fig. 1). The most important modifications took place during the fourteenth-fifteenth, sixteenth and nineteenth-twentieth centuries. The body of the walls is made of calcarenite stone, whereas the corners are made of lumaquela limestone and argillaceous limestone was used for the foundations.

1.2 *The effects of urban pollution*

Even though Vitoria-Gasteiz has been awarded because of its sustainable environmental policies, its monuments suffered the effects of acid gases (traffic and heavy industry), smog, particulate matter, etc. The most important impacts are the dry and wet acid gases depositions

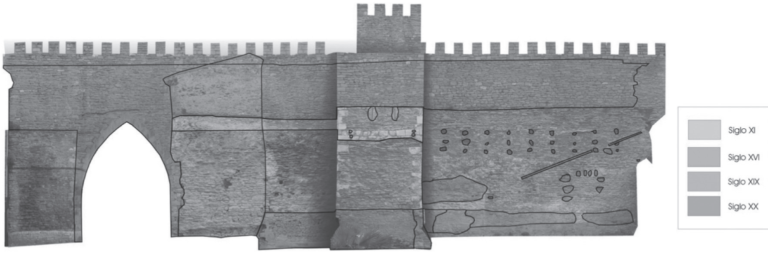

Figure 1. Scheme of one part of the city walls, where the modifications of the last centuries are visible.

over carbonaceous materials, which promote their degradation (Massey 1999). These acid gases can interact with basic anions, dissolving the stone by developing soluble salts. The presence of these salts can also degrade the construction materials, as it has already been described in literature (Tsui et al. 2003). One of the most visible effects of crystallization of soluble salts is the formation of the black crusts, which are mainly composed by calcium sulphate, soot, heavy metals and other compounds in less quantity. In fact, the presence of metals favours the formation of calcium sulphate (Zappia et al. 1998).

The objectives of the present work were to study the state of conservation of the city wall of Vitoria-Gasteiz, to determine whether the visible sulphation process was just punctual or spread, and to try seeing the effects of the road close to the wall.

2 EXPERIMENTAL

2.1 *Sampling*

The sampling area was limited to the first stretch of the wall. Close to this stretch there is a road with moderate traffic density. The study was performed in two parts. First, an in situ analysis was carried out by Raman and EDXRF handheld systems. Then, taken into account the obtained results, several samples (black crust, efflorescences, etc) were taken and sent to the laboratory in order to (a) be directly analysed by Raman and FTIR spectroscopy as well as SEM-EDS and (b) be extracted with water to mobilise the soluble ions and determine its concentration by ion chromatography.

2.2 *Analytical techniques*

In situ Raman analyses were carried out with a handheld InnoRam spectrometer (B&WTEK) equipped with a diode 785 nm laser. The spectrometer works in a spectral range from 65 to 2980 cm^{-1}. The maximum laser power of the system is 300 mW. Almost 400 spectra were taken with a measurement time varying from 0.5 to 10 seconds, in a spectral range from 100 to 2200 cm^{-1} and with a number of accumulations varying between 20 and 200. The laser power was reduced to 10% in order to avoid any thermal photodecomposition of the analysed materials. Laboratory Raman analyses were done by using a Renishaw RA100 System coupled to a micro-probe (785 nm excitation laser, CCD detector). Neutral density filters (1% and 10%) were used to attenuate the laser power on the samples (between 1 and 10 mW). The head of the micro-probe implements a 20X enlargement objective as well as a micro-video camera that helps to focus on the area under analysis.

A Jasco 6300 FTIR system was used in transmittance mode for IR analyses between 400 and 4000 cm^{-1}, at a resolution of 4 cm^{-1} and accumulating 30 scans per spectrum. Pellets were prepared under 10 tons pressure by mixing approximately 0.5 mg dry sample with 150 mg KBr.

Raman and FTIR spectra were processed by the Nicolet Omnic 7.2 software and the identification was based on a comparison of the recorded spectra with those of several spectra library such as e-VISART (Castro et al. 2005) or RRUFF (Downs 2006).

Elemental in situ analyses were carried out with a hand-held X-MET5100 EDXRF spectrometer (Oxford Instruments) equipped with a rhodium anode X-ray tube (operating at 45 kV). The instrument has a high resolution silicon drift detector (SDD). The measurements were taken in 50 seconds counting time.

SEM-EDX measurements were carried out to obtain the elemental distribution maps in the cross-sections of the samples and were performed using an EVO40 scanning electron microscope (Carl Zeiss) coupled to an X-Max energy-dispersive X-ray spectrometer (Oxford Instruments). EDX analyses were carried out using a working distance of 8–10 mm, a I Probe of 180 pA, an acceleration potential of 20 kV and 10 scans.

The ions from the soluble extracted salts were quantified by a Dionex ICS 2500 ionic chromatograph with an ED50 suppressed conductivity detector. Anions such as Cl^-, F^-, SO_4^{2-}, NO_3^- and PO_4^{3-} and cations such as Na^+, K^+, Mg^{2+}, Ca^{2+} and NH_4^+ were analysed. Details about the extraction methodology and chromatographic conditions can be found elsewhere (Prieto-Taboada et al. 2012).

3 RESULTS AND DISCUSSION

3.1 *In situ analyses*

In situ Raman analysis confirmed the nature of the stones used in the construction of the city walls as well as some decay products coming from the impact of environmental stressors on the surface. For example, calcite ($CaCO_3$, 1085 cm^{-1}), dolomite ($CaMg(CO_3)_2$, 1095 cm^{-1}) were determined. These compounds are present in lumaquela and calcarenite stones. Quartz (SiO_2, 465 cm^{-1}) was also characterised in calcarenite stone. In addition, gypsum ($CaSO_4 \cdot 2H_2O$, 1008 cm^{-1}) was determined all along the surface of the walls. The sulphation process of calcareous stone is a well known pollution affect promoted by SO_x acid gases. Besides, unwashed areas of the walls, gypsum was found together with soot (amorphous carbon, 1315 and 1600 cm^{-1}).

Sodium sulphate (thenardite/mirabilite, 992 cm^{-1}) as well as epsomite ($MgSO_4 \cdot 7H_2O$, 985 cm^{-1}) were also found, reinforcing the sulphation process thesis. Epsomite was found only over lumaquela limestone (due to the degradation of dolomite), whereas sodium sulphate was found over the surface of a new wall added in the twentieth century. Sodium sulphate can be found in two hydrated state: thenardite (Na_2SO_4) and mirabilite ($Na_2SO_4 \cdot 10H_2O$). The changes in the state of hydration due to changes in temperature and %RH can cause physic stress and tensions that degrade the surface of the walls. Furthermore, whereas gypsum usually precipitates over the surface, epsomite and sodium sulphate, much more soluble, penetrate through the bulk of the stone and cause more severe damages (Grossi & Brimblecombe 2002).

In situ EDXRF analysis revealed, together with the expected elements due to the composition of the stones, the presence of lead and sulphur. Sulphur was present over the whole surface of the walls (as expected after Raman analyses). Moreover, the concentration of sulphur decreased with the distance to the road near the wall. Thus, the presence of lead could be also related to the traffic present close to the sampling points. The concentration of lead was especially high in non rain washed black crusts.

3.2 *Laboratory analyses*

On the one hand, laboratory Raman analyses not only confirmed the results obtained in situ with regard to the sulphation process, but also revealed the presence of singenite ($K_2Ca(SO_4)_2 \cdot H_2O$, 982 and 1006 cm^{-1}), another sulphate formed as a consequence of the same deterioration process (see Fig. 2).

On the other hand, FTIR analyses of the samples taken from the city wall, calcite and quartz were determined together with gypsum. In some of the spectra, it was possible to see a weak peak around 1385 cm^{-1} that was consistent with the presence of nitrate. Besides, the main band of sulphate presented in some spectra a shoulder around 1035 cm^{-1} that could be assigned to the main band of lead sulphate. Thus, it could be set that the way that lead is immobilized inside the black crust is as lead sulphate.

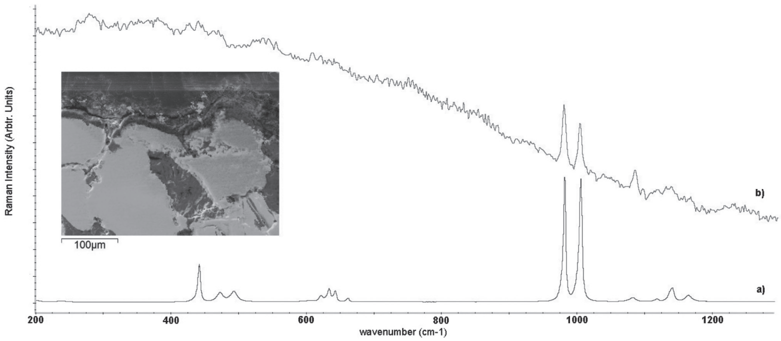

Figure 2. Raman spectra of singenite (a) standard and b) sample) and SEM-EDS image of sulphation process in a cross-section (green and blue are bulk compounds while violet shows the gypsum layer).

SEM-EDS analysis of some cross-sections revealed an uniform layer of sulphur (gypsum) over the stones' surface with a mean thickness of 50 µm. Unfortunately, lead could not be detected because it was under detection limit.

Looking for the best PCA (principal component analysis) model, it was possible to classify all the samples in 3 groups depending on the quantity of sulphate the distance to the road, corroborating the analysis carried out by in situ EDXRF.

4 CONCLUSIONS

Taking into account all the results, it is possible to set that there is a spread sulphation processes and the nearby road seems to play an important role because it has been demonstrated that the quantity of sulphate decreases with the distance to this road. The presence of lead sulphate would also point to the traffic as the main responsible of this decay.

ACKNOWLEDGEMENTS

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Alterations of materials at the façades of the church of San Pedro de Mezonzo (A Coruña, NW Spain)

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ABSTRACT: It is presented a study of alteration features in a 20th century church in A Coruña (NW Spain) where diverse materials were applied. The observational study detected the presence of diverse stains (that have been sampled and studied by scanning electron microscopy) and erosive processes affecting granite slabs and rendered walls. The association of the erosion in the granite stones and alkaline sulphate efflorescences suggest the contribution of mortars. There are is also indications of contribution of metallic materials and atmospheric pollution for some of the stains observed.

1 INTRODUCTION

Diverse decay processes can affect stony materials applied in historical and modern constructions resulting from characteristics of the materials and the surrounding environment (Arnold & Zehnder 1991, Siegesmund & Snethlage 2011).

Alteration processes affecting granite stones in historical works of A Coruña (NW Spain) have been extensively studied especially regarding the relations between atmospheric pollution (related to geogenic and anthropogenic sources) and the materials (Sanjurjo Sánchez 2005, Sanjurjo Sánchez et al., 2009, 2011) showing the widespread distribution of gypsum-rich black crusts and the occurrence of diverse other coating types (Sanjurjo Sánchez et al. 2012). In the present work results are presented of the study of a 20th century church not previously considered, focusing on the decay products resulting from the action of alteration processes involving also the contribution from the materials used in the building.

2 MATERIAL AND METHODS

The Church of San Pedro de Mezonzo is a 20th century church located in the centre of A Coruña (NW Spain), with WGS-84 UTM coordinates 29 T 548086 m; 4800696 m (according to Google Earth). It is placed roughly 400 meters of the A Coruña harbour and near high traffic lines. It has a main façade exposed roughly to the west (and to the automobile traffic) where several materials are applied. Most of the main façade is clad with slabs of leucocratic granite. In the main façade there is statuary work over the main façade. The side and rear façades are mostly covered with mortars and paint and granite stones at the base, openings, pilasters and cornices.

The performed study consisted initially of a visual inspection of the façades from the ground level for detection of alteration features for characterization of the general alteration patterns. Very small amount samples of alteration features were collected for studies by scanning electron microscopy. A sample of dust deposit on one side window was also collected and studied by scanning electron microscopy.

3 RESULTS

An observational study based on visual detection of alteration features showed diverse stains:

- Whitish efflorescences on the main façade granite ashlars (alkaline sulphates);
- Whitish stains with a run-off pattern that seem to be enriched in calcium carbonate but also with the presence of S and P (besides elements that are attributed to the substrate, Figure 1);
- Widespread darkish coatings on diverse materials including the carved statuary and that might attain the thickness of a black crust being as usually made by gypsum aggregates;
- Brown crusts on the sheltered portions of lintels also with gypsum aggregates (Figure 2);
- Dark brownish/reddish stains related to ferrous elements on the main façade that affect the façade slabs, the statuary and also the pavements consisting of a thin iron-rich coating covering the materials and where other elements such as P can be found. There are also erosive features affect the rendered walls and seem to mark water infiltration points and the salient features in the granite ashlars of the main façade. The

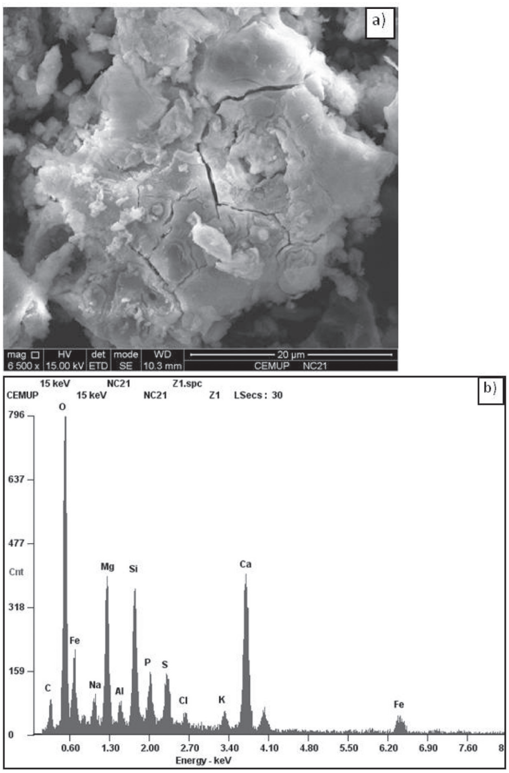

Figure 1. SEM observations of whitish coating (a) with energy-dispersive x-ray spectrum (b).

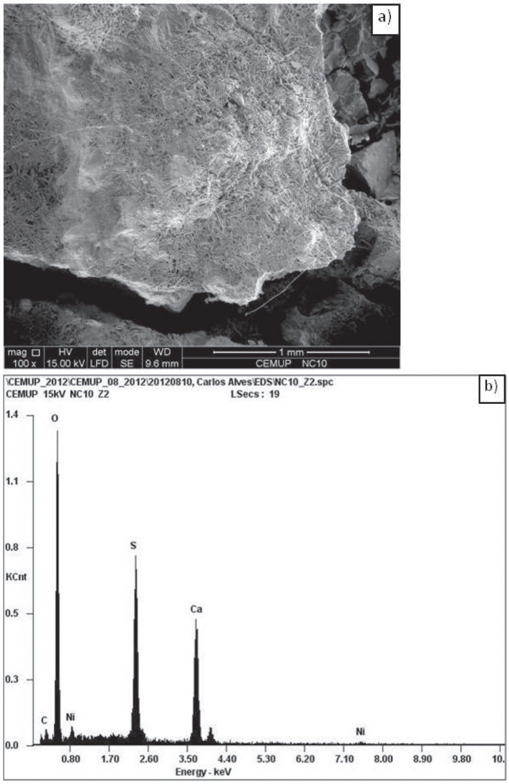

Figure 2. SEM observations of brown crusts showing the presence of gypsum aggregates and energy-dispersive x-ray spectrum (b).

proximity of the efflorescences to the erosive features suggests a causal association between the erosive features and salt weathering. The presence of alkaline sulphates is frequently attributed to the contribution of modern Portland cements (Arnold & Zenhder 1991).

The dust sample showed, besides the typical terrigenous particles, the presence of aggregates of calcium sulphate (Fig. 3).

4 FINAL CONSIDERATIONS

These decay features indicate that the decay of the materials result from the exogenous agents (water, atmospheric materials) but also form the materials that are used in the making of the church.

Of particular relevance are the ugly brown/reddish stains associated with the metallic elements and the intense erosive features observed on the granite ashlars that seem associated to the alkaline sulphates (frequently attributed to cement mortars), features that indicate the contribution of the materials used on the built structure.

The gypsum aggregates in the dust sample poses the hypothesis of gypsum formation from atmospheric particles but could also be related to migration from gypsum aggregates in the crusts that are present in the studied building or in the surroundings.

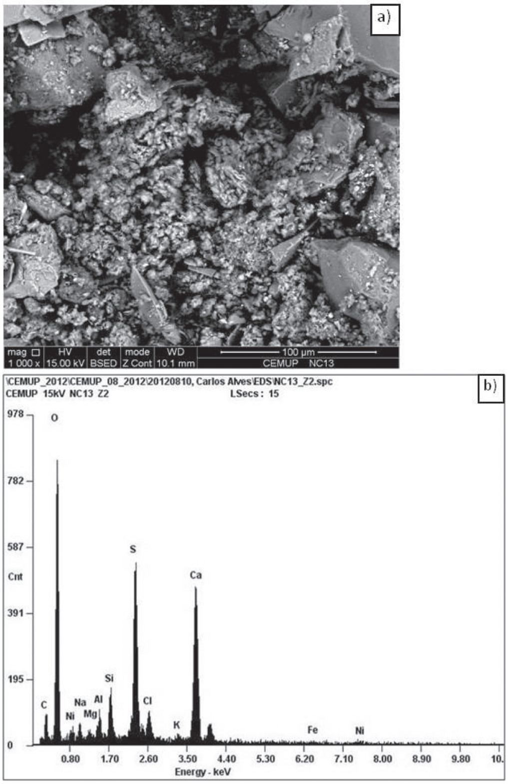

Figure 3. SEM observation of gypsum aggregates in dust sample (a) and energy-dispersive x-ray spectrum (b).

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Decay of building materials in the Circular Mausoleum, Necropolis of Carmona, Spain

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ABSTRACT: The Necropolis of Carmona (Seville, Spain), used during the first and second centuries AD, is one of the most significant Roman burial sites in southern Spain. With more than 600 tombs, the Circular Mausoleum is one of the best examples of a tomb affected by different decay mechanisms. The alteration patterns are varied and abundant, including host-rock fragmentation, loss of materials (mineral disintegration), surface modifications (efflorescences, crusts of various typologies) and biological colonization (mainly bacteria, algae and lichens). The different pathologies observed are discussed to the light of environmental parameters.

1 INTRODUCTION

The Necropolis of Carmona (Seville, Spain) was discovered accidentally during the years 1868 and 1869. It represents one of the most significant Roman burial sites in Southern Spain and was in use during the 1st and 2nd centuries A.D. The Necropolis comprises a large number of underground tombs excavated in the rock (about 600), predominating cremation over the burial ritual. Most tombs were collective mausoleums consisting of an underground chamber accessed by a staged well. Previous research works focused mainly on biological aspects of the deterioration (Ariño & Saiz-Jimenez 1997, Laiz et al., 2009) or in the salt damage processes leading to deterioration (Benavente et al., 2009).

In this paper, the weathering of the building materials in the Circular Mausoleum Tomb as one of the best examples of a tomb affected by different decay mechanisms is studied.

2 MATERIAL AND METHODS

A micro-environmental monitoring system was installed to record the microclimate inside the Circular Mausoleum tomb and eight other tombs belonging to the Archaeological Site of Carmona. A detailed description of the micro-environmental monitoring system was described elsewhere (Benavente et al., 2011). The microclimatic parameters measured within the tomb were air temperature, relative humidity and temperature of the rock surface. Data were recorded every 15 min from November 2007 to May 2008. In order to detect thermohygrometric anomalies, a study was conducted periodically with a thermal imaging camera.

Mineralogical, textural, petrophysical, and durability characterization studies of the host-rock, as well as a microbiological survey were carried out as previously described (Benavente et al., 2011, Ariño et al., 1997).

3 RESULTS AND DISCUSSION

The Circular Mausoleum (Fig. 1) shows a varied set of deterioration processes (Fig. 2), including host-rock fragmentation, loss of materials (mineral disintegration), surface modifications (efflorescences, various typologies of crusts) and microbial colonization (biofilms, diffusive pigments). The distribution of these alteration patterns is varied: microbial colonization mainly develops in areas near the ground; crusts appear in the intermediate zones and saline efflorescences and cracks appear in the upper zones and ceiling of the tomb.

Evidence of microbial activity is varied and widely extended. At the entrance and corridor walls, algae, cyanobacteria, lichens, and heterotrophic bacteria are found. Inside the tomb the distribution of the microbial colonies depends on the orientation of walls and its distance to the entrance and is ultimately controlled by microenvironmental conditions. Microbial colonization is more intensive in holes and rough substrates and shows a greenish colour due to the growth of phototrophic microorganisms (*Muriella terrestris*, *Muriella* sp., *Chlorella vulgaris, Ctenocladus circinnatus* among the chlorophyta; *Gloeocapsa rupestris, Gloeocapsa* sp., *Scytonema* sp., *Cyanothamnos* sp., *Chroococcidiopsis* sp., *Symplocastrum friessi*, among the cyanobacteria).

Crusts and efflorescences are mainly composed of gypsum and are distributed in all types of substrata. Crusts exhibit different forms ranging from thin, smooth and cryptocrystalline to globular crusts. Efflorescences present mainly acicular habit.

Climate monitoring has shown that, despite the outside weather conditions and strong water deficit of the Archaeological Site, effective condensation processes inside the tombs are very active and develop over long time intervals. The petrophysical properties of the different materials present in the tomb (host-rock and buildings materials) influence the amount of water condensed and retained by each substratum.

Condensation processes studied in the tomb are developed throughout most part of the annual cycle, which implies a considerable water availability time for the development of decay mechanisms (Fig. 3). In the current conditions, the cycles of condensation and evaporation in the tomb are usually short, which determines that the effective condensing intervals are also short (typically less than one day). Such a situation of high water stress with continuous wetting/drying processes was not experienced by the tomb before discovery. Thus as a result of the numerous interventions and restorations since its discovery, the tomb presents

Figure 1. The Circular Mausoleum and its 3D rendering.

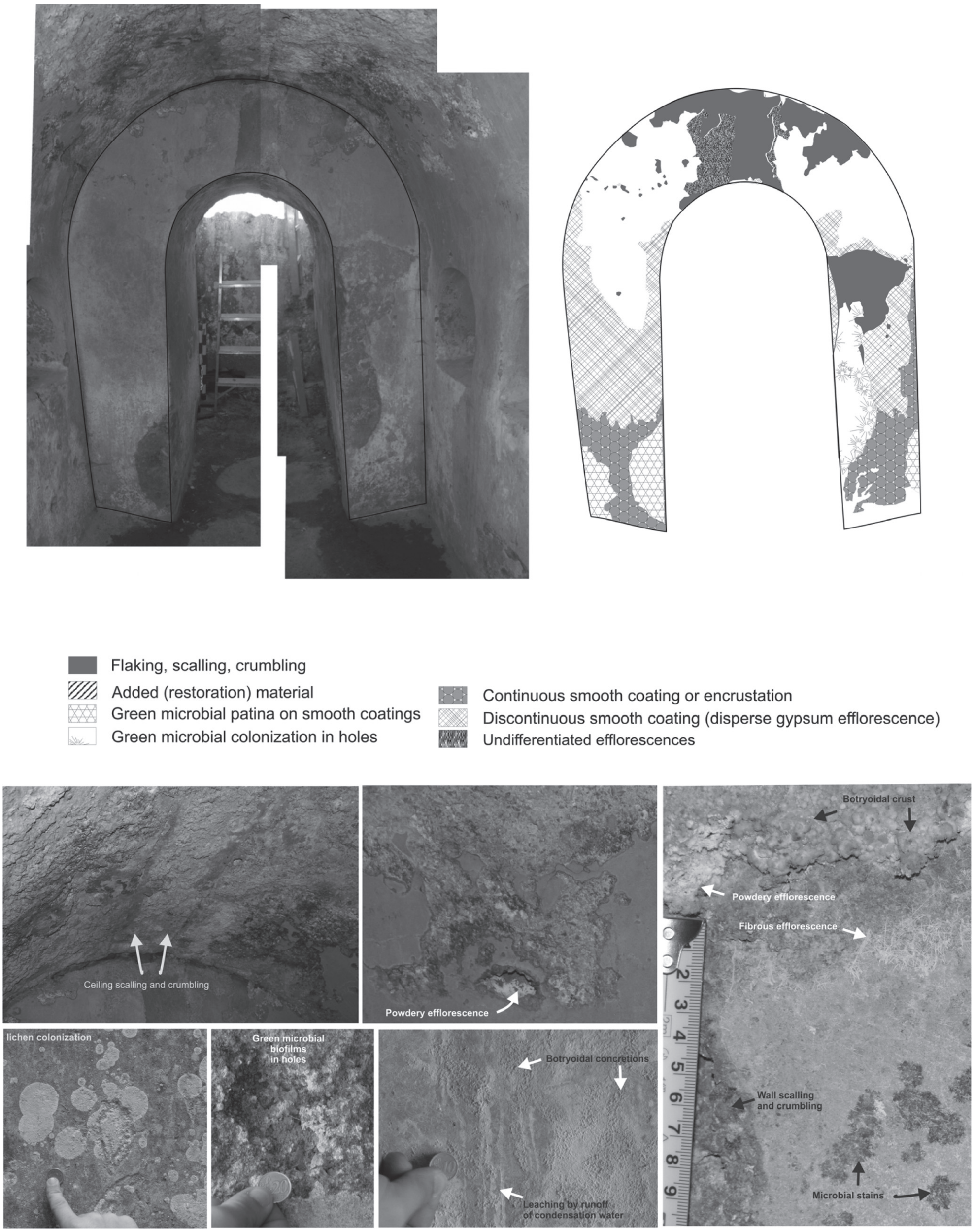

Figure 2. Distribution of weathering forms in the Circular Mausoleum tomb.

a high RH degree (78.9%, on average) and a general overheating near the ceiling surface (the mean temperature of the air-rock interface remains 1.2°C above the average air temperature). Moreover, vapour condensation is highly enhanced due to the porous structure of stuccoes, mortars and host-rock. Condensation is registered during more than 20 days per month reaching monthly amounts up to 1.6 kg/m^3 air (January and February).

All these factors cause a steep thermal gradient which leads to the heating of the ceiling in a high humidity environment. This result in a mechanical stress and the proliferation of microbial communities adapted to the different environmental conditions of the tomb. Ventilation is restricted and the intense thermohygrometic gradient induces decay mechanisms.

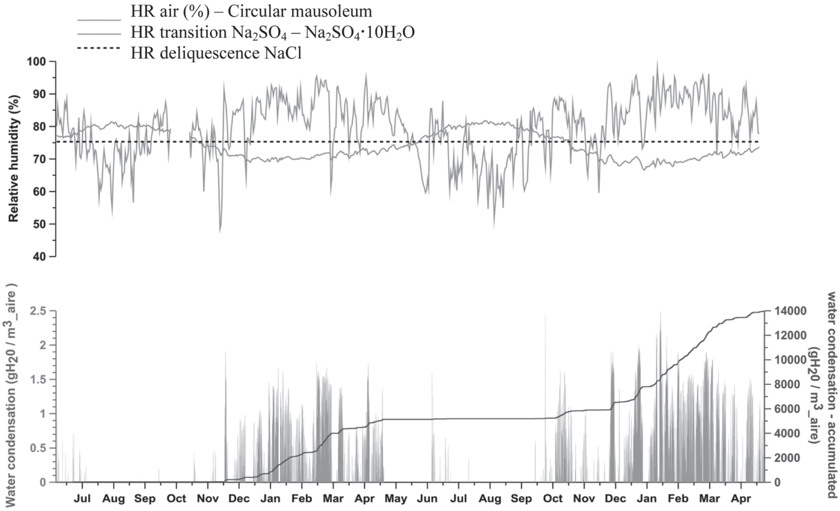

Figure 3. Time series of condensation process in the rock surface of the Circular Mausoleum Tomb (expressed as gH_2O/m^3 of air), from June 2007 to April 2009.

4 CONCLUSIONS

By means of different methodological approaches it can be concluded that the alteration processes experienced by the Circular Mausoleum are largely related with intense interventions suffered by the Carmona Archaeological Site since its discovery, which in most cases have enhanced the deterioration mechanisms.

The sequence of interventions after discovery of the tomb provoked exchange rates between the tomb atmosphere and the exterior that profoundly altered the environmental conditions. The tomb currently has high moisture content, high condensation rate and a high roof overheating Environmental monitoring, including increased ventilation during periods with increased humidity and the use of natural desiccant decrease the thermal imbalance of the tomb and the destructive wetting/drying cycles.

ACKNOWLEDGEMENTS

The authors acknowledge funding from the Consejería de Cultura (project "Estudio integral del estado de conservación del Conjunto Arqueológico de Carmona") and Consejería de Innovacion, Ciencia y Empresa (project P06-RNM-2318). Carmona Archaeological Site staff members are acknowledged for their collaboration throughout the whole research period.

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The erosion of granite surfaces: The Cathedral of Évora as example

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ABSTRACT: The evaluation of the erosion in the stone surfaces of a granitic monument highlights the severity of decay due to the presence of salts. The method used and reported here integrates different but relevant information: besides the quantity of material lost by the stone surfaces, their hygroscopic behavior was evaluated in different humidity conditions, complemented by the characterization of the microenvironment where the erosion process takes place. The method used contributes to a better knowledge not only of decay but also of the behavior of these materials over one year, illustrating the dynamism imposed by the presence of salts as the most relevant factor of decay. How to modify the behavior of decayed stone materials is the great challenge of conservation actions.

1 INTRODUCTION

1.1 *Overview of the subject*

Stone surfaces in historical buildings are usually dynamic and in permanent interaction with the surrounding environment. The impact of climate changes, risk evaluation and the quantification of stone surface recessions on stone buildings have been a main concern and a central topic of several European research projects in this field during the last decade.

From onsite observations or in laboratory/onsite tests, researchers try to quantify stone decay processes on carbonate materials, in order to anticipate the future and to define preventive measures. However, long-term results on stone decay are not so frequent and usually the information is qualitative rather than quantitative. In fact, the evaluation of damage and the identification of the active processes responsible for decay are particularly important, especially when the final objective is to find adequate solutions for the preservation of surfaces in a specific monument and, for this reason, this matter is also very relevant in conservation.

Visual inspection is widely recognized as the first approach to describe and to evaluate the decay state of surfaces. The use of a common language to describe decay patterns, proposed a long time ago by researchers (Fitzner 2002) or institutions (ICOMOS 2008), has been increasingly used although not without difficulties and ambiguities. It has been implemented as a good practice, allowing both description and a certain type of quantification, very useful for several relevant purposes required by the best practices in conservation. Besides purposes involving diagnosis or monitoring, it is very useful to report and document the actions taken during the intervention of conservation.

To express weathering and decay in numbers is not an easy task, in particular if we desire to obtain representative data using simple and generally applicable methods. More recently, more or less sophisticated techniques have been proposed to look at the surface and follow the gradual loss of surface using 3D laser scanning and LIDAR systems, but even when it is possible to use more complex methods, simple visual examination plays an important role in quantifying decay. Moreover, the use of simple methods is usually the only option available in real practice.

The examination of the surfaces depicts the state of the stone at a particular moment, but it does not capture the rate of decay. For this, a series of inspections is required, usually over a period of several years, and common photographs are used as documents although their objectivity can be questioned. What methods can be used to evaluate correctly and "easily" the weathering/erosion of the surfaces? The information derived from the academic exercise reported here can be very relevant to decide the most adequate measures to be undertaken during the conservation intervention.

1.2 *The objectives*

This paper presents the guidelines of the work carried out on a granitic monument to evaluate the factors responsible for decay and the methods used to quantify the erosion of surfaces in selected areas of the monument. The work was planned to integrate the preparatory research before the conservation intervention on the Cathedral of Évora (Portugal). Our goal was to understand the influence of the microenvironment on decay patterns observed on the granitic ashlars of the monument.

2 PLANNING THE WORK ON THE MONUMENT

2.1 *Some relevant aspects of decay observed on the monument*

The construction of the Évora Cathedral dates back to the late twelfth century and lasted for a long period of time, featuring the late Romanesque and Gothic styles. The diversity of materials used to build the monument expresses well the regional variability of the igneous complex from where the construction materials were extracted. For technical and economic reasons, the medieval builders used the upper parts of the rock mass outcrops, where the superficial materials are found naturally altered. As a direct consequence, the blocks present in the cathedral stonework exhibit an inherited alteration that pervades the entire block and examples of extremely poor quality stones may be found. This condition was the first determinant cause of severe degradation forms, namely contour scaling, sand disintegration and back erosion (Delgado & Costa 2008).

2.2 *How serious and how far can the damage reach?*

One of the most significant places in the monument is the lantern tower (*zimbório*). The interior surface is particularly critical concerning the erosion. The extensive rainwater infiltration is the major source of moisture. Incompatible materials widely used here, particularly cement-based mortars, are also important onsite decay factors. Originally, the masonry was covered by renders and a calcitic mortar was used to mimic the limits of the blocks. Meanwhile, the erosion partially removed the render and the blocks are now uncovered in large areas. Figure 1 (b) illustrates the weathering of the granitic masonry in a place where the stone is now mostly uncovered (the render is preserved on the right (zone delimited by dashed line).

Sand disintegration justified the installation of a platform under the vault. Afterwards, it was possible to collect the debris detached from the blocks. Since the vault was only accessible

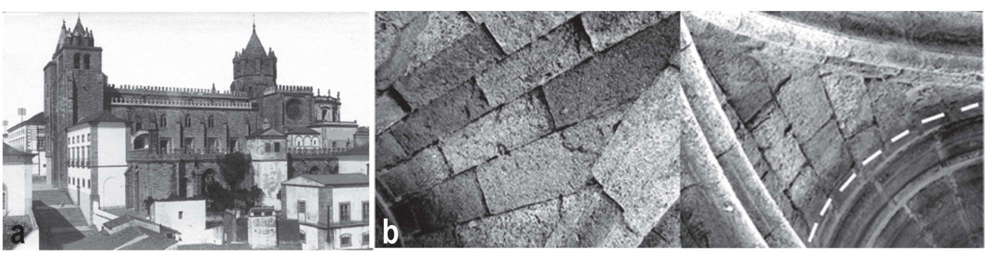

Figure 1. a) Cathedral of Évora (Portugal) in the 1940s (*reproduction of an old postcard*). The lateral façade, one of the towers of the main façade (on the left) and the *zimbório* (on the right); b) Extensive sand disintegration and erosion in the internal vault.

to researchers, the spontaneously detached grains could be collected, undisturbed, according to the orientation of the respective sectors and therefore a geographic distribution could be made (see Figure 2a). For about three years it was possible to quantify these materials. The data allows quantifying erosion of the internal surface in this significant space of the monument.

2.3 *Planning the work in the field*

Regarding decay, two general tasks were defined for this particular area: 1) Monitoring of the debris over time; 2) Characterization of the microenvironment (air envelope).

The objectives were to quantify the debris and its salt load content. As a complement, the influence of the microenvironment on the erosion process in progress was also analyzed.

3 SOME RESULTS

3.1 *The microenvironment*

The microclimate in Évora is characterized by hot summers and mild winters, but also by great daily variations, particularly in the relative humidity conditions. The indoor climate of the monument is controlled by the external conditions, although characterized by a narrower range of values, especially regarding temperature. Table 1 presents the relevant parameters (expressed in terms of the average values ± standard deviation and maximum and minimum values) of indoor climate measured in 2000, taken as example.

3.2 *The debris: How serious is the erosion process inside the lantern tower?*

Taking as an example one of the periods monitored (the year 2001), very high material loss were determined in some sectors, reaching 1.5 $g/m^2/day$ during the summer period. In the areas where the render is still partially preserved ("sec 3", "sec 4", "sec 5" or "sec 6" in Figure 3), the quantity of detached material is lower, around 0.3–0.6 $g/m^2/day$. Consistently, the quantity of material detached during the winter is lower than in the summer.

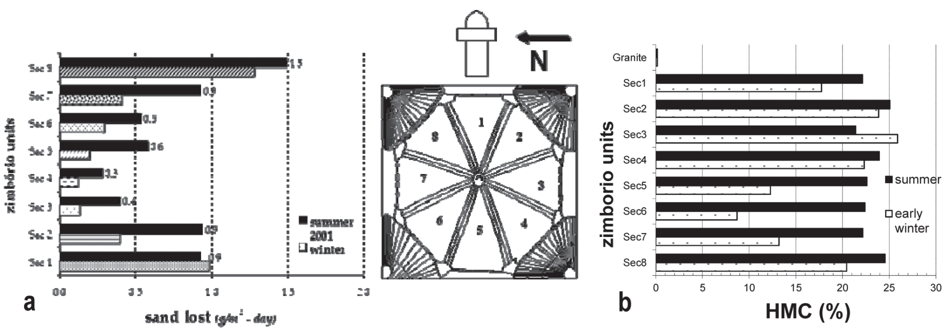

Figure 2. a) Erosion rates determined for the different sectors of the *zimbório* internal vault; b) Hygroscopic moisture content (HMC) of debris collected in summer and winter of 2001. Erosion rates determined for the different sectors of the *zimbório* internal vault.

Table 1. Indoor climate in the *zimbório*.

	Temperature (ºC)		Relative humidity (%)	
January	12.1 ± 0.6	(14.1–11.1)	60.6 ± 3.5	(73–50)
August	26.8 ± 1.7	(34.4–24.1)	38.9 ± 7.4	(54–16)

3.3 *The salts as efflorescences and the hygroscopicity of the debris: How serious is the salt load?*

Salt minerals present inside the stone are more difficult to analyze and to quantify than efflorescences. The hygroscopic moisture content determination of decayed samples is a very informative technique to quantify the amount of salts, in particular when it can be complemented with Ion Chromatography (IC) (Costa & Rodrigues 2008). It is worth noting the good correlation of the total salt content determined by IC and hygroscopic moisture content (HMC) values. The granites in the *zimbório* have sulphates and nitrates as suflorescences.The hygroscopic moisture content of the debris (Figure 2b shows some results) confirms the high amount of hygroscopic salts present as subflorescences (up to 3–4%, in the summer).

To complement the study, samples of efflorescences were collected in several points of the monument indicate that granitic materials are "contaminated" with complex mixtures of salts. Carbonates, nitrates and sulphates are present: i) sodium and magnesium carbonates (Trona, Hidromagnesite and Northupite); ii) magnesium, calcium or sodium sulphates (Epsomite, Gypsum, and Thenardite); iii) sodium and potassium nitrates (Niter and Nitratite). Complex salts like Aftitalite and Humberstonite, composed of sulphate and nitrate anions in several proportions, were also identified (Costa et al. 2004).

5 CONCLUSIONS

Nowadays, granites and similar rocks are considered very durable construction materials. Looking back into the past, several examples show that they can be very fragile, justifying the need for urgent intervention and conservation works. Sand disintegration and scaling are frequent decay patterns on monuments made of granite and similar varieties, with large areas are in risk of loss. In this research the Cathedral of Évora is presented as case study. This work was planned in the frame of the conservation intervention plan. During the work, it was possible to collect data on the degradation of the materials, in particular in the *zimbório* area, where this problem is especially relevant.

Some results obtained are presented here. The debris detached was collected over years; the material loss allowed evaluating objectively the erosion of the surfaces, which can reach the value of 1.5 $g/m^2/day$ during the summer period. The salt load content of these materials and the microenvironment characterization of this space were also relevant to better understanding the erosion process. The materials detached have a strong hygroscopic behavior due to the presence of salts. Complex mixtures, present as efflorescences but mainly as subflorescences, are the major responsible for the fast erosion and for the dynamic of the process in progress.

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Study of the long term stability of an industrial polyamide from a contemporary artwork

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ABSTRACT: The application of an analytical procedure mainly based on the use of Fourier transform infrared spectroscopy (FTIR) and other commonly used techniques for the characterization of polymers enabled identifying the constituent material of a contemporary artwork and predict its long term durability. Specifically, the main component of *Homo Felis* by *Esferobite DSk* was identified as an industrial polyamide, which exhibited good ageing stability under simulated ageing treatments and, by extension, under mild museum conditions.

1 INTRODUCTION

Synthetic polymers were used for the fabrication of artworks since their introduction as industrial materials and, as a matter of fact, sculptures (including assemblages, collages and installations) partially or completely made of plastics are ubiquitous in art collections and contemporary art museums. On the other hand, it is well known that polymers may be much more prone to oxidation and more in general to physical or chemical ageing, than other materials traditionally used by artists, even under protected indoor conditions such as those found in museums during display or storage (Shashoua 2008, Lazzari et al., 2011, Toja et al., 2012).

In the framework of a comprehensive project aiming to develop an analytical procedure to evaluate the degradability of polymeric materials in contemporary works of art, herein we focus our attention on the long term stability of a plastic-made installation (*Homo Felis* by *Esferobite DSk*) from the collection of the contemporary art museum of Santiago de Compostela, with the final aim to address its conservation and management strategy. Recognition of the polymeric components was carried out by attenuated total reflectance—Fourier transform infrared (ATR-FTIR) analysis and differential scanning calorimetry (DSC), whereas their weathering was investigated under simulated conditions of ageing in which the processes of degradation occurring under natural conditions were accelerated by an isothermal treatment or through the irradiation of polymer samples in a photoageing device. Monitoring of structural and molecular changes was performed not only by instrumental techniques for polymer characterization, essentially FTIR and UV-vis spectroscopy, and DSC, respectively, but also through not instrumental measurements, such as weight loss determination.

2 EXPERIMENTAL

2.1 *Samples from the artwork and reference material*

Small fragments were collected from the inner part of one of the 8 white flat masks constituting the artwork partially shown in Figure 1. In addition, large amounts of the white powder

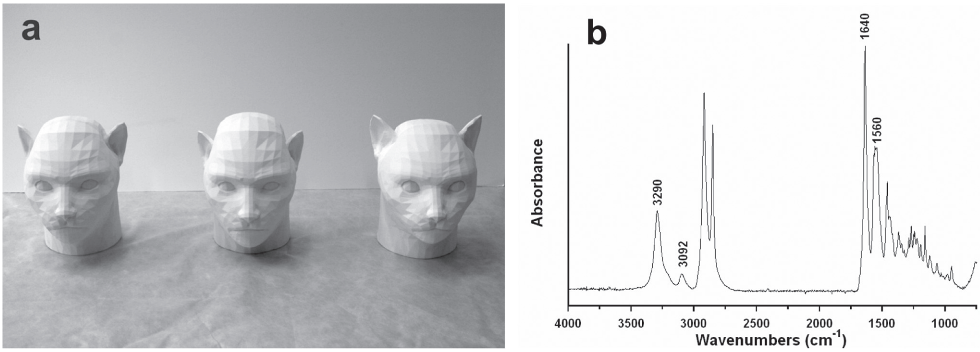

Figure 1. Partial view of *Homo Felis* (a) and FTIR spectrum of the powder used for its fabrication (b).

used to fabricate the sculptures by selective Laser sintering (Gurr & Mülhaupt. 2012) were also available as remainders from the artist's studio.

2.2 *Instrumentation and ageing treatments*

IR absorption spectra were collected with a Thermo Nicolet FTIR Nexus instrument, eventually equipped with a Smart Endurance device for ATR measurements, and a deuterated triglycine sulfate detector, at 4 cm^{-1} resolution. Spectroscopic acquisition and data treatment were performed using Omnic version 6.1 (Thermo Nicolet). Spectra in the UV and visible region were measured with a HP8452 diodearray spectrophotometer (Hewlett-Packard). Finally, DSC measurements were carried out with a Q200 differential scanning calorimeter (TA Instruments), with a scanning rate of 20°C/min, under a nitrogen atmosphere.

The samples for ageing treatments were prepared in the form of thin films with a thickness of around 100 μm. The film thickness was deduced from the amount of *m*-cresol solution used for the preparation, considering a uniform deposition. Samples for FTIR and UV–vis spectroscopy were supported on KBr or quartz windows, respectively, whereas for all other determinations they were prepared on 76 mm × 26 mm glass slides. The accelerated thermal ageing was carried out in a forced-air circulation oven (Memmert), whereas the accelerated photoageing was carried out in a Suntest CPS high-speed exposure unit (Heraus), equipped with a xenon light source having constant irradiation at a power of 765 W/m^2; a glass filter with cut-off at $\lambda \leq 295$ nm was used to exclude radiation more energetic than that of outdoor solar exposure. Finally, weight losses of polymer films induced by degradation were determined gravimetrically, carrying out measurements in triplicate.

3 RESULTS AND DISCUSSION

3.1 *Compositional analysis*

FTIR spectra of both fragments from the artwork and the white powder used for its fabrication showed very similar patterns (see Fig. 1b as an example). Apart on some commonly encountered bands due to aliphatic structures, such as those at 3,000–2,800 cm^{-1} (C–H stretching) and 1,450–1,350 cm^{-1} (C–H bending), a series of other characteristic absorptions at 3,290 and 3,092 cm^{-1} (hydrogen bonded N–H stretching), and 1,640 and 1,560 cm^{-1} (C=O and N–C=O stretching, respectively) may be ascribed to a polyamide structure. Notwithstanding, the exact type of aliphatic polyamide could only be identified through the determination of the temperature of fusion by DSC. The observed value of 173°C is only compatible with a polyamide 12. Along with the sensitivity of the applied techniques, it is worth mentioning that no additives or other minor components were identified.

3.2 *Simulation of the ageing*

In order to simulate under artificial conditions the same chemical changes occurring in the long term under environmental conditions, we carried out two common tests of accelerated ageing which consisted in an isothermal treatment in a forced-air circulation oven or in a photo-ageing treatment in a device equipped with a xenon lamp.

The isothermal treatment at a constant temperature of 140ºC, chosen to speed up the natural ageing without triggering unwanted processes (Feller 1994, Lazzari & Chiantore 2000) only induced negligible degradation for rather long time of ageing, i.e. up to 300 h. On the other hand, reference samples submitted to accelerated photo-ageing displayed dramatic changes of physical and chemical properties. The polymer started to loose weight since the beginning of the treatment, reaching 35% and 77% weight loss after 500 h and at the final treatment time (1000 h), respectively, whereas its optical properties, mainly transparency, and UV spectrum did not show significant modifications. Fast weight loss is associated to the structural changes visible in Figure 2, where the FTIR spectra before and after 500 and 1000 h treatment are depicted for comparison. Apart on a progressive decrease of principal absorptions, indicating loss of low molecular weight molecules produced by the degradation and involving all parts of the structural units (Lazzari et al., 2001), the new spectral features resulting from the photoinduced oxidation are: progressive increase of a peak centered at 1710 cm^{-1}, associated to the formation of new carbonyl groups, namely aldehydes, and appearance of a small peak at around 3450 cm^{-1}, which is assigned to free N–H stretching vibration bond. At the longest ageing time, the original pattern is hardly recognizable. In particular, the formation of a broad band and, at the same time, the disappearance of the original peaks in the 3500–3000 cm^{-1} region associated to N–H groups involved in hydrogen bonding, possibly indicate an extensive destruction of the crystalline structure. As a matter of fact, DSC of samples aged for increasing time (Fig. 3) showed a progressive decrease of the temperature of fusion of the polyamide, from the initial value down to 168ºC after 1000 h treatment.

On the basis of these preliminary results, and remembering that the understanding of the mechanism of photoxidation is crucial for predicting the natural ageing, it is possible to suggest an approximate mechanism for polyamide 12. Following the typical mechanism of hydrocarbon oxidation, the initial step reasonably consists in a hydrogen abstraction from the methylene group adjacent to the amide N–H, followed by oxygen addition and formation of a hydroperoxide intermediate. The ease of breakdown of the hydroperoxides then generates the corresponding alkoxy radicals and finally the aldehydes identified by FTIR. At the same time, the formation of volatile product of degradation may be a direct consequence of the contemporary formation of aldehydes at adjacent amide groups.

At the end, it may also be supposed that exactly such structural modifications and the corresponding decrease of the molecular weight through polymer chain scission are the respon-

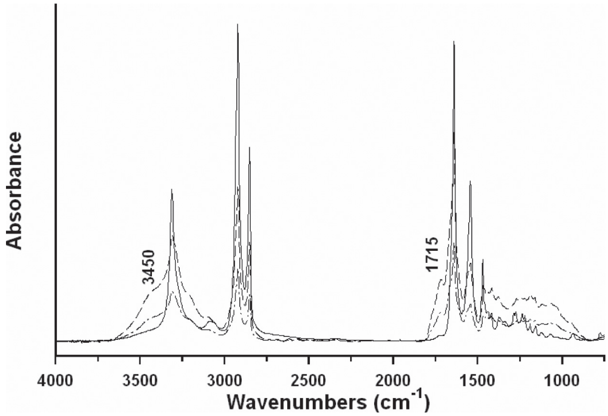

Figure 2. FTIR spectra of polyamide 12 thin films before (solid line) and after 500 h (dashed line) or 1000 h photo-ageing (dash-dotted line).

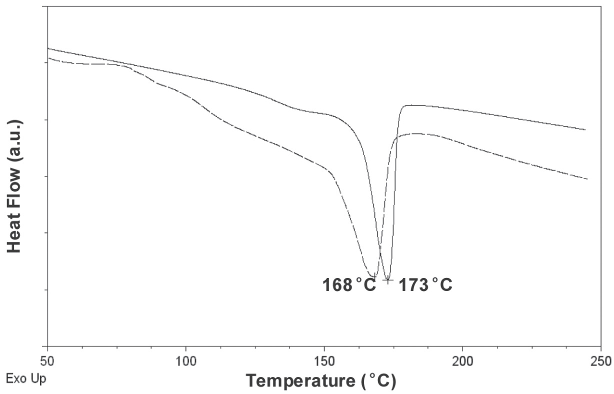

Figure 3. DSC curves of polyamide 12 before (solid line) and after 1000 h photo-ageing (dashed line).

sible of the changes in the crystalline form, strongly dependent on the extent of hydrogen bonding.

4 CONCLUSIONS

Applying a very simple method based on the use of analytical techniques generally applied for the characterization of industrial polymers we disclosed the composition of plastic-made sculptures and predicted their durability through simulated ageing treatments. Despite the approximation in comparing results obtained after short accelerated tests with those expectable after much longer natural ageing under indoor conditions, mainly due the complexity of the thermodynamic and kinetic of involved oxidation reactions, it may be affirmed that the polyamide 12 used for the fabrication of the artwork exhibited good ageing stability. Apart from some limited structural modifications of the polymer, the most important aspects related with the appearance of *Homo Felis*, such us color and gloss, did not show relevant changes along the ageing treatment. However, in order to minimize such irreversible processes of deterioration, some general suggestions of preventive strategies may be delivered, mainly addressing the storage/displaying of the artwork under stable environmental conditions which slow down the unavoidable weathering (Lazzari et al., 2011).

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Study of the corrosion products of the lead blocks from the historical organ Jean Pierre Cavaillé of Vinça, France

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ABSTRACT: This paper describes for the first time the study of the severely corroded blocks that are fundamental components of the reed stops, and that affected strongly the quality of the sound from the Organ of Saint Julien et Sainte Basilisse of Vinçá (France). The blocks were corroded in bulk through a progressive peeling of the corrosion layer. Two corrosion products had been identified through X-ray powder diffraction, FTIR and μ-Raman. Plumbonacrite $[Pb_{10}O(OH)_6(CO_3)_6]$, as initial corrosion product that most likely convert to the more stable hydrocerussite $[Pb_3(CO_3)_2(OH)_2]$, as principal corrosion products. This study evaluate their possible cleaning and restitution, or their replacement for new others blocks if necessary.

1 INTRODUCTION

The organ of Saint Julien et Sainte Basilisse of Vinçá was constructed by the French organ builder Jean-Pierre Cavaillé (1743–1809), who was working at the area of the south of France and Catalonia during the second half of the XVIII century, leaving instruments as important as this one and other organs in Saint Guilhem-le-Désert (France), in Torroja del Priorat (Tarragona) or in Barcelona (Santa Catalina). The organ had been entrusted to the organ builder Joseph Cavaillé, uncle of Jean-Pierre, although the last one was who realized most of the work. Its construction was carried out between 1760 and 1765, having stopped the works in 1762 for lack of funds and being taken up again three years later. The case was arranged in the Catalan way, in the third side chapel of the nave of the Gospel, but in 1862–1864 it was moved to the current position, in a tribune to the foot of the nave. The author of these works was Henri Thébault (Luzzato 1977, Klotz 1995, Jambou 1999) who extended the number of keys of the keyboards and modified the stops. The organ has three manuals and pedalboard. Both the Great Organ and the Choir Organ have an extension of 50 notes, while the Recitative has 27 notes, and the Pedal originally 14 notes.

This organ was restored by the firm Grenzing S.A., which returned the instrument to the original character of Jean-Pierre Cavaillé, although preserving two Thébault stops and extending the pedalboard up to 26 notes (Fig. 1a). During the restoration process, it was observed a corrosive process located in some wind ducts made of lead, and especially in the blocks of the stop of Oboe (Fig. 1b), which, in addition to the strong corrosion, were provoking the blockade of the tuning wires, and therefore avoiding the correct tuning of the pipes. The blocks, constructed in pure lead, are perforated cylindrical elements that serve to assemble the set of pieces that compose the

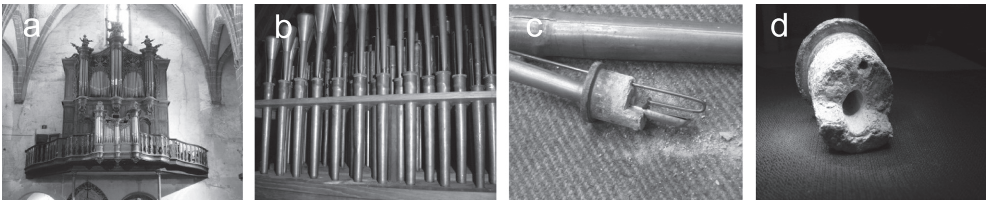

Figure 1. (a) Organ Jean-Pierre Cavaillé (b) Rank of Oboe pipes (c) Boot and block with resonator, shallot, tongue, wedge and tuning wire (d) Detail of a strongly corroded block.

reed pipes: on the one hand the shallot, wedge of wood, and the reed that vibrates and produces the sound, and for other the resonator that amplifies the sound produced by the reed. It is interesting to note that neither the components made of brass (reeds, shallots and tuning wires) nor the boots and resonators presented alteration sings (Figs. 1c, d). All the components of the pipes were moved to the restoration workshop and the laboratory to analyze the components and their alteration products, and evaluate the possible recovery of the altered components.

2 EXPERIMENTAL

The analyses were carried out in seven blocks. One of them was cut in order to observe in cross-section from the unaltered lead of the body of the block. In addition, a small sample of one the boots were analyzed in order to know the difference in the degree of corrosion between the blocks and the internal part of the boots, because all are subjected to the same atmosphere.

Observations of the transversal cross-sections blocks were performed by Optical microscopy using a stereo loupe microscope using a 20–50 X magnification objectives and equipped for microphotography using a digital camera (Nikon COOLPIX 4500). The morphology studies of the corroded layer for untreated blocks samples surface were carried out using a Scanning Electron Microscope (SEM) HITACHI S4800. An energy dispersive X-ray analyser (EDS) coupled to the SEM, was employed for elemental analysis. Quantification of Pb and C were carried out by EDS analysis of the metallographic cross-sectional samples. A Siemens D5000 diffractometer with a Cu target and Grazing Incident Diffraction (GIXRD) device was used to identify the crystalline phases present at the surface of the untreated sample and at the bulk of the metallographic cross-sections of the blocks. FTIR (JASCO-6200) microscope measurements were performed on the white powder found on the lead surfaces blocks. All the FT-IR spectra were obtained at a 4 cm^{-1} resolution and 100 scans. Micro-Raman measurements were carried out to identify the compositions of the black spots found into the white corrosion layer of the blocks. Spectra of the samples were acquired using a LabRAM Horiba Jobin Yvon spectrometer equipped with a Full area CCD detector, using 785 nm CLDS point mode diode laser for confocal Raman measurements. The wavelength range of recording was of 100–1800 cm^{-1} using a 50–100 X magnification objectives. Raman spectra were collected for 3–6 min with a spectral resolution of 2 cm^{-1}.

3 RESULTS AND DISCUSSION

The observation under optical microscope (OM) in the blocks prepared in cross-section showed that the corrosion affected not only the external surface of the blocks but the interior of the holes drilled to accommodate the shallots, the tongues and the tuning wires (Fig. 2a). X-Ray diffraction of the powder show the characteristic diffraction peaks of the two basic lead carbonates hydrocerussite and plumbonacrite (Fig. 2b).

The typical morphology of the white corrosion layer found into the surface of the untreated sample SEM image (Fig. 3a) was covered by a continuous layer of flake-shaped crystals. The EDS chemical analysis performed on the different zone of the transversal cross sample

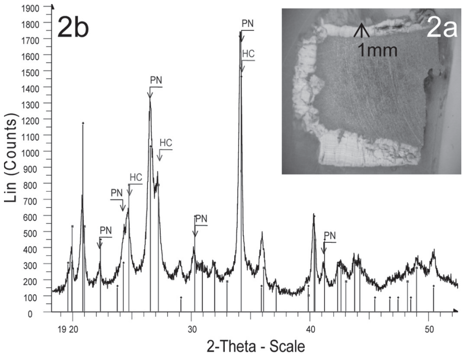

Figure 2. (a) Cross section (OM) of the block and the corroded surface (b) XRD of the corrosion products (PN: plumbonacrite, HC: hydrocerussite).

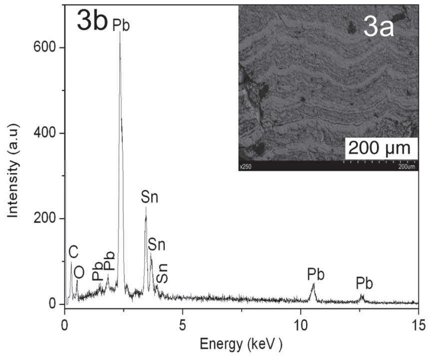

Figure 3. (a) SEM image of the banded corrosion layer (cross section) (b) EDS analysis of the boot.

included in Fig. 3b indicates the existence of small amounts of C together with the expected major component Pb element. Under the optical microscope, very small inclusions of dark colour in the mass of the corroded material were observed. The analysis by EDX showed that are constituted by Pb.

Micro-Raman analysis clearly showed the difference between the initial lead oxide (PbO) and lead carbonates (hydrocerussite and plumbonacrite mostly) whereas PbO associated to the black inclusion features progressively appears in the spectra. (Figure not shown) The initial lead oxide phase shows only the bands at 124 cm^{-1} and 279–329 cm^{-1} but with dominant bands from 106, 664 and 1048 cm^{-1} associated with lead carbonates (Figure not shown). FTIR corroborated the presence of two lead carbonates.

It is well known the effect of carboxylic acids in the atmosphere on the degradation of metals (Echavarria et al. 2003). The problem of the objects in an environment surrounded by wood, like the showcases in museums or the pipes in the pipe organs is the high concentration of volatile organic compounds, fundamentally low molecular weight organic acids, as studied by Tétreault et al. (2003), Chiavari et al. (2008), Gibson & Watt (2010), Schieweck & Salthammer (2011). Oikawa et al. (2005) studied the effect of volatile organic compounds from different species of wood on pigments and metals (iron and copper). Even the volatile organic acids evolved from the alteration of cardboard in humid atmospheres alter lead artworks to hydrocerussite and plumbonacrite (Duran et al. 2009). During the operation of an organ, the reeds are the less used stops. Normally, the flue pipes in different combinations are the basic stops used to interpret the scores. The flue pipes are open to the air, and therefore the air introduced from the windchests to produce the sound is easily diluted with the air from the surrounding atmosphere when they are not playing. However, the blocks in the reed stops are kept in a quite confined environment for a long period of time due that the minute space between the reed and the shallot hinders a quick interchange with the surrounding atmosphere by convection. That means that after been played, the air contained in the boot remains in contact with all the components of the stop for a long period of time.

We found that the blocks were corroded from the surface to the bulk to the two basic lead carbonates hydrocerussite and plumbonacrite. On the other hand, the analytical results of the brass components (64% Cu-36% Zn) and the interior side of the boot (made of an alloy of 75% Pb and 25% Sn) showed no sign of corrosion. Even pipes with high content of lead did not showed signs of corrosion. According with the bibliography the very intense corrosion of the blocks must be due to the attack of volatile organic acids produced by the hydrolysis of acetyl groups in the hemicellulose from the wood of the windchest. The basic lead acetates are quickly transformed into basic lead carbonates with reaction with the atmospheric CO_2. In our studies on metallic components of pipe organs from Spain and Portugal (Herrera et al. 2010, Justo-Estebaranz et al., 2011, 2012), we have never found such degree of alteration in the lead components. We assume that the difference must be due to the type of wood used in the cases and windchests. The study of accelerated corrosion experiments in climatic chambers with different species of wood and on different lead-tin alloys is being performed by our group in order to try to clarify the problem.

As conclusion, due to the deep corrosion of the blocks, it was considered to be impossible to recover their functionality, being necessary their replacement. Attending that the blocks are not essential components in the conservation of the tone of the instrument (as are the shallots, reeds and resonators), new blocks were constructed following the parameters of the originals except in the chemical composition, in which a certain proportion of tin was added to the lead in order to give major stability to the corrosion. Finally the stops were incorporated to the instrument, entirely recovering its functionality and original tone.

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Science and Technology for the Conservation of Cultural Heritage –
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Causes of decay of Eduardo Chillida's Monument to Tolerance in Seville (Spain)

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ABSTRACT: The Monument to Tolerance was created in 1992 by the sculptor Eduardo Chillida (1924–2002). On the Muelle de la Sal (Salt Pier), next to the river, this work was created in reinforced concrete around an inner steel framework using formworks and moulds.

Since the moment of its construction, this work has undergone weathering due to its own characteristics and to its exposure to high environmental humidity. This has impacted both its structure and the cohesiveness of the concrete. Consequently, it has been subjected to numerous preventative attempts that have nonetheless been unable to halt the decay process. The study, together with a partial reconstruction, addresses both the composition of the materials and the pathologies affecting them. Restoration and maintenance are proposed.

1 INTRODUCTION

The Monument to Tolerance, designed by the prestigious Basque sculptor Eduardo Chillida, is a homage by the city of Seville to the co-existence of the distinct cultures that have resided here throughout history: Christian, Jewish, and Muslim. The concrete structure represents arms open wide for an embrace, and its location next to the Guadalquivir River symbolizes the role of this water course as the backbone of the city's history (Fig. 1).

The sculpture's emplacement, the environmental conditions, and the character of the reinforced concrete used in its execution are crucial in understanding the decay it has undergone since it was unveiled in 1982.

In the 1990s, vandalism left the inner metal structure visible, thereby requiring restoration work to counter the accelerated corrosion of the steel. Since this intervention, the most serious changes have derived from high environmental humidity, which has little by little caused corrosion of the steelwork and partial spalling of the concrete due to expansion of the iron oxides. On a purely aesthetic level, graffiti damage has had to be cleaned on several occasions.

Figure 1. Monument to Tolerance on the Muelle de la Sal (Salt Pier) in Seville.

Figure 2. Spalling due to corrosion of reinforcement in the upper zone.

As concerns the quality of the materials used, the sculptor's intention in his reinforced concrete works was to achieve a rust-coloured finish that would provide, from the start, the type of patina only time can give. Therefore, as far as can be gathered from the documentation gathered, the artist resorted to including steel shavings in the composition of the concrete with the aim of causing general corrosion so that the products of this corrosion would alter the original colour of the concrete. This solution involved a problem due to the microstresses produced throughout the mass from the expansive nature of the reactions, which has favoured the partial spalling.

2 MATERIALS AND METHOD

For the concrete study, we used fragments spalled from the lower (M1) and upper (M2) part of the monument due to corrosion of the reinforcement (Fig. 2), avoiding further damage to the structure.

The concrete samples were characterized by determination of major and trace elements by X-ray fluorescence with a Panalytical spectrometer (AXIOS model). Subsequently, the chloride content was estimated from the chlorine content and expressed as a percentage by weight of cement. The mineralogical study used X-ray diffraction (Bruker-AXS D8 Advance model), determining the bulk mineralogy by the powder method. The phenolphthalein test was used to estimate the concrete pH, and the carbonation depth was determined in accordance with the UNE-EN 14639:07 standards. Finally, open porosity and apparent and real densities were determined in accordance with the UNE-EN 1936:2007 standard.

3 RESULTS AND DISCUSSION

3.1 *Chemical analysis*

The results of the chemical composition are given in Table 1.

The high SiO_2 contents are mainly attributable to the quartz and to silicates from the aggregate and from the cement used to make the concrete. The CaO is primarily attributable to the calcium hydroxide deriving from the cement hydration, which is partially carbonated. The sulfur content expressed as SO_3 was low (0.24%), deriving principally from the gypsum used as a setting regulator for the cement, and is of scant importance. Finally, the presence of chloride in both samples (even though in amounts of parts per million) is a parameter that needs evaluation due to the depassivating effect it has on the reinforcement (Cobo 2001). The chloride ion locally destroys the passivating layer that initially protects the steel reinforcement when it is encased in concrete. When it reaches the steel, chloride easily corrodes it by pitting corrosion.

In order to calculate whether the chloride content in the concrete exceeds the allowable maximum, (0.4% by weight of cement, EHE-2008), the cement content of the concrete must be established

Table 1. Chemical composition of major elements in the concrete samples (%).

	SiO_2	Al_2O_3	Fe_2O_3	MnO	MgO	CaO	Na_2O	K_2O	TiO_2	P_2O_5	SO_3	Cl(ppm)	L.O.I.
M1	70.17	4.48	6.49	0.05	0.32	9.14	0.72	1.24	0.17	0.03	0.24	816	5.61
M2	64.60	4.46	6.10	0.05	0.38	12.35	0.79	1.10	0.16	0.03	0.24	1918	7.75

(CTI, 2002). Given that no mineralogical phases with chlorine in its composition were indentified, the chloride content will be the same as the chlorine content. However since that information was not available, two theoretical estimates were made with the EHE ranges for a concrete density of 2560 kg/m^3 (average sample value, Table 2), one with a maximum cement dosage of 350 kg/m^3 and the other with a minimum dosage of 200 kg/m^3. The results of the estimation show a chloride content ranging from 0.59% to 1.04% for M1 and from 1.40% to 2.45% for M2 by weight of cement. It can be seen in all cases that the chloride content was higher than the maximum allowable limit, thereby confirming the potential corrosion of the reinforcement by pitting.

3.2 *Mineralogical analysis*

As concerns the mineral composition, most of the phases identified in the two concrete samples are as expected given the nature of the components. The cement hydration phases (tobermorites, aluminates, etc.) are not easily observed due to poor crystallinity or low contents in the bulk sample.

The quartz, feldspars, and dolomite derive from the aggregate for the concrete, whereas the calcite may derive from the carbonation of the portlandite when the cement hydrated or from a calcareous fraction of the aggregate. We have also detected traces of mineral phases of sodium, potassium, and magnesium sulfates that may correspond to cement efflorescence.

3.3 *Carbonation study*

Concrete is a physical barrier separating the steel from the atmosphere. The steel-concrete interface forms a passivating, self-regenerating film (Gancedo 1989) due to a basically electrochemical process (Sagoe 1989) that depends on the high alkalinity of the concrete (pH of 12.5 to 13.5) caused by the calcium, sodium, and potassium hydroxides dissolved in the aqueous solution of its pore network (CEIB 1984) and on the existence of a suitable electrochemical potential in accordance with the Pourbaix diagram for iron. In this way, the steel will remain passive indefinitely unless there is a decrease in pH, which would trigger the destruction of the passive state.

The stripping away of the protection of the concrete framework is basically due to the presence of depassivating ions, especially chlorides, and to carbonation at a rate that depends mainly on relative humidity, the availability of CO_2, the grade of concrete, and the environmental temperature where the concrete element is placed (Neville 1995). In any case, the carbonation process allows a local or general occurrence of a pH below a critical value in the concrete.

As soon as the hardened concrete begins to undergo carbonation, even at atmospheric carbon dioxide concentrations of 0.03% by volume (Sirvent 1997) or similar, the concrete will have two zones with a different pH, an inner pH of over 12 and an outer pH near 7. When the framework lies within the zone undergoing carbonation, at a pH of under 11, the passive film of the steel disappears.

As the phenolphthalein test confirms, the original concrete is completely carbonated, with the reinforcement depassivated and therefore entirely unprotected from corrosion.

3.4 *Physical properties*

The data from the physical analysis of two concrete samples can be viewed in Table 2. These data correspond to a concrete with medium density but with porosity at the upper limit, thereby making this a permeable, low-density (<10%) concrete more susceptible to attack by external agents.

Table 2. Physical properties.

	Porosity (%)	Apparent density (kg/m^3)	Real density (kg/m^3)
M1	11.5	2260	2550
M2	9.0	2340	2570

4 CONCLUSIONS

The results from the sample analysis indicate that the decay process is the product of a poor-quality concrete and its execution in addition to a series of negative environmental effects. Surprisingly, chloride is more abundant in the sample from higher in the monument than in the lower sample. This means, in theory, that chloride percentages are random and may be due to such causes as, for instance, the use of chlorides as set accelerators ($CaCl_2$) or to induce corrosion during batching of the concrete.

Another interesting datum is the presence of metal particles distributed throughout the piece. From an analysis of the creative evolution of Eduardo Chillida and his aesthetic intentions, it can be gathered that he intended for this work to quickly acquire a rust-coloured outer patina. This purpose was not achieved, hence the fact that the restoration work in 1999 artificially coloured the entire work, possibly with yellow iron hydroxide and an unknown binder.

Finally, it is worth noting that in another, more recent, restoration, the conservation technicians opted for using lime mortars for the repairs, thereby doing the original work a disservice.

Given the clearly adverse conditions beginning with the very materials comprising the monument, a conservation and restoration intervention is a complex issue. It would start with re-alkalinisation by electrolysis of the structure and, even so, the problem of metal particles scattered throughout and the presence of chlorides would remain.

In the meantime, in our consideration, in addition to performing the pertinent repairs to the monument appropriately and duly documenting them, its conservation is based on maintaining it perfectly water repellent, preventing contact with environmental humidity and with rainwater insofar as possible.

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Analysis of heat effects due to fires on calcareous stones

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ABSTRACT: Fires are one of the frequent anthropogenic hazards for Cultural Heritage, these events occur usually during armed conflicts or may be due to poor maintenance of electric net or gas pipeline systems. The aim of this study was to analyze the behavior of three limestones submitted to heat effects at 300 °C, 400 °C, 600 °C and 750 °C in order to evaluate the effects of the temperature generated from a fire in the monuments. The thermal tests have been studied on fresh samples of limestone from Jerez de la Frontera (Cadiz, Spain), Puerto de Santa Maria (Cadiz, Spain) and Pedrera (Seville, Spain). Specimens from the three quarries show color changes from 400 °C, meanwhile the highest temperature (750 °C) produce mineralogical and textural changes due to the presence of portlandite, which is accompanied by fractures, fissures and high loss of weight.

1 INTRODUCTION

Fires are one of the frequent anthropogenic hazards for Cultural Heritage, these events occur usually during armed conflicts or may be due to poor maintenance of electric net or gas pipeline systems. Hajpál (2008) and Gómez-Heras (2005) have highligheted that the heat of a fire can cause irreversibles changes on stones which influence the mineralogical composition, porosity, compressive strenght or statical behaivour, depending on the lythotypes.

RIVUPH is a project of the Andalusian government based on the multidisciplinary analysis of environmental risk and hazards in Historical Cities in order to develop global conservation strategies that can minimize the deterioration of Cultural Heritage. With these purposes, the heat effects of stones, that suffered fires in Monuments of Seville (Spain) 80 years ago, are being analysed. The fires destroyed most of the structures of these buildings and only part of the walls or facades was maintened. The current weathering forms of the stone facades have been recorded and the post-fire effects and damages are being analysed in comparison with heat effects on similar quarries stones.

2 METHODOLOGY AND MATERIALS

2.1 *Methods and analytical techniques*

The heat tests have been carried out in an oven model 12-PR/200 BB series at different temperatures: 300 °C, 400 °C, 600 °C and 750 °C in order to evaluate the effect of the temperature generated from an inner fire in the monuments.

Several analytical techniques have been employed to determine changes due to heat effects: a) Observation of the weathering forms obtained, b) Mineralogical analysis with a X-ray difractometer brand Bruker (model D8 Advance), using CuKα., c) The ultrasound transmission speed has been studied by a PROETISA STEINKAMP equipment, model

Table 1. Properties in the analyzed lithotypes and provenance.

Quarry/Location	Lythotype/Code	Quartz (%)	Is(50) kg/cm^2	Colour L*a*b*	Porosity (%)	US km/s
Puerto de Santa Maria/(Cadiz)	Calcarenite C	25–40	1.5	45,1,9	38.0	2.4
Jerez de la Frontera/(Cadiz)	Biosparite B	2–15	5.3	71,3,10	33.2	3.2
Pedrera/(Seville)	Oolitic limestone OL	<1%	32.7	73,1,9	13.3	5.1

* Is(50): point-load strength test, US: Ultrasound Speed.

BP-5, at 55 KHz, d) color changes have been followed by a X-RITE equipment Series SP60, and e) The loss of weight has been measured.

2.2 *Lythotypes*

Stone specimens come from quarries of Puerto de Santa Maria (Cadiz), Jerez de la Frontera (Cadiz) and Estepa Mountain, Pedrera (Seville). These three quarries have been widely used on monuments of Andalusia (South Spain). Martín et al. (1987), Guerrero (1990), Bello & Martin (1992, 1997) and Colao et al. (2010) have recorded the use of this quarries in Seville University, Town Hall, Cathedral and several Churches from XII to XIX Centuries.

The samples of these quarries are classified into the following three groups biosparite, oolitic limestone and calcarenite. The main petrographic differences among them are due to the quartz content, clasts/cement ratio, size of clastic and bioclastic grains and number of pores and pore size distribution (Ortiz et al. 1994, Guerrero 1990).

Quartz Content and main physical-mechanical characteristics are summarized in Table 1.

3 RESULTS

San Julian, San Roman and Omnium Sactorum were some of the Churches burnt in Seville between 1931–1933. San Roman Stone Facade was recently restored with replacement of stones materials, while San Julian and Omnium Sanctorum have only had partial restoration of their stones Facades. The weathering maps carry out in the Church of Omnium Sanctorum show erosin, missing parts and redish chromatic alteraion (Escudero et al. 2011). This colour change is also visible in San Julian, and other stone facades that have suffered fires in the past.

In order to undestand the influence of heat effects on this stones, an oven test was carried out at 300 °C, 400 °C, 600 °C and 700 °C on quarries stones of Puerto Santa Maria (Cadiz), Pedrera (Seville) and Jerez de la Frontera (Cadiz). The measurements of the changes due to heat effects are shown in Table 2.

The heating test produces well-marked colour changes at 300 and 400 °C at the different lythotypes. Specimens from the three quarries, which colours are light yellow or white, show a reddish colour at 300 °C and 400 °C that revert to whitish and greyish colour at the highest temperature.

This redish colour changes (Δa* 2.8–0.6) at 300–400 °C is associated to the presence of iron on the matrix, meanwhile at the highest temperature (750 ° C), the white and grey colour is due to the collapse of calcite structure and the loss of CO_2.

After being on the oven at 750 °C, the samples were leaved at room temperature and humidity, and the CaO suffers the transformation in portlandite. According to DRX results, near 25%w/w of portlandite is measured in oolitic limestone, while this new mineral arise arround 50% in calcarenite and biosparite. This new mineral implies a volume increase of 20% in average which is accompanied by fractures, fissures and missing parts.

This mineralogical change causes the desintegration of specimens. The losses of weight reach above −36% after 48 hours on bioesparite (Fig. 1) while they are around −5% in calcarenite and oolitic limestones. The losses increase with relative humidity over 75% (Escudero et al. 2011).

Table 2. Results of heating tests.

Code	Temperature	Weathering forms	ΔL*	Δa*	Δb*	LW (%)	Δ_{US} (%)
C	300 °C	Chromathic Alteration, pinkish	–5.8	2.1	0.0	–0.1	–13
	400 °C	Chromathic Alteration, pinkish and white on edges	–5.5	1.8	–1.4	–0.2	–17
	600 °C	Chromathic Alteration, whitish and greyish, sanding on corners	–3.1	0.1	–3.0	–0.4	–32
	750 °C	Chromathic Alteration, whitish, sanding on edges, crackings, missing parts	4.5	–0.9	–4.2	–5.3	–52
B	300 °C	Chromathic Alteration, pinkish	–4.8	2.3	–0.7	–0.7	–1
	400 °C	Chromathic Alteration, pinkish	–6.9	2.8	–2.9	–1.7	–1
	600 °C	Chromathic Alteration, whitish and greyish	–8.1	–1.1	–4.6	–1.8	–7
	750 °C	Chromathic Alteration, whitish and greyish, cracking and missing parts	–1.8	–0.4	0.6	–33.9	–12
OL	300 °C	Chromathic Alteration, pinkish	–20.8	0.6	–2.8	–0.04	–6
	400 °C	Chromathic Alteration, pinkish and brownish	–10.9	–0.2	–4.3	–0.1	–7
	600 °C	Chromathic Alteration, grayish with white spots	–23.2	–1.0	–6.9	–0.1	–7
	750 °C	Chromathic Alteration, whitish in the inner part and greyish outside and missing parts	1.8	–1.7	–6.6	–4.9	–56

* C: Calcarenite, Puerto Santa María (Cadiz), B: Bioesparite, Jerez de la Frontera (Cadiz), OL: Oolitic Limestone, Pedrera (Seville). ΔL: $L^* - L^*_{initial}$, Δa*: $a^* - a^*_{initial}$, Δb*: $b^* - b^*_{initial}$, LW: Loss of weight, Δ_{US}: Ultrasound speed variation.

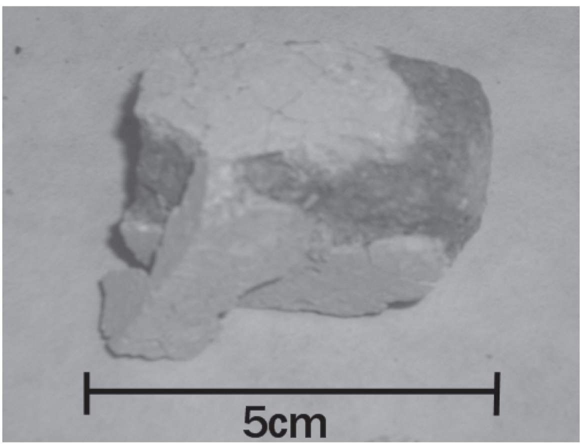

Figure 1. Missing part in the Biosparite at 750 °C (Jerez Quarry, Cadiz).

A clear decrease in the ultrasound wave speed has been detected. This change is higher in calcarenite and bioesparite (Δ_{US}: −17, −13%). Previous studies carried out by Hajpál (2008) have associated microcracks at quartz and feldspar grain boundary of sandstones to the transformation of α-quartz to β-quartz at 580–595 °C by petrographical microscope observation, although the compressive strength test does not decrease clearly. Nevertheless, the downfall of ultrasound wave speed in quarry samples, could reveal in these cases that the porosity system is changing since 300 °C. In any case, further studies must be carry out to understand if this changes are due to micro-cracking or pore size distribution changes.

During a fire in a monument, the temperature depends on the distance to the focus, fuel, fire-charge of the building and environmental conditions. According to this paper, calcareous stones that reach temperatures around 300 °C in a fire could appear reddish. Reddish chromatic zones in San Julian and Omnium Sanctorum Stones could be due to this effect, and it would be interested to analyse the inner weathering degree to assess porosity changes.

4 CONCLUSIONS

Heat effects take place in texture and mineralogical composition of the studied calcareous stones since 300 °C, and must be taken into account during a restoration after a fire on stones monuments. The mineralogical composition, quartz content, texture and porosity of these calcareous stones define the resistance to heat caused during a fire.

Colour changes found on calcareous stones at 300 °C are similar to those found in San Julian or Omnium Sanctorum Church, though those stones could appear enough well-conserved, there could be microtextural changes that could accelerate other post-fire weathering processes.

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Degradation of plastic artifacts: Case study of a "drafting machine" made of different cellulosic plastics

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ABSTRACT: This paper presents the results of the analysis made for the identification of the materials used in the manufacture of a drafting machine and the study of the relationship between its composition, conservation condition and VOCs produced during its degradation. According to the results obtained by FTIR spectroscopy, the artifact is made of two plastic materials: cellulose nitrate plasticized with camphor and cellulose acetate plasticized with triphenyl phosphate. Both plastic materials produce VOCs, acetic acid, nitric acid and nitrogen oxide that have promoted the corrosion of metallic parts. The research has shown, also, the negative influence of the piece made of cellulose nitrate in the conservation of the cellulose acetate one.

1 INTRODUCTION

Since the mid-19th century, semisynthetic plastics have been widely used in making all kind of things used in daily life of people. Now, many of these objects have entered ethnographic and history museums and have become the main source of interest of significant conservation research (Shashoua 2008, Fernández-Villa et al. 2010).

The Cartography and Geographic Studies Archive of the Spanish Ministry of Defense houses a relevant collection of topographic, geodesic and photogrammetric instruments. Some of them have been manufactured with plastics, as it occurs in the case of certain instruments used in technical drawing. As it is well known, some of these old plastics are susceptible to particular type of degradation, as it occurs in cellulose derivatives, which can lead to the complete destruction of the artifacts. Figure 1 shows the image of a "drafting machine" constructed with plastic and metal. Its current condition is an excellent example of plastic degradation and the synergies produced by the degradation products. A drafting machine is a device which is attached to a drafting table to aid a draftsperson in preparing an architectural or engineering drawing, combining the functions of a graduated parallel ruler and a graduated protractor.

This paper presents the results of the analysis made for the identification of the materials used in its manufacture and the relationship between its composition, degradation, VOCs produced during its degradation and the conservation condition of the artifact. This study is an illustrative example of the consequences of the combined use of extremely unstable materials (cellulose nitrate, cellulose acetate) and metals and the connection with their conservation (development of cracking, crazing, exudates, loss of transparency, distortion and yellowness of the plastic, as well as corrosion on metallic parts) (Figs. 1b, c, d, e).

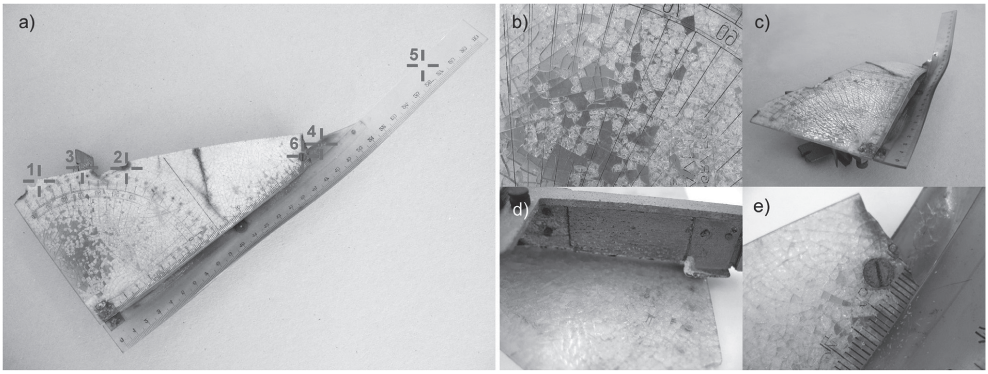

Figure 1. a) Drafting machine (numbers indicate sampling areas); examples of the different deteriorations: b) cracking, crazing, brittleness, exudates, loss of transparency and oxidation; c) yellowness, oxidation, distortion and shrinkage; d) and e) corrosion on metallic parts.

2 EXPERIMENTAL

In order to identify the plastic materials and their degradation products, six samples have been analyzed. Samples M1 and M5 have been taken from less degraded areas and samples M2 and M4 are from the most degraded. Samples M3 and M6 correspond to corrosion products of the metallic parts. The analytical techniques used have been FTIR-ATR spectroscopy and XRD.

Measurements of acid emissions have been performed with passive samplers by keeping the piece into a desiccator during around 300 h. Palmes diffusion tubes were used for quantification of formic and acetic acid and IVL' s diffusive samplers for nitrogen dioxide and nitric acid (Grywacz 2006). Measurements have also been taken outside the desiccator to have a reference of the VOCs concentration into the room in which it is placed.

The concentration of pollutants was calculated applying Fick's first law and considering the diffusion coefficients of acetic and formic acid ($0.110 \pm 0.003\ cm^2 \cdot s^{-1}$ and $0.127 \pm 0.005\ cm^2 \cdot s^{-1}$, respectively) (Gibson et al. 1997). The concentration of acetate and formate was identified by ion chromatoraphy. The concentration measurements of nitrogen dioxide and nitric acid were performed by the IVL Swedish Environmental Research Institute.

3 RESULTS AND DISCUSSION

At a glance, it is appreciated that this device is made of several types of plastic materials and metals. It is also evident that they show different degradations. The protractor shows crazing, cracking, brittleness, exudates, loss of transparency and areas with intense yellowing; these yellow zones are associated to the cracking lines. The millimeter rule exhibits yellowness, distortion, stiffness and shrinkage and the most damaged area is the one in contact with the protractor. Regarding metallyc parts, some of them show green color corrosion and others display rust. In both cases, the corrosion is more evident in the areas in contact with the protractor.

The FTIR-ATR spectra of the plastic material of the protractor (samples M1 and M2) show characteristic bands corresponding to cellulose nitrate. These are: $\nu_{C\text{-}OH}$ at 3394 cm^{-1}), $\nu_{C\text{-}H}$ at 2964, 2872 cm^{-1}, ν_{NO_2} at 1633 cm^{-1} and at 1276 cm^{-1}, $\nu_{C\text{-}O\ (ester)}$ at 1046 cm^{-1}, $\nu_{N\text{-}O}$ at 839 cm^{-1}, δ_{NO_2} at 751 and 621 cm^{-1}. The presence of plasticizer camphor is shown by the bands at 1724, 1448, 1373, 1046 and 1021 cm^{-1} (Fig. 2a).

The FTIR spectra corresponding to the plastic material of the millimetre rule (M4 y M5) present absorption bands of cellulose acetate. These are: $\nu_{C\text{-}OH}$ 3500 cm^{-1}, $\nu_{C\text{-}H}$ at 2943 and

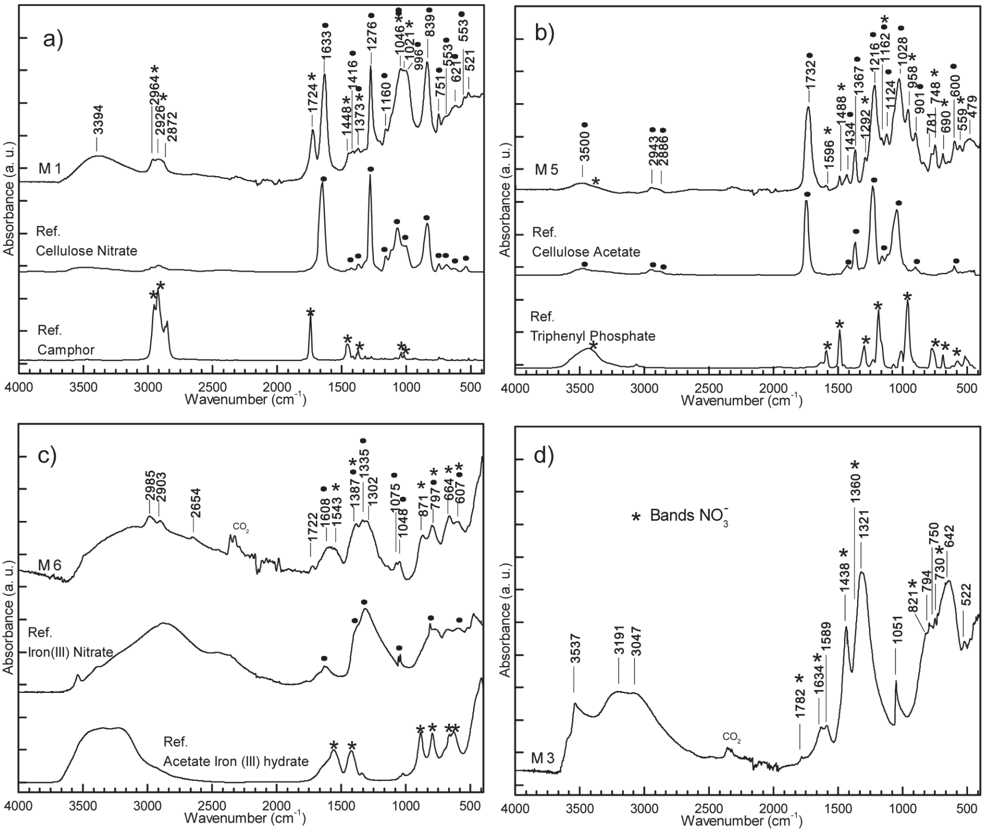

Figure 2. FTIR spectra: a) protractor (M1), b) millimeter rule (M5), c) screw rust (M6), d) green corrosion on metal (M3).

2886 cm^{-1}, $\nu_{C=O}$, at 1732 cm^{-1}, δ_{CH3} at 1367 cm^{-1} and $\delta_{C\text{-}O\text{-}C\ (ester)}$ at 1216, 1162 and 1028 cm^{-1}. There are also features attributed to the plasticizer triphenyl phosphate (1596, 1488, 1292, 1162, 958, 748, 690 and 559 cm^{-1}) (Fig. 2b).

The corrosion products identified in sample M6 by FTIR spectroscopy have been iron (III) nitrate and iron (III) acetate (Fig. 2c). With regard to sample M3 a complex spectrum has been obtained which shows features that can be attributed to nitrate and acetate groups (Fig. 2d) (Miller & Wilkins 1952, Socrates 2001, San Andrés et al. 2010). Analysis by XRD have confirmed the presence of copper (II) nitrates [copper nitrate hydrate-JCPDS pattern: 00-052-0081, and ammonium copper nitrate-JCPDS pattern: 00-051-1762] and copper (II) acetates [tris(hidroxo) acetate-bis copper hydrate-JCPDS pattern: 00-050-0407].

Figure 3a shows FTIR spectra to samples M4 and M5. Both correspond to millimeter rule, but the first one is next to the protractor and is more deteriorated. The spectrum of sample M4 displays bands that can be attributed to nitrate group besides characteristic bands of cellulose acetate. A similar comparative study has been realized between samples taken from different areas of the protractor. Figure 3b shows spectra corresponding to samples M1and M2. In both, bands attributed to cellulose nitrate can be appreciated. However, in sample M2 a decreasing of features attributed to camphor (plasticizer) may be observed as well as an important increasing of bands corresponding to nitrate groups.

Regarding the results of VOCs´ analysis, the emission of acetic acid (1.43 mg · m^{-3}), nitrogen dioxide (0.072 mg · m^{-3}) and nitric acid (<0.22 · 10^{-3} mg · m^{-3}) have been confirmed, but formic acid has not been detected.

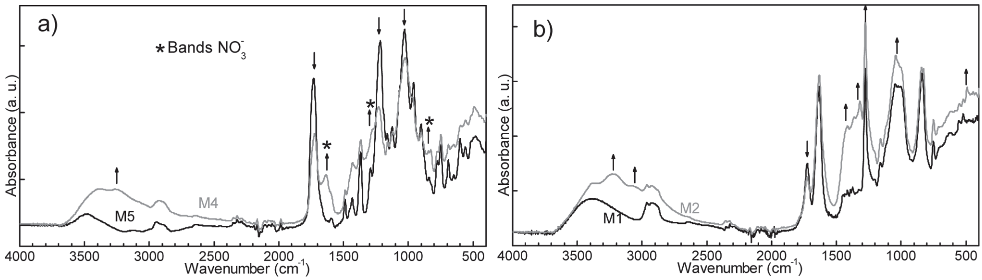

Figure 3. FTIR spectra comparison of degraded areas (M2 and M4) and no apparent deterioration (M1 y M5): a) protractor b) millimeter rule.

4 CONCLUSIONS

The drafting machine investigated is made of two plastic materials: cellulose nitrate plasticized with camphor and cellulose acetate plasticized with triphenyl phosphate. Both materials show an important degradation state that is appreciated in a visual exam. The piece of cellulose nitrate (protractor) increases the degradation of the piece of cellulose acetate (ruler millimeter) as it is proved by the results obtained by FTIR spectroscopy. Sample corresponding to cellulose acetate attached to cellulose nitrate shows bands attributed to nitrate group (NO_3^-).

Both plastic materials produce VOCs, acetic acid, nitrogen dioxide and nitric acid that have promoted the corrosion of metallic parts. The corrosion products identified have been copper (II) salts (nitrates and acetates) and iron (III) salts (nitrates and acetates).

The degradation process of these materials is in progress as the results corresponding to analysis of VOCs have proved.

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Evaluation of mural paintings biodeterioration by oxalate formation

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ABSTRACT: The microbiological study of the paintings in the Low Choir of the Convent of Nossa Senhora da Saudação Church allowed the characterisation of several bacterial strains (bacilli and cocci), filamentous fungi belonging to the genera *Cladosporium, Penicillium* and *Nectria*, several mycelia and yeast strains of the genera *Rhodotorula*. Proliferation of filamentous fungi on the painting was detected by scanning electron microscopy in microfragments of mortars. It was possible to observe the penetration of fungal hyphae in the microstructure of the mortars that may be responsible for cracking and detachments in some areas of the painting.

The alteration of the green pigment malachite was detected by Raman microscopy, being the result of the metabolic activity of microorganisms present on the paintings, which promote the formation of calcium oxalates. The results show a strong relationship between the most deteriorated areas of the paintings and higher microbial contamination.

1 INTRODUCTION

Biodeterioration is an undesirable process, triggered by living organisms, such as bacteria, fungi, algae and lichens which can affect cultural heritage and economically important materials (Capodicasa et al. 2010, Pangallo et al. 2009). The main parameters which affect microbial development are physical factors such as humidity, temperature, light and chemical factors like the nature of the substratum (Heyrman & Swings 2003). Some authors suggest bacteria as the first agents in the colonization of the mural paintings, thus providing organic matter to the next colonizers (fungi and lichens). On the other hand, the growth of biological agents such as fungi is identified as a determinant factor in the degradation of the murals (Rölleke et al. 1996). The microbial activity can cause structural and aesthetics damage in the paintings such as discoloration of its surface, detachment of fragments and biofilms formation (Guiamet et al. 2011, Milanesi et al. 2006).

Green pigments, such as malachite, are known to suffer chromatic alterations, often associated with the oxalate formation, which can have chemical or biological origin. According to the second hypothesis, microorganisms such as bacteria, fungi, algae and lichens have been identified as the main responsible for their formation (Edwards et al. 2000, Rampazzi 2004). In fact, the metabolism of these microorganisms secretes oxalic acid ($H_2C_2O_4$), which can react with the calcite ($CaCO_3$) present in the painting giving rise to calcium oxalate (CaC_2O_4), leading to the formation of efflorescences and consequent deterioration of the paintings (Guggiari et al. 2011). Calcium oxalate formation can also occur as a defence mechanism of the microorganisms in situation with excess of calcium, to prevent the toxicity to the cell (Pinna 1993).

The aim of this work is the isolation and characterisation of the microbial communities involved in the biodeterioration phenomena affecting the wall paintings of the Low Choir of the Convent of Nossa Senhora da Saudação Church (Montemor-o-Novo, Portugal) and the identification of a pigment deterioration product caused by oxalic acid, in order to plan appropriate restoration treatments.

2 MATERIAL AND METHODS

2.1 *Sampling*

The minimum amount of sample required for the different analyses and sufficient to ensure the representativeness of the paintings was collected, under aseptic conditions, with sterile swabs and scalpels, placed in a suspension of transport MRD medium (Maximum Recovery Diluent, Merck). Mortars and paint layers were also collected to allow the technical study of the paintings as well as for studying the microorganisms and to assess the extent of proliferation of microbial communities.

2.2 *Characterisation of the microorganisms present in the mortars*

The mortars collected were analysed by scanning electron microscopy (SEM). The samples were air-dried, coated with gold (Balzers Union SCD030), during 30 s, and observed in a Scanning Electron Microscope (Hitachi 3700 N) in high vacuum with accelerating voltage 10–20 kV.

2.3 *Isolation and characterisation of microorganisms*

The samples recovered with sterile swabs were mechanically shaken for 1h and inoculated, under aseptic conditions, in different culture media, specific to each microorganisms: Nutrient Agar for bacteria, Malt Extract Agar and Cook Rose Bengal for filamentous fungi, and Yeast Extract Peptone Dextrose Agar for yeasts. The cultures were incubated at 30°C for 24–48 h and for 4–5 days at 28°C, for bacteria and fungal development respectively. The identification of the microbial isolates was performed based on the observation of macroscopic and microscopic features, such as texture and colour of the colonies, hyphae morphology and reproductive structures (in the case of spore isolates), and observed with an optical microscope (OM)(Leica DM 2500P) whose images were acquired in a camera Leica DFC290HD.

2.4 *Analysis of the alteration products*

The analysis of alteration products was performed by Raman microscopy, using a HORIBA Xplora Raman microscope, with capacity increased to one hundred times, and CCD (Charge Coupled Device) detector. The samples were analysed without any preparation. The lasers used were 638 nm and 785 nm, and 10–50% filter, to avoid destruction of the sample. Raman spectra were obtained in scanning mode, after 5 scans, with acquisition time of 10–20 s and spectral resolution of 5 cm^{-1}.

3 RESULTS AND DISCUSSION

3.1 *Identification of the microbial contaminants in the paintings*

Microfragments of mortar were analysed by SEM allowing the observation and identification of the microbial communities thriving in the paintings. The images obtained by SEM (Fig. 1B) allowed the observation of fungal hyphae and mycelial structures of filamentous fungi penetrating the microstructure of the mortars, therefore promoting the proliferation of these microorganisms in depth, which may explain the presence of some cracks in the paint.

Figure 1. (A) Detail of the painting, (B) SEM micrograph of the mortar, (C) Macroscopic and D) OM characterization of *Penicillium* sp.

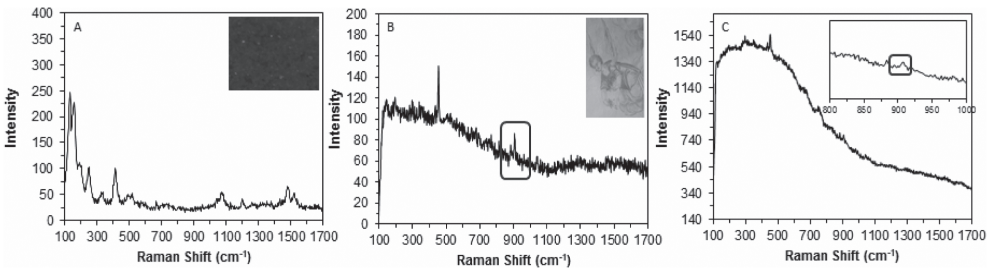

Figure 2. Raman spectra of the standard malachite (A), microfragments of mortars (B) and mixed cultures to simulate oxalates production (C). The peaks corresponding to oxalates are marked in the spectra.

To evaluate the microbial population present in the paintings, an *in vitro* growth assay was envisaged using different culture media. The characterisation of the isolated microorganisms was performed according to macroscopic and microscopic characteristics. Although this approach does not enable a full characterisation of the microbial community, since some microorganisms do not have the capacity to grow under *in vitro* conditions, is extremely important because it gives a first idea on the predominant microflora and allows obtaining a high density of cells for the other assays.

The microbiological study allowed theisolation and identification of several bacterial strains (bacilli and cocci), yeast strains of the genera *Rhodotorula* and filamentous fungi of the genera *Cladosporium*, *Penicillium* (Figs. 1C, D), *Nectria* and mycelia (without identification of reproductive structures). All the panels analysed have biological contamination, either by bacteria or filamentous fungi proliferation, chromatic alterations, which seem to be associated with the development of biofilms, cracking and the detachment of some areas of the painting (Nugari et al. 2009, Zammit et al. 2011).

3.2 *Alteration of malachite pigments and analysis of the oxalates in simulated assays*

Microfragments of mortars with green areas deteriorated, standards of malachite (Fig. 2A) and oxalic acid were analysed by Raman microscopy to detect oxalate compounds. The spectra in Figure 2B show the presence of the bands at 455, 909 and 1440 cm^{-1} characteristic of the presence of weddellite in the samples studied. It is also observed in all samples the peak at 1080 cm^{-1}, characteristic of calcite (Daniilia et al. 2008), which may be a source of calcium available to react with the oxalic acid produced by the bacteria and fungi found in these paintings (Nevin et al. 2008, Sarmiento et al. 2008).

In the case of mixed cultures of bacteria (Fig. 2C) it was possible to detect the presence of whewellite (885 and 1464 cm^{-1}) and weddellite (455, 908 and 1490 cm^{-1}) (Hernanz et al. 2007). This is consistent with those obtained in real samples, where were also detected these oxalates.

The results clearly show the influence of the microorganisms, particularly bacterial communities, in the alteration of the paint polychromy, and in the formation of surface oxalate biofilms.

4 CONCLUSIONS

This study indicates that the paintings of the Low Choir, Convent of Nossa Senhora da Saudação Church, have been colonized by filamentous fungi, yeast and also by bacteria, which seem to be responsible for the biofilm formation that promotes chromatic alterations in the painting.

There seems to be a strong relationship between the most deteriorated areas with structural damage such as cracking and detachment of the paint layer, and a higher microbial contamination. In these paintings calcium oxalates resulting from the metabolic activity of the microorganisms were detected.

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Study of the influence of black dyes in the physico-mechanical behaviour of silk fabrics

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ABSTRACT: The aim of this research is to understand the implications of the chemical structure of some natural dyes in the physico-mechanical behaviour and degradation of dyed silk fabrics. More specifically, this study focuses on black natural dyes such as logwood (*Haematoxylum campechianum L.*), commonly used in dyeing silk fabrics. For this purpose, a multi-method approach is proposed combining optic and spectroscopy techniques together with tensile tests in order to characterize the behaviour of silk fabrics as a function of the dyes present in their composition. According to this, different recipes from treatises led to the preparation of different dyed silk samples in order to characterize them physically, mechanically and chemically. Stress-strain curves evidenced the stiffness and flexibility of silk as well as their elongation and strength to failure within specific environmental conditions and dyeing procedures. Previous research carried out on the behaviour of silk fabrics led to the correlation of results and evidenced an increase of silk's stiffness as a function of the type of dye and therefore its chromatism and pH of the bath solutions.

1 INTRODUCTION

Until the discovery of South America, recipes used for obtaining black colour were extremely complex and the addition of different dyes (i.e. indigo and madder), as well as other auxiliary substances were needed to achieve a stable and bright black. These coexisted chronologically with simple recipes as iron-tannate dyes, which resulted in lower quality dyes and caused the short-term damage of the fibre due to the high corrosion of the dye baths (Cardon 2007, Hofenk de Graaff 2004, Wilson et al. 2012). The use of logwood in the European context meant obtaining high quality blacks, solving some ancestral technical problems. Despite its low stability, logwood turned into a revolutionary product due to its ability to provide deep blacks in high concentration. Logwood recipes for silk dyeing were gradually replacing the recipes cited above reducing costs and obtaining less aggressive dye baths for textiles. Black obtained with logwood coexisted with synthetic dyes until the 19th century (Roquero 2006). The conservation of black silk textiles means a great challenge for textile conservators due to the specific characteristics of dyes used for achieving this colour throughout history as well as the susceptibility of textile fibres to damage.

The aim of this research is to understand the implications of the chemical structure of different black dyes in the physical-mechanical behaviour and degradation of dyed silk fabrics. This study focuses on dyeing with logwood (*Haematoxylum campechianum L.*) as well as gallnuts. These dyes were essential constituents of the most representative black recipes since the 16th century (boom of Spanish black fashion) and until its decay when synthetics dyes were widely developed in the 19th century (Roquero 1997, Santos 2009).

2 EXPERIMENTAL

2.1 *Dyes and fabrics*

Raw dyes were purchased from Kremer Pigmente (Germany). The selected natural dyes correspond to black tones and shades and include logwood and galls compounds. A plain woven silk habutae (taffeta, 60 × 60 yarns/cm, 44.88 g/m^2, fabric thickness 0.175 mm) supplied by Testfabrics, Inc. was used as test fabric.

2.2 *Preparation of reference specimens*

2.2.1 *Preparation of the fabric*

The new silk fabric was washed with non ionic surfactant in deionised water at room temperature to remove surface soil (S). Part of the washed silk fabric was processed at same conditions of the dyeing baths (PS) to compare it with dyed silk. In order to prepare silk (S) for dyeing these were pre-mordanted in a 10% iron solution (Fe) for 1 hour at 70°C.

2.2.2 *Dye extraction*

Logwood dyeing bath: 25 g of logwood pieces were soaked in 250 mL of deionised water for 24 hours at room temperature. Then the solution was heated at 50°C for 1 hour, and filtered with a nylon filter. Then the dyeing solution was diluted to 500 mL so that a dyeing bath (Pc) was obtained (pH = 4.4–4.97).

Galls dyeing bath: 31.64 g of galls nuts powdered were soaked in 800 mL of deionised water. Then the solution was heated at 50°C for 1 hour, and then filtered with a nylon filter. Then the dyeing solution was diluted to 1600 mL so that a dyeing bath (A) was obtained (pH = 3.12–3.17).

2.2.3 *Dyeing procedure*

Several wetted pre-mordanted silk samples were immersed in the dyeing solution of logwood or galls at 70°C for 1 hour. After cooling, the dyed silk (FeA: pre-mordanted silk Fe dyed with galls A, FePc: pre-mordanted silk Fe dyed with logwood Pc) was rinsed off with deionized water and dried in the shade. One of the wetted pre-mordanted silk was first immersed in the dyeing solution of galls for 1 hour at 70°C and in the dyeing solution of logwood for 1 hour at 70°C in a second stage. After cooling, the dyed silk (FeAPc: pre-mordanted silk Fe firstly dyed with galls and then with logwood Pc) was rinsed off with deionized water and dried in the shade.

2.3 *Instrumentation*

Colorimetric analysis. Minolta CM-2600d spectrophotometer interfaced to a PC. Measurements were taken with the specular component excluded and included (SCE and SCI), using illuminant CIE D65 (6500 K) and 10° standard observer (KONICA MINOLTA SENSING, Inc.)

FTIR Spectrometry. IR absorption spectra were performed in ATR mode with a Vertex 70 Fourier transform infrared spectrometer (BRUKER OPTIK GmbH) with a FR-DGTS temperature-stabilized coated detector made by BRUKER OPTICS® with a MKII Golden Gate Attenuated Total Reflectance (ATR) accessory (ATR crystal-Diamond 45°, 2 mm × 2 mm, depth of penetration 2.0 µm for sample of Refractive Index 1.5@1000 cm^{-1}, maximum applied force 100 cNm (torque) 160 lbs or 1.78 Kbar). Number of co-added scans: 32; resolution: 4 cm^{-1}. Data was processed with OPUS software, version 5.0. The baseline correction was first applied to the original spectra (Rubberband correction method and 150 number of baseline points).

Tensile testing. Tensile tests were performed on a testing machine donated by the *Smithsonian Museum Conservation Institute* (Washington D.C.) that consists of a rectangular methacrylate box that contains several tensile testers with calibration constants. This box acts as a climatic chamber where relative humidity (RH) and temperature (T) can be kept constant. Tests were run at room temperature (23°C ± 1°C) and controlled relative humidity (45% ± 5%).

3 RESULTS AND DISCUSSION

3.1 *Colorimetric analysis*

The values L* a* b* (CIELab) of the undyed and dyed silk standards in Table 1 show the chromatic coordinates obtained from the dyeing processes for each sample. According to the chromatic coordinates CIEL* a* b*, it can be concluded that the tones obtained of each sample correspond to those described in treatises (Chevreul 1830, Fernandez 1778, Macquer 1771) from brown to black for galls and bluish/black in the case of logwood.

3.2 *FTIR*

IR spectrum (1800–600 cm^{-1}) of silk sample (S) compare to dyed silk samples (FeA, FePc and FeAPc) shows a moderate increasing of the profiles, higher in those dyed with galls (Figure 1). Appearance of a shoulder to 1723 cm^{-1} evidence the presence of carboxylic acids explaining the addition of acidic to silk fibre. Decreasing in the profile of the FeAPc silk samples compare to those dyed only with galls could be explained as a function of the presence of logwood, that could modify the structure of the iron-tannate complex.

3.3 *Tensile testing*

Table 1 shows differences between maximum deformation and strength prior to failure of silk sample (S), processed silk sample (PS) and silk samples subjected to dyeing with different recipes (FeA, FePc, FeAPc) using logwood and galls. The decreasing strength values obtained from processed silk (PS) compared to (S) silk samples evidence the weakening of processed silk probably due to the specific conditions of dyeing processes.

Figure 2 shows the force-strain curves obtained from the analysis of the behaviour under stress of the dyed silk specimens compared to processed silk (PS). Despite a slightly decrease

Table 1. L* a* b* (CIELab) values, bath dyeing pH, strength and elongation (%) of the undyed and dyed silk samples.

	Chromatic coordinates			Tensile testing		Bath dyeing
Sample	L*	a*	b*	Strength	Elongation (%)	pH
(S)	–	–	–	1.12	15.7	–
(SP)	–	–	–	1.03	16.1	–
FeA	40.4967	40.4944	3.0705	1.12	15.6	3.04
FePc	0.0903	0	0	0.99	16.1	5.1
FeAPc	10.8371	20.9391	18.4858	1.05	14.3	5.72

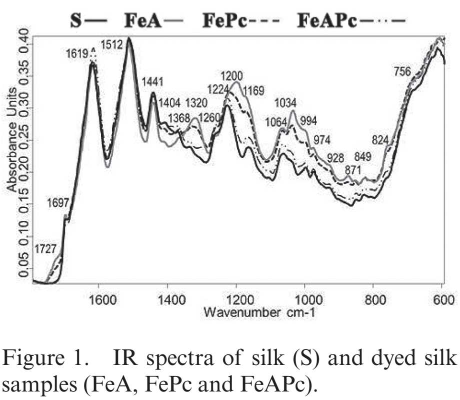

Figure 1. IR spectra of silk (S) and dyed silk samples (FeA, FePc and FeAPc).

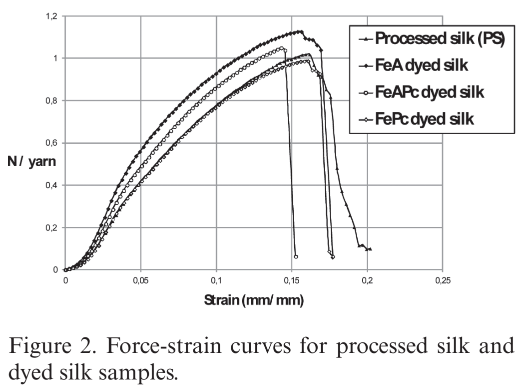

Figure 2. Force-strain curves for processed silk and dyed silk samples.

in the strength (0,99 N/yarn), FePc dyed silk shows a similar behaviour to processed silk ones. This indicates that logwood seems not to influence the mechanical behaviour of silk significantly. However, it is evident that dyed specimens with gallnuts (FeA and FeAPc) present a higher modulus. FeA dyed silk shows the highest change in modulus and evidenced the highest strength to failure (1.13 N/yarn). This change in modulus evidence an increasing stiffness of the fibre due to the acid of the iron-tannate complex. FeAPc shows a lower increase of the yarn force (1.05 N/yarn) and a significant loss of percentage elongation, around 12% compared to processed silk (PS). The addition of a second dyeing bath with logwood seems to soften the effects produce by dyeing with galls, as it can be observed in the results obtained by FTIR Spectrometry.

4 CONCLUSIONS

Tones/shades obtained reproduce those described in treatises when dyeing with galls or logwood. Results obtained by tensile testing and FTIR spectroscopy are coincident. Dyeing with logwood do not change significantly the behaviour of the silk. However, dyeing with galls provides the highest degree of acidity, stiffening the fabric significantly. This seems to decrease with the addition of logwood.

Additional tests must be conducted on artificially aged samples in order to evaluate the degradation induced by relative humidity, temperature and light.

To conclude, further research is needed to determine the effect of the different dyes (the ones corresponding to black tones) in the degradation of silk.

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VARIM 2.0: Non invasive NIR hyperspectral imaging for analysis of cultural beings

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ABSTRACT: A new image acquisition and mosaicing system (VARIM 2.0) for studying artworks in the near-infrared range has been developed to incorporate multispectral and hyperspectral imaging. The spectral window used ranges from 1000 nm to 1700 nm. Different pigments used in old master paintings, as well as modern ones, have been tested. Other materials related to the paintings as gypsum in different forms have also been inspected. The first results are in agreement with those obtained with other analytical techniques and anticipate this system to be a powerful tool in the study of paintings assisting in the restoration and conservation.

1 INTRODUCTION

As a result of the collaboration between the Visual Telecommunications Application Group of the Universidad Politécnica de Madrid and the Physics Studies Department of the Instituto del Patrimonio Cultural de España (IPCE), a whole system for the automatic acquisition and formation of the reflectographic mosaic called VARIM (http://www.gatv.ssr.upm.es/wikivarim) was developed. Originally, the system was equipped with a VIDICOM camera. The replacement of this element by an InGaAs detector camera significantly improves the results and allows increasing the acquisition speed. This system, working from 2004 to 2010, has provided the underdrawing of hundreds of paintings including those of big altarpieces in situ without dismantling (http://www.gatv.ssr.upm.es/wikivarim/index.php/Resultados).

During the last 10 years, several European and American centers have developed multispectral and hyperspectral imaging techniques, mainly in the visible spectral range, with interesting results (Liang 2012). Only a few groups have begun addressing the same techniques in the infrared range (Ricciardi et al. 2012).

For our new project, an imaging spectrograph covering the range from 1000 nm to 1700 nm was acquired. The spectrograph includes an input slit, collimating optics, transmission grating and focusing optics in a package. The generated spectrum in the near-IR region consists of overtones and combinations of the mid-IR region fundamental vibration modes. For this reason some pigments can be identified and the hyperspectral imaging can be use to determine spectral bands, which can be selected for a multispectral imaging study. This technique requires a careful monitoring sensor calibration to get the spectra and a high-precision movement to compose images in each wavelength. The design of the system is versatile as it is also planned for carrying out automated reflectography broad band and narrow band, including mosaicing.

The system is able to work in situ and on pieces of different sizes which can be located at different heights.

2 EXPERIMENTAL DETAILS

The hardware architecture is composed by an InGaAs detector camera model XENICS XEVA-FPA-1.7-640-90 Hz whit spectral range, between the 900 nm and 1700 nm. The digital images have 640 × 512 pixels of 20 microns size each. The camera may acquire images of 8 and 14 bits up to 90 fps and is connected with a PC via USB. The camera mounts a hyperspectral set of lenses (Specim ImSpector Enhanced N17E). This is a linear device able to diffract the incoming light and project the pattern in one unique grey-scale image in the InGaAs detector. Its spectral range is equal to the detector one and the bandwidth of each pixel line is around 2,25 nm. The set of lenses provides hyperspectral information for only one slice of the object to be analyzed. In order to compose images at a any wavelength, a 1-D mechanical device, able to move vertically the camera-ImSpector set, is included. This system consists of a motorized translation linear guide, 12,5 microns resolution path, which allows a linear movement of 40 mm/s. It can load an additional illumination system because it has a charge capacity of 15 kg. In order to automate the process, this device is controlled by VARIM software application.

For the acquisition of reflectographic images in narrow and broad bands, a positioning structure composed by a frame and an easel stand was designed. The frame is a linear 2-D guides system able to load up to 40 kg. It has a precision of 40 microns, with a repeatability of 5 microns. The easel stand can extend the detector position up to 2,2 m. The whole structure has two independent multipoint telemetry lasers with a LCD displaying the distance to the artwork with an error of ±1.5 mm, enough for fixing the required parallelism between the detector and the scanned surface. Reflectographic images in discrete bands are obtained by using 10 filters, 1 inch diameter each, which are mounted on an automated rotating wheel.

An upgrade of the VARIM control software has been developed to fulfill the new requirements of the system. Together with the mechanical controls, the new version implements a method for controlling the luminosity of the images (Torres & Menendez, 2005), a geometrical distortion correction technique (Torres & Menendez, 2004), a noise suppression algorithm and “monochromatic (2.25 nm)” imaging reconstruction from the hyperspectral captures.

First trials has been done on controlled samples of pigments commonly used by old master painters (azurite, cinnabar, lead-tin yellow, verdigris) bound with egg tempera and applied over several layers of gypsum and rabbit skin glue as binding medium. The paint layer reaches a thickness of approximately 60 microns. Additional trials have been made with powdered pigments in test tubes and on real paintings.

Standard and modified old enlarger objectives were used depending on the capture needs, such as distance to the object and field to be covered. As lightning system, the halogen lamps OSRAM (64515–300 w/NAED 58524 or 64502-150 w) has been selected.

Image analysis to obtain the spectra was performed with a Matlab® program taking into consideration the spectral calibration, ImSpector alignment, noise and discontinuities of the sensor and the optical distortion of the used lens. A white calibration tile (CAL/tile300 from Specim, 300 × 25 × 10 mm, 99% reflectance) was used as reference for reflectance values.

3 RESULTS AND DISCUSSION

3.1 *Ancient pigments tests*

Figure 1 shows the reflectance spectra for four ancient pigments samples (azurite, cinnabar, lead-tin yellow and verdigris) bound with egg yolk. These results agree with those obtained using other techniques as “Fiber optics reflectance spectroscopy” (http://fors.ifac.cnr.it/index.php). Figure 2 (left) shows the results from the same pigments in powder. The characteristic reflectance curves for every pigment are seen in both sets of data. The main difference between painting layer and powder results is observed at 1200 nm and in the range from 1400 to 1550 nm. This difference is much less evident for cinnabar sample.

Due to the transparency of the pigments to IR light, a distortion of the spectra coming from the molecules of the gypsum preparation layer could be expected. The spectra obtained

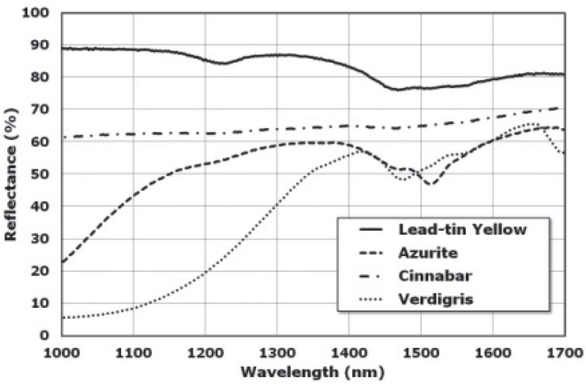

Figure 1. Reflectance spectra for four ancient pigments samples bound with egg yolk.

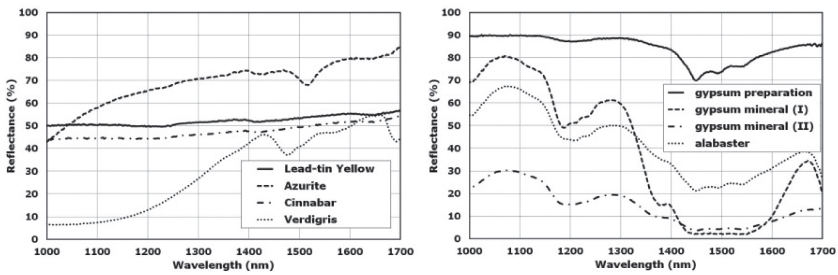

Figure 2. Reflectance spectra for four ancient pigments samples in powder (left). Reflectance spectra for the gypsum preparation layer, 2 gypsum minerals with different side of crystals and alabaster (right).

for the gypsum preparation layer used in the samples together with the spectra from 2 gypsum minerals samples with different side of crystals and the spectra of a piece of alabaster are shown in Figure 2 (right). The main component in all these materials is calcium sulfate dihydrate. The absorptions bands observed between 1400 and 1550 nm are an inherent characteristic of the gypsum molecule as well as a band at 1200 nm. Therefore, the differences observed in the spectra of powdered and layer of painting samples can be explained as due to the transparency of the pigment once mixed with the binding medium.

3.2 *Application with broad band and narrow band reflectographies*

Tests on a 16th century piece of art being restored in the IPCE have been performed (Fig. 3). Five narrow band reflectographies, progressively increasing wavelengths, and a reflectography in broad band were performed. The images show that a greater transparency at higher wavelengths for blues and greens is achieved and the shaded drawing in the figures and robes also becomes more transparent. However, the intensity of the main drawing lines of the overall composition of the scene do not change. This result may provide information about the way of working in the workshop of the painter.

In addition, the reflectography performed at 1000 nm revealed composition changes in a more clearly way that the one performed on broad band. One of those changes is the presence of the figure of God Father in the sky, not seen in the painting to the naked eye (Figure 3). From the result of the broad band reflectography, one might think that this is a change of composition at the drawing stage, but, in fact, the different grey levels of this figure respect to the background, indicates that it is a paint rectification. The significance of this change has a meaning broader than a mere esthetic formulation and it could be related to religious matters, involving an old modification of the painting by a different artist. Other imaging

Figure 3. *The Annunciation* (Bartolomé de Castro, XVI Century). Lázaro Galdiano Museum (Madrid). Photography in visible range; broad band reflectography (900–1700 nm); detail on narrow band (1000 nm).

techniques normally used in the IPCE, initially did not help in this case since the piece was cradled in a previous restoration making difficult the radiographic reading and not discontinuity was observed with fluorescence induced by ultraviolet radiation.

4 CONCLUSIONS

A new VARIM system for studying artworks in the near-infrared range has been developed to incorporate multispectral and hyperspectral imaging. The resulting spectra of the samples prepared for this study allow a reliable identification of some pigments and reproduce those obtained for other techniques working in the same spectral range but for small areas and touching the piece of art. Broad and narrow band reflectography of completed painting can be performed quickly and automatically. The results provide important information on the painter's way to work as well as layer's differentiation of great value in the process of restoration, conservation and history of art.

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Non-invasive recording technologies for the study and conservation of prehistoric rock art: The Dolmen of Dombate

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ABSTRACT: The work presented here describes the methodology used for the recording of the megalithic art (painting and engravings) preserved in the Dolmen of Dombate (Cabana de Bergantiños, A Coruña). This recording is linked to the plans for the construction of a permanent canopy over the mound (built in 2010), which raised the need to undertake direct interventions inside the chamber, especially on the paintings. Therefore, it became essential to obtain an accurate recording of the preserved art, to verify the current condition of the paintings, as well as to assess any possible damages and alterations throughout the implementation phase of the project and the processes involved in conservation and restoration activities.

These recording tasks were always carried out by means of non-invasive and indirect techniques, mainly consisting in the execution of digital tracings and alteration maps from orthoimages of the stone slabs obtained by close range photogrammetry and structured-light 3D scanning.

1 INTRODUCTION

The Dolmen of Dombate is one of the most outstanding megalithic monuments in Galicia, remarkable by its monumental architecture and by the identification of a large body of interesting prehistoric evidences. Maybe above all, the most significant patrimonial issues are the prehistoric engravings and paintings preserved inside. The archaeological excavation of the monument was conducted between 1987–1989 under the direction of J.M. Bello Diéguez, and the main results have been published in various articles (e.g. Bello & Carrera 1997). It consists of a passage grave with a short corridor oriented SE (130º), and highly differentiated both in plan and section. The chamber is made of seven megalithic slabs, and the corridor of six, three on each side. This huge structure demarcates an internal area of approximately 22 m^2 and a volume of 57 m^3. The megalithic structure is protected by a fine-grained earth mound (possibly obtained by sieving), covered with a continuous layer of stones.

The latest recording tasks had been carried out in 1992, when the Dolmen was protected with a provisional wooden cover, and the paintings inside were cleaned and consolidated. After that intervention, no further recording, cleaning or consolidation treatments were undertaken, even when the paintings revealed different changes in its state of preservation that suggested the need to update this documentation. These changes became more evident in the lower part of the orthostats (where the preserved pictorial elements are more frequent), which is covered with a thick layer of surface soil.

The construction of the permanent canopy over the burial mound (built in 2010–2011), reaffirmed the need to develop a new series of direct interventions to guarantee the preservation of the monument and, especially, of the paintings inside. This project, as well as the recording and conservation works described below, was funded by the Diputación de A Coruña, owner of the monument.

The exhaustive documentation of all the phases of the project was considered a fundamental element among all the targeted interventions: the previous state of the megalithic ensemble and of the art preserved inside, the recording of its state of preservation before and after the works, the recording of each and every direct intervention implemented, etc. The aim was to obtain a precise documentation of the preserved art and to verify the state of the paintings before and after the works, so as to evaluate possible damages and alterations during the construction works.

Among the works carried out, this work focuses on the application of indirect geometric techniques for the documentation of the art, explaining how this information was analysed in order to achieve the objectives set out in this project.

2 TECHNIQUES AND RECORDING STRATEGIES

For the recording of the Dolmen of Dombate, several different graphic and geometric recording techniques have been used. Such techniques have allowed us to analyse and record in detail the paintings and engravings and their state of preservation, as well as generating a high-accuracy documentation that could be used in future musealization or dissemination works.

For the general recording of the Dolmen of Dombate, a photographic and video report was made, in order to register the inner and outer space, the burial mound and the layer of stones that covers the mound, as well as all the works undertaken. As a complement, several panoramic photographs were created, covering fields of view of up to 360 degrees. All of these photographs were processed using the software PtGui v7.2 Pro.

A more specific recording of the preserved art was also conducted, carrying out, among other tasks, a photographic report of the state of preservation of the paintings before and after the cleaning treatments, taking photographs of the whole orthostats as well as detail photos of the paintings and of the remnants preserved in the upper area of the slabs. Furthermore, efforts have been made to repeat the same photographs before and after the cleaning, allowing to verify the level of cleaning and, when they exist, all possible degradations occurred during this process.

Two indirect geometric recording techniques were also employed, using a passive system (close-range photogrammetry) and an active sensor (structured-light scanning). With these two systems, our main aim was to obtain a series of orthophotographs of the orthostats, which, through the use of different analytical techniques, could be later used to obtain digital tracings of the engravings and paintings and alteration maps of the orthostats. Both these registering tasks were undertaken at the beginning of the project, before the cleaning of the paintings and the building of the permanent canopy.

In the case of structured-light scanning, the recording was executed with a *Nub3D* scanner, *Sidio Advance* model, and the software *Triple*, which includes an equipment that projects optical markers that are used as references in order to accurately line up the different data acquisitions. This equipment allows us to create a detailed three-dimensional archive, which represents the paintings and engravings with great detail accuracy (below 20 microns), with the added benefit of an RGB registering of the surface. So as to obtain a reasonable homogeneous color register, the scanning was executed in absolute darkness. Depending on the different working distances, the scanner was configured in two ranges: a distance of 1,20 m and a resolution of 0,375 mm (a measured point each 375 microns) for the orthostats of the chamber and two of the corridor, and a distance of 0,70 m and a resolution of 0,250 mm for the four remaining slabs of the corridor. All the individual scans (approximately 25 per orthostat) were lined up and assembled together by employing the digital optical markers projected onto the stone slabs, thus avoiding direct contact with the paintings and increasing the accuracy of the alignment. Subsequently, all this information, organized by orthostats, was processed in Polyworks to obtain the final results, improve their alignment and merge all the scans, eliminating residuals, performing the orientation for orthophotographs, etc.

Concerning photogrammetry, the process for the generation of orthophotographs is quite simple, and basically consists on taking three pictures of each orthostat from three different points of view. In these images, during processing, at least six common points to all photos must be identified; to this end, several removable targets were placed on the surface of the slabs, targets that significantly facilitated this process. All the images for photogrammetric restitution were taken with a Nikon D300 digital camera with 12 mm and 18 mm lenses.

The drawing of the orthostats was executed in *AutoCAD* by using the scaled orthophotographs generated with photogrammetry. Also the documentation of the paintings and engravings was performed using these orthophotographs as a basis, by executing the digital tracings in *Adobe Photoshop*. Nevertheless, the methodology to execute these tracings turned out to be quite complex, due to the condition of the megalithic monument in the moment of the photographic report, with very thick soil deposits, especially in the lower part of the orthostats. For this reason, it was absolutely necessary to treat these photographs before executing the digital tracings so as to improve the visibility of the paintings:

– By the use of polarising filters while taking photographs, so as to eliminate light reflection by blocking the radiation of a particular orientation (Vicent et al. 2000). This translates into a contrast enhancement, particularly highlighting—in megalithic art- red pigments (Carrera 2011).
– By the digital treatment of the orthophotographs generated with photogrammetry. This makes easier to view the preserved painting remains, even on those areas where the pigments are barely noticeable. This task was executed by using the *ImageJ DStretch* software, which has proved to be highly useful to enhance red pigments and, to a lesser extent, black pigments and even caolin.

The original orthophotographs were combined with those digitally manipulated in order to better identify the different types of pigment, being able to execute the digital tracings in *Adobe Photoshop*. While performing these digital tracings, different auxiliary materials were constantly used, thus trying to review and improve the tracings: detail and macro photography, orthophotographs obtained with structured-light scanning, comparison with previous direct tracings, first-hand on site observations, etc.

For the recording of the engravings, a very similar process based on orthophotographs was followed, but introducing some variations in the methodology. In this case, the necessary photographs for photogrammetric restitution were taken by illuminating the surface with a range of different lighting angles (generally under oblique light), employing a methodology similar to the one proposed by Cassen and Robin (2010). Once the processing of the pictures was concluded, we obtained several identical orthophotos but with different lightings, orthophotos that were overlapped as layers in Adobe Photoshop. Each of these photos was analysed (separately or combined) to determine which parts of the traces are more visible in each of them.

A similar process was performed with the 3D models obtained with the structured-light scannning, but in this case, the engravings of the untextured model were digitally illuminated at a shallow angle in *Polyworks*. This allowed us to better perceive the form and the extension of the traces, generating a series of representative orthophotographs of them.

The recording of the state of preservation consisted in the execution of detailed alteration maps of each of the orthostats and of the decorated areas. Each of the detected forms of alteration was precisely registered on those maps: fractures, fissures, lichens, fungi, algae, etc. Moreover, all these forms of alteration were photographically documented, paying special attention to the areas that still preserve painting remains.

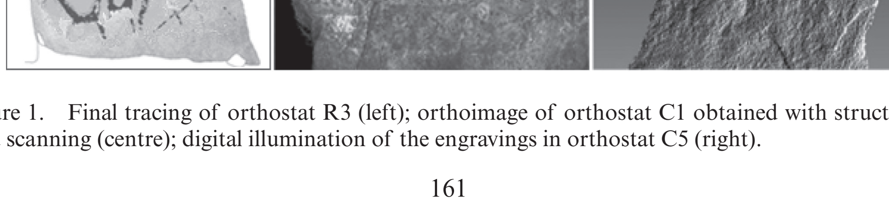

Figure 1. Final tracing of orthostat R3 (left); orthoimage of orthostat C1 obtained with structured-light scanning (centre); digital illumination of the engravings in orthostat C5 (right).

Finally, all the documentary products achieved so far (recording of the orthostats, paintings, engravings and state of preservation) were overlapped in *Adobe Photoshop*, generating a .psd file with multiple layers collecting all the information registered (orthophotographs of the orthostats, painting and engravings, alteration maps, digital tracings of the painting (caolin and red and black pigments) and the drawing of the orthostats (executed employing its respective orthophotograph as a basis). It was about using all the available information to generate an accurate drawing of each stone slab with the painting and engravings preserved on them, and at the same time, obtaining an appealing result for public presentation.

3 CONCLUSIONS

All things considered, we think that a clear positive value of this project has been the combination of different remote registering technologies (photography, photogrammetry, 3D scanner) to record such a fragile cultural heritage element as the paintings of Dombate.

It may be worth emphasising the application of metric registering methods, which have provided an excellent basis for the analysis and representation of different aspects of the paintings and engravings. They provide a good documentation of the object, avoiding any type of deterioration since they are techniques that require no direct contact with the surface being documented, with no light or heat emission. The high-quality products obtained with them have allowed us to undertake further analysis of the art preserved inside the megalith and of its state of preservation. In the case of structured-light scanning, a series of detailed three-dimensional archives was created, which represents the paintings and engravings with great detail and accuracy. This makes it possible the digital preservation of the paintings, but it also gives access at any time to this three-dimensional information, thereby enabling us to handle it: supervising the state of preservation, automatically comparing it with previous and subsequently recording works and so on.

Comparing the results of both methods, in the case of photogrammetry it is important to point out the speed of field data capture, although, concerning this case, the procedure was complicated to carry out, considering the extra difficulty of the rather short distance involved (between the slabs and the photographic camera) and the difficulty for a uniform illumination of the whole orthostats. The work process is quite simple and the equipment required is cost-effective, being limited mainly to a digital photographic camera and the software (*Photomodeler*). Structured-light 3D scanner is, on the contrary, a high-cost equipment, which requires very specific illumination conditions, but it allows to obtain a high-quality three-dimensional register, with detail and colour, and with an improvement in accuracy with regard to photogrammetry.

After this experience, we suggest the interest of applying indirect technologies as a necessary part of a conservation and evaluation methodology for this kind of art. There are further possibilities than those explained here: the recorded data are suited for further analyses, thus enabling the improvement of accuracy, assessment capacity and analysis as opposed to the more traditional techniques, but it also opens up the possibility of exploring further ways of dissemination and presentation to the public and colleagues. This is a way to be explored.

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Modern methods of documentation for conservation—digital mapping and automated 3D object documentation in software metigo®

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ABSTRACT: Several years of experience of heritage documentation have given the author a background to develop methods of cartography and digital evaluation. The outcome of which is the development of a 2D-mapping software with integrated image rectification over a period of more than 10 years. Based on true to scale mappings quantity surveys of areas and lines can be calculated automatically. Digital maps were used for the documentation of damage types, for planning of required action and for calculation of costs.

Digital stereo-photogrammetry allows users an automatic evaluation of the spatial dimension and the surface texture of objects. The integration of image analysis techniques simplifies the automation of evaluation of large image sets and offers a high accuracy. An adapted expansion- and matching algorithm offers the possibility to scan the object surface automatically and to generate a Digital Surface Models (DSM). This is the basis for calculation of true to scale ortho photos or digital 3D mapping.

1 MODERN METHODS OF 2D DOCUMENTATION

1.1 *Rectification*

Included image rectification and montage allow creating image plans as a true to scale mapping base. The projective image transformation can be used, if the object surface describes sufficiently precise a plane. For image rectification only distances measured on the object surface and geometric information (rectangle, parallel lines) are needed.

The image montage allows to combine several pictures with different qualities (resolution, scale, RGB/Grayscale) and content (infrared, UV-light, historical image) in one mapping project. CAD-Files, drawings and old mappings can be integrated by scaling function.

1.2 *Structure of a mapping project*

In a mapping project the user can define classes (layer, planes, shapes …) of different types (area-, line-mapping, detail photos, vector signatures, annotations and measurements). These classes can be grouped individually, e.g. for special combinations of classes of materials or damages for better interpreting of mapping. On the base of the grouped classes a legend can be created automatically. One finally created mapping project can be used as "mapping template" for new mapping projects of the same type.

1.3 *Digital mapping*

Different drawings can be used. There are different CAD-tools and cutting functions for processing the contours of bordering areas and working in enclosures. All mapping elements are vector based and always allow their editing and offer high quality for output in different resolutions. Based on true to scale mappings quantity surveys of areas and lines are calculated

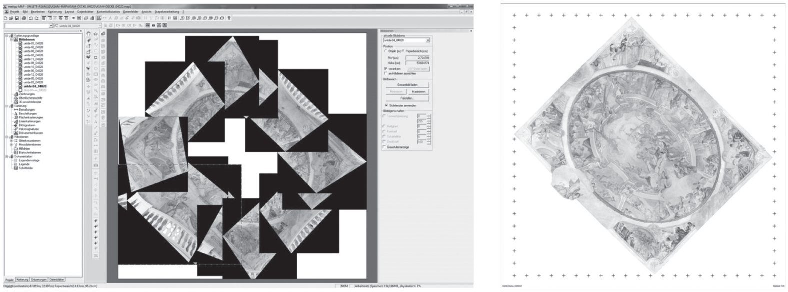

Figure 1. Image rectification and montage (left) allow true to scale object documentation, Castle Ettlingen, 'Asamsaal' (Germany).

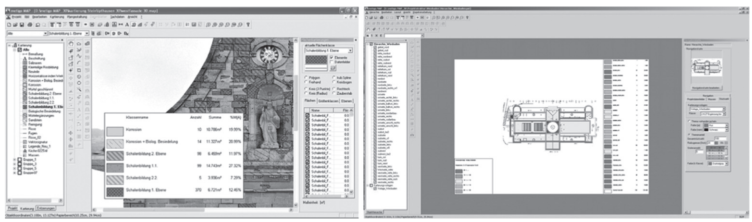

Figure 2. Left: Mapping-legend with current statistic of mapping; Pilgrame church Ipthausen (Germany), H. Romstedt. Right: Navigation map of object hierarchy for analysis of large mapping projects, Kurhaus Wiesbaden (Germany), J. Kaminsky.

automatically. So it is possible to evaluate the current statistic of mapping at all time. This statistic of mapping can be shown in the legend. For every mapping class data fields can be created (for findings or technological information), that can be assigned with values.

1.4 *Object hierarchy*

With the help of object hierarchy large conservation projects with many mapping projects can be managed and evaluated comprehensively. Subprojects can be adjusted over mapping templates. The complexity of object hierarchy is dependent of the object. At first it is very easy to define a project-tree with different mapping templates and subprojects. The software organizes the project and image files on hard disc. In the next step the user can import a navigation map and define links (areas, lines and signatures) to the subprojects on it for better navigation. By assignment of user defined project information (for example material, derivation, responsible conservator …) an easy evaluation of the mapping projects can be obtained, by automatic colouring of the links. In the same way it is possible to show the extent of damage of a special mapping class over all subprojects by filling the link areas of the navigation map with different colours.

2 CURRENT DEVELOPMENTS

2.1 *Automated detail rectification with image matching*

Correlation techniques provide automated measurements of subpixel precision for corresponding image points and congruently rectification. Therefore it is necessary to rectify one image to scale. The resulting rectified image is used as matching reference. The user has to define only an approximate rectangle on the first rectified image for each of the other images.

This is useful to compare existing documentation with additional documentations or to create a new documentation in higher quality by rectification of images in higher resolution.

Figure 3. Detail rectification with image matching church Creglingen (Germany), St. Christopher, fokus GmbH Leipzig.

2.2 *Module for calculation*

For a long time the quantity surveys of a mapping project were exported to spreadsheet by the customer to process the further calculation there. In the preparation process of a mapping project, while creating mapping classes the user can include additional factors for work and materials. Thus, the workload can be described in several work steps with persons of different skills. With different prices for material and working time several variants can be calculated and compared. All these calculation functions are collected in a separate module (optional for *metigo MAP*).

2.3 *3D mapping*

In the new version of the mapping software 3D surface models (STL, VRML, shp) can be imported as mapping base. These surface models can be created by scanning systems or by photogrammetric systems with automated image matching like in metigo 3D. This offers the base for true to scale mapping on the object surface. For 2D output the user can define different views with orthogonal projection on the object surface, which allows a true to scale output.

3 AUTOMATED 3D OBJECT DOCUMENTATION

3.1 *Image recording*

At least one digital calibrated SLR camera (full frame sensor) is used for 3D evaluation on the base of stereo models in an image set taken from the object. Using a receiving rail (on a tripod), where 2 cameras are attached, the workflow and the evaluation accuracy can be improved. For the scale distances at the object or between both cameras have to be measured. Additional three dimensional reference points at the object can be measured by tacheometer.

3.2 *Automated model assignment, automated model orientation*

After creating a project in the software the evaluation accuracy and resolution are defined, and the images are loaded into the project. The inner orientation is established for every image by linking the images to the corresponding camera. Control points are automatically detected by the evaluation software in the images (identical points at the object). The calculation of orientation of both images of the stereo model is made on the base of the known control points.

3.3 *Automated generation of point cloud and surface model*

In addition to the single-point measurement object surfaces can be scanned with appropriate expansion algorithms. With consideration of the evaluation accuracy for every stereo model the right step size (point distance) for matching is determined in dependence of the images

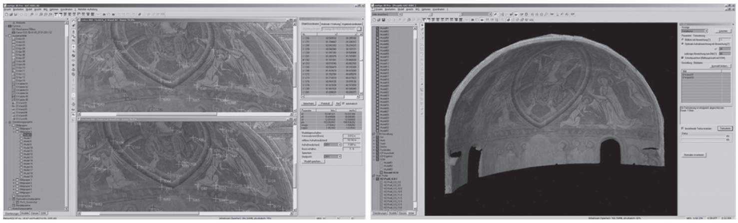

Figure 4. Left: Receiving rail for stereoscopic exposures with defined bases; middle: Orientated stereo model (coloured image coordinates with different states); right: 3D surface model with image texture; castle Katzenstein, fokus GmbH Leipzig.

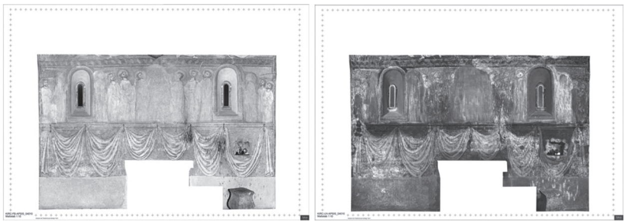

Figure 5. Left: Unwrapped image plan of a calotte (ortho-projection onto cylinder); congruent unwrapped image plan of apse with ortho-projection onto cylinder; colour image (middle) and UV-light image (right).

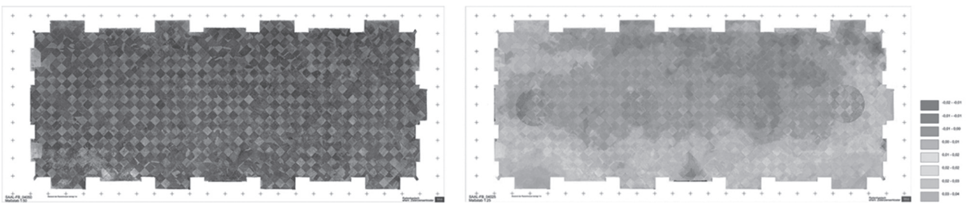

Figure 6. Left: Congruent image plan and deformation photo of floor; right: deformation photo on the base of scanned point cloud (scanned by laserscanner); Steinerner Saal, Raitenhaslach (Germany), fokus GmbH Leipzig.

scale. With batch processing all existing stereo models can be "scanned". With a triangulation algorithm a digital surface model is generated by a point cloud.

3.4 *Unwrapping/digital ortho-projection*

For the projection of images onto a plane or another unwrapping geometry, user coordinate systems can be defined related to overall coordinate system, with the help of a partial set of points (balancing plane) or with measured reference points taken by tacheometer on site. The ortho-projection onto the unwrapping geometry is made in a user defined image scale and image resolution on the base of the orientated images and the surface model.

3.5 *Deformation photo*

With the help of user defined coordinate systems it is not only possible to project textured surface models onto plane but also to show the deformations to user selected coordinate planes. Such orthophotos can be used as a base of a drawing and also for the evaluation in the mapping software *metigo MAP*.

4 SUMMARY

The mapping software *metigo MAP* was developed by fokus GmbH Leipzig and is on the market in Germany and other European countries since 2000. *Metigo MAP* is available in German, English, French, Polish, and since 2012 in Spanish.

The described functions for automated generation of 3D surface model are available within the software *metigo 3D* (currently only German) developed by fokus GmbH Leipzig. Both developed software are stand-alone applications, so no further software is required.

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Innovative testing solutions for safeguarding architectural heritage

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ABSTRACT: The paper presents several innovated or newly developed techniques for testing historic materials which enable to acquire material characteristics not achievable in another way due to specific constraints posed by the conservation policies. Affordable methods for surface sorption and for assessment of surface cohesion are presented with non-standard testing strengths of materials and strengthening effects of various consolidation agents. In contrast, the paper includes references to modern equipment supported methods, e.g. digital image correlation measurements or x-ray microtomography.

1 INTRODUCTION

In situ testing of historic materials as well as assessment of conservation treatment effects requires development and application of special non-standard testing methods. They typically exploit combination of simple approaches with modern technology for recording and evaluation of the measured data. Of course, more sophisticated methods and analytical tools can be used, too. The paper shortly presents some examples and informs about new research infrastructure built for investigation of cultural heritage problems.

2 AFFORDABLE INNOVATIVE TESTING METHODS

2.1 *Measurement of surface sorption of liquids*

Let us start with a simple method that can be applied for *in situ* measurements of surface sorption of liquids. We suggest this test for *in situ* water uptake measurements instead of using the so-called Karsten tube. The Karsten tube method was introduced into stone survey practice several years ago, though it was originally developed for a different purpose. The method is not user friendly, and its application leads to many difficulties. The main problem is with fixing a heavy glass tube to a vertical surface. In addition, measurements cannot be made on inclined surfaces and ceilings, and two operators are needed, one for observing the water movement in the scaled glass tube, using a stop-watch, and another who records the readings. There are also problems with sealing the contact ring area, and soiling the surface with the sealing putty.

The innovated microtube system for water uptake measurements is based on the ability to make electronic recordings of the data, the ability to record the water sorption from the very beginning, the ability to make continuous measurements of the water infusion into the surface, the ability to make measurements on any inclined surfaces, and the ability to make measurements of so-called "point" characteristics. The microtube system does not need to be fixed to the surface, and no special sealing is required (Drdácký et al. 2011, Drdácký et al. in press a).

The version for *in situ* measurements is shown in Figure 1. The mechanical part of this pistol-like device consists in a scaled capillary tube or some other scaled glass tube in a swivel connected tube holder that is adjustable in horizontal or vertical position, a connecting

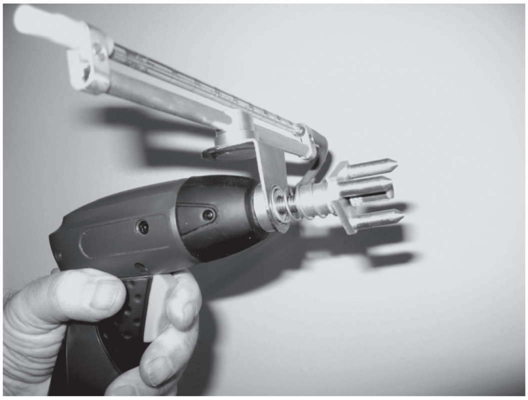

Figure 1. Pistol like device consists in a scaled capillary tube in a tube holder adjustable in horizontal or vertical position (swivel connected), a connecting plastic hose ended with an outlet hinged head with a three point support and cigarette filter "sponge" transferring liquid into measured surface, a switch for manual recording data, and a connection cable to data storage unit.

plastic hose, an outlet hinged head with a three-point support, a switch for recording the data manually, and a connection cable to the data storage unit.

The unit records time intervals corresponding to the defined volume of water absorbed by the tested material. The water uptake velocity is observed on the scaled microtube. The microtube is kept in a holder, which is fixed to the pistol with a magnet. The horizontal capillary tube can be used for measurements on inclined surfaces, for example vaults or ceilings. The trigger of the pistol is modified in the form of a micro-switch, which controls the recording of the instantaneous real time value into the processor memory in the relevant set of the open group of measurement data. The trigger is pressed when the water meniscus in the capillary tube crosses the scale line that corresponds in a typical capillary tube to a value of 0,01 ml. Of course, other scaled tubes can be used. The trigger is connected to the electronic unit through a cable with a connector. The device enables 40 measuring groups to be recorded. Thus measurements can be recorded in 40 places. Then the records should be skipped into a computer, the memory should be erased, and the device is ready for another series of measurements. The measurement is very fast and suitable for work in complicated situations—e.g. on complex sculptures, cliffs etc.

For laboratory work the scaled tube is replaced by a calibrated tube (water container) into which a float has been inserted. The float carries a core which moves inside a fixed coil of electrical inductive sensor and the movement of the float corresponding to the water level movement is thus transferred to electrical output which is continuously recorded and can be further elaborated. During the measurement the tube is repeatedly filled with a given amount of water and the movement of the water level in the tube is recorded. The outlet is connected to the tube by means of a flexible hose and provided with a paper cigarette filter which functions as a sealing interface between the outlet and the measured surface.

2.2 *Peeling test of consolidation effects*

A peeling test is used to determine the surface cohesion ("strength") of the material. It can be used for assessing surface degradation and/or for assessing improvements in surface properties after application of a consolidation agent. In the course of the test, adhesive strips are attached sequentially and then removed from the same place, and the weight of the removed material is determined by laboratory scales. The process model anticipates that some asymptotic value of the removed material will be reached by the end of the test (and denoted as A [g]). This value characterizes the surface cohesion strength, and can be related to the overall strength of the material, (Drdácký et al. in press b). The main application strategy exploits repeated peeling in the same place on a surface in order to eliminate the effect of the natural decrease in the detached material from the subsurface layers, which might be incorrectly interpreted as a consolidation effect. The measurement procedure and a discussion of the influences on the measurement are presented in detail e.g. in (Drdácký et al. 2012a). An approximation form describing the sequence of weights of the removed material m(n) is also suggested in the form

$$m(n) = A + B\,e^{-Cn} \quad (1)$$

where n is a sequence of measurements in a given place, m(n) mass (weight) of the released surface material at this n-th sequence, and A, B, C constants.

A peeling test ("Scotch Tape Test") has been used for more than forty years in conservation practice for assessing the consolidation efficiency of degraded stone without support of any standard or reliably verified recommendations for its application. Its applicability was overestimated, and its unrestricted use without adequate knowledge and sufficient understanding lead to non-comparable, non-reproducible and, in many cases, incorrect and severely biased results and assessments. Therefore, a reliable procedures and a "standard" protocol for testing the cohesion characteristics of brittle and quasi-brittle materials, mainly mortars and stones has been established and verified.

3 NON-STANDARD TESTING OF MECHANICAL CHARACTERISTICS

Well known limitations for sampling of historic materials from existing buildings or monuments force the investigators to apply methods and techniques exploiting destructive tests on small size non-standard specimens. For this purpose several methods have been developed and introduced into research and engineering practice. Let us focus on quasi brittle materials (mortars) only, even though small sample testing is also well treated in the field of timber structures. However, testing of historic timber is in recent time preferred on site without extraction of material samples, and for such a purpose new methods and devices have been developed, too, e.g. (Kloiber et al. 2011, Tannert et al. in press, Kloiber & Drdácký 2012, Kloiber et al. 2012).

Tests of mortars are carried out on specimens made of materials extracted from historical objects, and their dimensions are typically non-standard, because it is usually possible to extract pieces of masonry joint mortar or plaster only about 20 mm in thickness. The compression strength attained on non-standard flat specimens is always higher than the strength measured on standard specimens. The author derived semi-empirical correction coefficients applicable for assessing the equivalent standard compression strength from tests on non-standard specimens for lime mortars of very low standard strength of about 0,365 MPa, corresponding to degraded historic mortars, in the form

$$f_c = f_e/(h/a)^{-1,9} \quad (2)$$

where f_c denotes the computed equivalent standard compression strength, f_e is the experimentally attained compression strength, and h/a is the slenderness of the specimen. The formula is valid for specimens with length a of the base side of about 40 mm and with low strength (the lime: sand mixture was only 1: 9 (vol.)). Short length of "beams" made of extracted samples of material taken from the structure can be for bending tests supplemented symmetrically on both ends to the required length, with two "prostheses", in order to satisfy Navier's assumption of linear stress distribution along the cross section in flexure. Wood has been found to be a suitable material for mortar prosthesization,and the tested material is placed at the centre of such a beam. Correction of small size effects is described in detail e.g. in (Drdácký 2010).

Research of subtle effects of consolidation or protection treatments usually calls for design of specific test specimens, mostly thin walled in order to allow for complete penetration throughout the whole profile of the tested specimen, e.g. (Drdácký & Slížková 2012).

4 COMPUTER BASED METHODS

Even though the above mentioned devices and methods take advantage of computer supported recording or evaluation of the measured data, they are not dependent on sophisticated numerical methods and massive computations. However, this technology opened doors for development and introduction of new high tech experimental approaches and methods also in the field of cultural heritage research and study of behaviour of historic materials subjected to various loads.

The extent of this paper does not allow for a more detailed review of such modern methods. It is possible just to refer to some of them and let the reader to find further information in the relevant literature, e.g. (Drdácký et al. 2008). One of the most powerful tool can be seen in the digital image correlation which enables to test for example material characteristics of natural fibers, or material response over 2D areas (Valach & Drdácký 2008). Generally, the methods and techniques enabling study surface characteristics over an area are preferred in contrast to the point wise measurements. Further, the computer tomography offers an insight into 3D structure of materials and its which is appreciated in description of porous materials and gives data not available in another way.

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Assessment of laser treatment on dolostones colonized by microorganisms and lichens

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ABSTRACT: The preliminary results of the laser assessment for biofilms removal on rock surfaces are shown. The procedure consisted of laser irradiation (Nd:YAG, 1064 nm, 10 ns, 200 mJ) on a dolostone colonized by microorganisms (mainly cyanobacteria) and lichens. Samples were taken to assess the effectiveness of laser treatment on both the lichens thalli and microbial communities (SEM-BSE and TEM), and also on the stone substrate (SEM-SE + EDS). The results show that lichen thalli were eliminated only partially. The laser fluence applied was not enough to efficiently eliminate and/or damage the majority of lichen thalli, which is in accordance with previous laboratory results, where it was demonstrated that a higher fluence is necessary to clean and make inactive lichen symbionts. No damage was found in the dolomite crystals after laser radiation. Roughness and color were recorded before and after laser treatment. Continuous monitoring of the thermal processes during laser irradiation showed that thermal gradient is extremely high.

1 INTRODUCTION—AIMS

Diverse groups of microorganisms such as heterotrophic bacteria, cyanobacteria, free-living algae and fungi are responsible for biodeterioration in stones used to construct heritage buildings and monuments (Caneva et al. 2008). Lichens are also common colonizers of monumental stone. These biological agents can colonize the surface of the lithic substrate, as well as the internal zone of the stone, where they develop complex interactions with the mineral substrate (Ascaso et al. 1998, Caneva et al. 2008). It is known that fungi are the major biodeterioration agents of stone with significant roles in mineral dissolution and secondary mineral formation (Gadd 2007).

Methods to control biodeterioration have proven their technical and environmental limitations (Caneva et al. 2008, Doehne & Price 2010). In the field of cultural heritage, laser cleaning is a well established technique because it provides a fine and selective removal of superficial deposits and encrustations such as biological and black crust (Cooper 1998, Pouli et al. 2008 & 2012, Maravelaki-Kalaitzaki et al. 2003). However, despite the widespread use of lasers in conservation, few laser cleaning studies have been carried out dealing with the removal of biodeterioration agents, as epilithic lichen and fungi, from stone (de Cruz et al. 2009, Speranza et al. 2012).

The objective of this study is the approaching to the biofilms removal on stone by means of laser irradiation under a multi and inter-disciplinary perspective considering the laser operation conditions and the efficacy on the microbial colonization remotion, the modification of the stone surface, and the recording of the temperature during the process.

To our knowledge, this is the first study dealing with the potential detrimental effect of laser irradiation performed on the quarry on harmful microorganisms colonizing the lithic substrate that contribute to the biodeterioration of monuments.

2 MATERIALS AND METHODS

The Redueña stone was selected for this study because of its use in traditional construction in the Central area of Spain. It is a cream-colored dolostone, mainly composed by dolomite and calcite, with a moderate to high open porosity (10–25%). Some other characteristics of this stone, as well as its decay pattern can be found in Fort et al. (2008). The quarry in which this study was developed belongs to a Cretaceous geologic formation from the North of Madrid. Stone quarries are an ideal natural environment to carry out this type of study since there is a non-limited supply of sample material and the information obtained is directly transferable to any nearby monuments built out of the same rock, besides any possible damage to the stone of a monument is avoided. The microbial colonization of the fronts of this abandoned quarry has been previously studied (Cámara et al. 2011), obtaining a predominant presence of the lichen *Verrucaria nigrescens* and endolithic microorganisms. Also some laser cleaning studies have been previously carried out dealing with the removal of biodeterioration agents in this same stone (Speranza et al. 2012).

In situ laser irradiations in the quarry stone front were performed on selected areas, colonized by cyanobacteria and lichens, using, according to the previously mentioned experiments, the fundamental wavelength (1064 nm) of a Q-switched Nd:YAG laser (CTS Art Laser) that delivered pulses of 10 ns (FWHM). The laser beam, with maximum energy of 200 mJ, was focused on the surface of the stone delivering fluences up to 1.5 J/cm^2 (below the stone ablation threshold, Speranza et al. 2012) at 30 Hz repetition rate. The fluence was determined as the ratio of the laser pulse energy and the area of the irradiated spot, measured by the print left on an unplasticized polyvinyl chloride sheet.

Others in situ measurements performed were color and roughness readings on the stone surface before and after laser irradiation. Color was measured by means of a spectrophotometer (Minolta CM-2002, CIELab system, with CIE Standard Illuminant D65 and a 10° observer angle), obtaining the global color change ΔE*:

$$\Delta E^* = \left((\Delta L^*)^2 + (\Delta a^*)^2 + (\Delta b^*)^2 \right)^{1/2} \tag{1}$$

where L* = Luminosity; a* = green-red coordinate, b* = blue-yellow coordinate, and Δ reflects the variation between the values obtained before and after laser irradiation. Surface roughness was determined by an optical surface roughness meter (TraceIT, Innowep), obtaining the Rz roughness parameter, which is the arithmetic mean value of the sum of the height of the 5 tallest peaks and the depth of the 5 lowest valleys, expressed in micrometer (μm). These two parameters are used to assess the efficiency of stone cleaning methods (Vazquez et al. 2012).

Continuous monitoring of the thermal processes during laser irradiation with an infrared microbolometer-based videocamera (Optris PI infrared camera) was performed, working within the 7.5 to 13 μm spectral range.

Scanning electron microscopy (SEM) was used to study both the biocolonization (DMS 960 Zeiss, in back scattered mode BSE) as well as the effects on the stone substrate (JEOL JSM 6400 with an Oxford-INCA energy-dispersive X-ray spectrometer EDS, secondary electrons mode, SE) on samples from the selected area of the quarry front.

Samples for transmission electron microscope (TEM) study were prepared following the process described in de los Ríos and Ascaso (2002), and observed in a Zeiss EM910 equipment.

The procedure followed in the field was the selection of square-rectangular areas of approx. 40–50 cm side, facing South. Color and roughness were first measured in situ, and some samples of biocolonized dolostone surface taken for microscopic analyses. Secondly the surfaces were water sprayed and laser irradiated. Color and roughness were measured again, and some samples taken to compare with the previous ones before laser treatment. Temperature monitoring was performed during the whole process of laser irradiation.

3 RESULTS & DISCUSSION

Laser-treated rock areas showed signs of visual superficial cleaning, especially the areas harboring epilithic cyanobacteria biofilms, as the color measurements will prove too. However, at a microscopic level, the effects were not so positive. The laser produced a specific damage within the lichen thallus (Figure 1a, asterisks). There are areas with hyphae totally damaged and in the proximity appear zones composed by cells with appearance of a high cellular integrity (Fig. 1a, arrows). The images obtained by TEM, shows the maintaining of the structure of the fungal cell walls as well as the integrity of the organelles present in its cytoplasm (Fig. 1b). In this experiment, the laser treatment induced the destruction of the majority of the algal cells in the algal layer of the lichen thallus, since this is what is shown by the appearance of empty areas in the SEM-BSE images. Probably some fungal cells are destroyed but many remain, as shown by the images obtained. Fungal cells remaining in the thallus after laser irradiation show good cell integrity, which we have known through the use of TEM. In a previous experiment in laboratory conditions the irradiation with a Q-switched Nd:YAG laser revealed as a promising and effective procedure for the control of important biodeterioration processes produced by epilithic and endolithic microorganisms (Speranza et al. 2012). Moreover, a certain resistance to the thermal laser effect was observed in the fungal cell walls. It is well documented that the extent of laser cell damage depends on both the fluence and time of exposure to laser light, and that this could be enhanced by the presence of pigments (Maravelaki-Kalaitzaki et al. 2003, Vural et al. 2007).

Figure 1c shows a cross section SEM image of a dolostone sample after laser irradiation. No damage to the dolomite crystals can be seen, which is due to the fact that laser irradiation fluence did not reach the stone ablation threshold fluence (Speranza et al. 2012).

Table 1 shows the results of color and roughness measurements, before and after laser treatment of the biocolonized stone surface, and, in the case of color, compared to a reference value (fresh rock) for obtaining the global color change. The ΔE* values obtained indicate that the laser treatment makes the stone color surface closer to that of the reference one, meaning that the laser irradiation was at least efficient in removing part of the biofilm, but not all. With respect to roughness there is a trend towards diminishing the roughness of the biocolonized surface after being irradiated with laser, although it highly depends on the type of biofilm, in this specific case, lichen thalli or cyanobacterial communities.

The maximum temperature attained in the higher albedo cleaned areas is around 63.4°C, while in the lowest albedo zones, corresponding to the dark *Verrucaria nigrescens* reach up to 84.3°C. In absolute terms, temperature does not go up to values that could generate thermal decay per se, but the high temperature gradients (reaching up to the equivalent of well

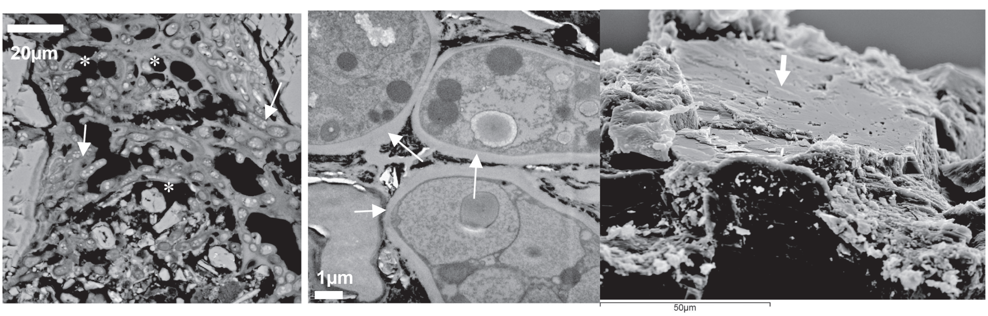

Figure 1. Microscopic images of the stone surface obtained after laser irradiation: a) SEM-BSE, b) TEM, c) SEM-SE.

Table 1. Color and roughness results measured in situ on the stone surface.

Sample field area	Color				Roughness	
	L*	a*	b*	ΔE*	Rz (μm)	ΔRz (%)
Reference	61	3.1	15.2	–	–	–
Biocolonized	40	1.5	7.0	22	35	–
Laser irradiated	48	2.5	10.6	14	33	–2

over 500°C per second) generate significant thermal shocks that could lead to an increase of cracks density in the first few outer millimeters.

4 CONCLUSIONS

The preliminary results show that laser fluence applied in the field was not enough to efficiently eliminate lichen thalli, as observed by TEM and SEM-BSE. This is in accordance with previous laboratory results, where it was demonstrated that a higher fluence is necessary to clean and make inactive lichen symbionts. It was also proved that no damage was found in the dolomite crystals after laser radiation. Laser treatment did not generate an undesirable increase in the stone surface roughness. Color parameters measured on the stone surface after laser irradiation were closer to those of the fresh cut of the rock, but not clearly enough. While maximum temperatures attained during the laser treatment hardly exceed 55°C, thermal gradients can be extremely high (5°C/0.01 s), especially in low albedo lichen species such as *Verrucaria nigrescens*.

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Effect of wavelength and pulse duration on laser cleaning of paints

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ABSTRACT: In this study, we report on the analysis of the influence of laser wavelength and pulse duration on the modifications induced on paint constituents by using pulses of femtosecond, picosecond and nanosecond duration and wavelengths in the ultraviolet and the infrared spectral regions (213, 248, 265 and 1064 nm). The study was performed on model samples consisting of shellac varnished and unvarnished traditional artist's pigment temperas, and on raw pigments. Comparison of the obtained results using different pulse durations and wavelengths illustrates the participation of mechanisms of diverse origin according to the pigment, binding media and varnish chemical composition, and highlights the importance of the optimization of the laser parameters by using laser wavelengths efficiently absorbed by the varnish and the binding media in combination with ultrashort pulses.

1 INTRODUCTION

During last decades, studies aiming at the characterization and understanding of the phenomena associated with laser-induced pigment discoloration covered a wide range of commonly used pigments, both in raw form or mixed with various binding media. Investigations have been undertaken with lasers emitting from the ultraviolet (UV) to the visible and infrared (IR) spectral regions and have shown that darkening of pigment particles and of the pigment–binder mixture occurs in various extents and may vary according to the composition of the mixture or the irradiation parameters (Castillejo et al., 2001, 2002, Oujja et al., 2010, Pouli et al., 2000, 2003).

Various authors have studied the color changes of historically pure pigments used since antiquity, as well as modern pigments used since 18th and 19th centuries, and in mixtures with organic binders (Castillejo et al., 2003), induced by irradiation with the harmonics of the Q-switched Nd:YAG laser (266, 355, 532, 1064 nm). These investigations have resulted in the determination of the threshold fluences for alteration for each material as a function of laser wavelength.

Recently (Oujja et al., 2010, 2011, 2012) have investigated the effect of shorter laser pulses in the picosecond (ps) and femtosecond (fs) range on paints. These investigations have undertaken studies on the physicochemical modifications induced on model unvarnished tempera paints with pulses of 150 ps and 260 fs at 213 and 265 nm respectively, and have shown that a high degree of control on the extent of the induced modifications may be achieved.

This paper reports on the effects induced by laser irradiation using wavelengths from UV to IR and pulse durations ranging from ns to fs domains on aged model samples consisting of shellac varnished and unvarnished traditional artist's pigment temperas, and on pellets of raw pigments. The obtained results allowed understanding the discoloration phenomena associated with painting materials and reflect the importance of using laser wavelengths highly absorbed by the binding media and varnishes in combination with ultrashort pulses during laser processing of paint artworks.

2 EXPERIMENTAL

2.1 *Samples*

The samples used for this investigation consist of unvarnished and shellac varnished temperas, and pellets prepared from raw pigments. The selected pigments were vermillion (HgS), lead chromate ($PbCrO_4$), azurite ($2CuCO_3 \cdot Cu(OH)_2$) and malachite ($CuCO_3 \cdot Cu(OH)_2$). Samples of unpigmented tempera (egg yolk) were also prepared to perform a comparison. For the varnished systems, purified (platina) shellac varnish, prepared by dissolving purified shellac resin in ethanol (1:2, w/w), was applied over the tempera layer resulting in a thickness of 10 μm.

2.2 *Laser irradiation*

Laser irradiation of samples was carried out in air by using three types of laser systems delivering pulses in ns, ps and fs domains. The ns and ps laser systems consist of the fundamental and fifth harmonic of Nd:YAG lasers emitting at 1064 and 213 nm with pulse durations of 15 ns and 150 ps. On the other hand, laser pulses of 500 fs at 248 nm and 260 fs at 265 nm were generated with a XeCl excimer pumped dye laser system and a Ti:Sapphire laser respectively.

Irradiation tests were performed on a single-spot basis for various fluences, in order to determine ablation and discoloration thresholds, as well as on a scanning basis in order to achieve a homogeneously irradiated area (approximately 10×10 mm^2) on which further analysis could be performed. In the case of laser beam at 265 nm, 260 fs, the irradiation was based on a multipulse approach (100 pulses).

2.3 *Analytical techniques*

Different analytical techniques such as optical microscopy, colorimetry, laser induced fluorescence (LIF), Raman spectroscopy and X-ray photoelectron spectroscopy (XPS) were used to assess the physico-chemical changes induced by laser irradiation.

Optical microscopy images were taken with an optical microscope equipped with a CCD camera. A spectrocolorimeter served to measure the chromatic properties of the samples. LIF measurements were carried out using laser excitation at 266 nm and a 0.30 m spectrograph with a 300 lines/mm grating coupled to an intensified charged coupled detector. Micro-Raman spectra were collected using a Raman microscope with sample excitation produced by a Helium-Cadmium laser operating at 442 nm, equipped with a microscope and an electrically refrigerated CCD camera. Finally, XPS measurements were carried out under an operating vacuum better than 1×10^{-7} Pa, using Mg Kα radiation (130 W) and an analyser transmission energy of 200 and 50 eV for the wide and narrow scan spectra, respectively.

3 RESULTS AND DISCUSSION

Discoloration and ablation thresholds of the different systems are reported in Table 1 and were determined by measuring the energy at which darkening and loss of material were observed under the optical microscope.

Table 1. Ablation and discoloration (in parentheses) thresholds in mJ/cm^2 for the treated samples. (*) and (…) means no discoloration observed and not determined respectively.

		1064 nm 15 ns	1064 nm 150 ps	265 nm 260 fs (100 pulses)	248 nm 500 fs	213 nm 15 ns	213 nm 150 ps
Unpigmented		…	800(*)	230	…	450(*)	250(*)
Shellac varnish		…	…	100(*)	…	140(*)	
Tempera paints	Vermilion	…	400(70)	170	…	260(*)	160(*)
	Lead chromate	…	400(80)	200	…	250(60)	150(50)
	Azurite	…	…	130	…	…	…
Raw pigments	Vermilion	1076(150)	440(72)	…	25(<25)	190(80)	25(15)
	Lead chromate	1350(400)	400(72)	…	35(<35)	150(80)	15(15)
	Malachite	1200(400)	380(72)	…	20(<20)	150(90)	15(15)

Laser-induced morphological changes on different samples were assessed using optical microscopy. Discoloration effects were observed under any laser irradiation conditions except for tempera paints when using wavelengths highly absorbed by the binding medium or shellac varnish (213 nm, 15 ns or 150 ps).

In our study on unvarnished tempera paints (Oujja et al., 2010), we have examined the alterations of the unpigmented tempera (binder-only) in comparison with those observed in the pigmented temperas. By using LIF and Raman spectroscopy we deduced that laser irradiation causes enhanced photodegradation of compounds which are present in the egg-yolk-based binder. However, in the colored temperas, the binder bands remain unaltered upon laser irradiation. This has been attributed to the effective channeling of the photon energy to the pigment related chromophore which prevents the photo-oxidation of the binder compounds. However, while in some cases the pigment shields the binder against modifications induced by laser action, the latter sometimes acts as protective buffer for the pigments. This is due to its high absorptivity to the applied laser radiation, a fact that restricts the interaction of the laser beam with the material at its external surface, as observed when using irradiation wavelengths at 213 nm with any pulse duration, and thus prevents from undesired alterations to the pigments (Oujja et al., 2010, 2011). Irradiation of unvarnished tempera paints revealed the role of the binding medium on the mechanisms of paint discoloration occurring upon laser exposure (Castillejo et al., 2003, Oujja et al., 2010). Unpigmented, vermilion and lead chromate based tempera were irradiated at 213 nm (150 ps and 15 ns) and at 1064 nm (150 ps). The vermilion system was found to behave differently at the two wavelengths; the pigment features (fluorescence and Raman bands) remained unaffected upon irradiation at 213 nm and disappeared under irradiation at 1064 nm. Differently, lead chromate was observed to discolor irrespective of laser wavelength or pulse-duration.

On the other hand, previous studies on model varnished tempera paints (Castillejo et al., 2003) have served to demonstrate the viability of UV laser cleaning as a tool for removing polymerized superficial varnish layers on painting substrates. Discoloration of the pigments upon direct laser irradiation was observed to occur in some cases, but no unsafe effects were detected when a thin protective layer of varnish was left on the surface. The remaining layer of varnish absorbs the ultraviolet light and protects the underlying paint. In cases where laser light interacts with the pigment layers, color and chemical changes were few and restricted to the material near the surface. Recent investigations have been carried out using two UV laser irradiation approaches in the fs and ns domain for the removal of shellac varnish on egg yolk based temperas (Oujja et al., 2011). In a multipulse approach with pulses of 260 fs duration at 265 nm it was found that the varnish experiences irreversible modifications of the initially smooth superficial texture in the form of a laser generated foam that reduces its transparency. Together with this inacceptable varnish degradation, the underlying paint layers undergo colour changes, in various extents depending on the nature of the pigment, that are interpreted as due to chemical degradation caused by exposure to the transmitted laser light. On the contrary, irradiation with pulses of 15 ns at the highly absorbed wavelength of 213 nm, allows the controlled pulse by pulse micrometric layer removal of the varnish and preserves the colorimetric and spectral properties of the underlying paints.

Latest investigations aimed at studying the effect of wavelength (213, 248 and 1064 nm) and pulse-duration (15 ns, 150 ps and 500 fs) on laser-induced changes of raw pigments (vermillion, lead chromate and malachite) (Oujja et al., 2012) revealed that vermilion experiences a change of phase from α-HgS to β-HgS allotropic form and, in turn, lead chromate and malachite discolor under the action of a reduction process of chromium and copper respectively. The XPS results obtained on vermilion pellets irradiated under laser conditions cited above have shown a negative binding energy shift in the position of Hg $4f_{7/2}$ and S $2p_{3/2}$ peaks. This physical transformation confirms the previously proposed mechanism by Zylberajch-Antoine et al. (Zylberajch-Antoine et al., 1991). With respect to lead chromate, the XPS results obtained herein have demonstrated that laser irradiation induces a decrease in the CrO_4^{2-}/Cr^{3+} ratio indicating the formation of chromium (III) oxide (Cr_2O_3) in various extents depending on the irradiation conditions. The reduction mechanism has also been reported to play a major role in the discoloration of lead chromate-based tempera paints subjected to 248 nm, 25 ns, laser irradiation (Castillejo et al., 2002). In the case of malachite, the obtained XPS and micro-Raman results reveal the participation of a reduction mechanism yielding cuprite (Cu_2O) from the original $CuCO_3 \cdot Cu(OH)_2$ compound. The laser-induced darkening of the highly sensitive pigment malachite has been reported in previous studies and has been attributed to the formation of oxides of copper (Castillejo et al., 2002, 2003).

4 CONCLUSIONS

The effect of laser irradiation on varnished and unvarnished tempera paints and on raw pigments was studied under different laser irradiation wavelengths (IR, UV) and pulse duration (ns, ps, fs). It was found that vermilion experiences a change of phase from α-HgS to β-HgS allotropic form and, in turn, lead chromate and malachite discolor under the action of a reduction process of chromium and copper respectively. These induced modifications were attenuated when using shorter pulses (ps, fs) with wavelengths in the UV region (213 and 248 nm). The comparison of the results obtained on tempera paints and on raw pigments allows to better understand the laser-induced discoloration of different pigments used commonly in paintings, and highlights the importance of using laser wavelengths efficiently absorbed by the binding media and varnish in combination with ultrashort pulses during laser processing of paintings.

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

Pigments and painting preparations of Gonzalo Bilbao analysed by non-destructive XRF technique

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ABSTRACT: Several paintings made by Gonzalo Bilbao between the end of the 19th and the beginning of the 20th centuries have been analysed by non-destructive XRF technique. The aim was to identify pigments used by the painter through different periods of his artistic activity, as well as to find out what kind of preparation he applied on canvases. There was a major interest in finding out, whether his palette and the system of preparing the painting ground were differing through time. The results showed that Bilbao was changing his painting preparations from exclusively lead white (denoted by the presence of Pb peaks in the XRF spectra) in his early works, which later on was gradually replaced by zinc white (Zn) and at the end by lithopone (Zn, Ba). Pigments showed even more complex changes. Bilbao was introducing new pigments as soon as appeared on the market, combining them with traditional ones.

1 INTRODUCTION

In November 2011 an exhibition dedicated to the Spanish painter Gonzalo Bilbao (1860–1938) was opened in the Fine Arts Museum of Seville. He is considered one of the most outstanding artistic personalities of Spanish painting of his time. The exhibition offered a possibility to analyse his works also from the material point of view, during the conservation and restoration process previous to the opening. For this purpose, fourteen artworks from different periods of time were selected: *Portrait of Elena Sánchez* (1890), *Portrait of María Luisa Ramos de Sánchez* (1891), *La madrecita* (1899), *Patio de los Bojes* (ca. 1905), *Portrait of Maria Roy* (ca. 1910), *Taller de Bordadoras* (ca. 1910), *Plaza de Zocodover, Toledo* (1890 or 1910), *La gitana* (sketch, 1910), *La casta Susana* (ca. 1914), *Las cigarreras* (sketch, 1911), *Las cigarreras* (1915), *Portrait of Teresa de Igual* (1918), *Claustro Mayor de la Merced de Sevilla* (1920) and *Portrait of Francisco Rodriguez de Marín* (1934) (Márquez 2011).

2 OBJECTIVES AND METHODOLOGY

The principal aim of the present research was to identify pigments used by Bilbao through different periods of his artistic activity, as well as to find out what kind of preparation/priming he applied on canvases. There was a major interest in finding out, whether his palette and the system of preparing the painting ground were changing through time, according to new materials and pigments that emerged especially at the end of the 19th and in the beginning of the 20th centuries. The analysis was carried out by a non-destructive X-ray Fluorescence (XRF) technique (Fig. 1). We used a portable equipment composed by an EIS X-Ray generator RX38 with a W anode and a SDD detector with 140 eV of energy resolution. All paintings were measured under the same fixed conditions, which allowed the direct comparison among the results of the different points analysed and a semi-quantitative analysis. These conditions were: 80 μA of cathode

Figure 1. *In situ* XRF analysis of Gonzalo Bilbao's *Las Cigarreras*.

current, 29.5 kV of applied high voltage and 300 s of preset live time. This non-destructive analysis offers the identification of inorganic materials on the basis of their characteristic chemicals elements present in an irradiated point. The pigments were identified according to the characteristic energy (keV) of the X-ray peaks in each obtained spectrum, which correspond to specific chemical elements (Volpin & Appolonia 2002, Seccaroni & Moioli 2004, Artioli 2010).

3 RESULTS AND DISCUSSION

3.1 *Canvas preparation*

In the preparation of canvases it can be clearly observed how, through time, Gonzalo Bilbao was changing the principal material of priming, according to new materials that were appearing on the market. In his paintings from the end of the 19th and beginning of the 20th centuries, i.e. in his early stage, Bilbao used only lead white ($2PbCO_3 \bullet Pb(OH)_2$), a common material for preparation since the beginning of canvas painting in the 15th century (Wehlte 1967, Townsend et al., 2008). When approaching the second decade of the 20th century, he started to introduce zinc white (ZnO). The quantity of this white pigment applied as priming gradually increases, while at the same time the use of lead white decreases. Finally, in his last works he stopped to use lead white and introduced a new material, lithopone ($ZnS + BaSO_4$) (Fig. 2).

3.2 *Pigments*

Results obtained on pigments show even more complex from traditional to modern materials. Bilbao was introducing new pigments as soon as appeared on the market, while at the same time, he gradually stopped to use traditional ones from his early period (Wehlte 1967, Montagna 1993, West Fitzhugh et al., 1987–2007, Gómez 2000, Eastaugh et al., 2008) (Table 1).

3.2.1 *Before 1900*

In his early works almost exclusive use of traditional pigments can be observed: lead white ($2PbCO_3 \bullet Pb(OH)_2$), yellow ($Fe(OH)_3$) and red (Fe_2O_3) ochres, umber (Fe_2O_3), vermilion (HgS), bone black ($Ca_3(PO_4)_2 + CaCO_3 + C$) and a copper based green pigment, probably copper resinate ($Cu(CH_3CO)_2 \cdot 2Cu(OH)_2 \cdot nH_2O\text{-}Cr_2O_3 \cdot nH_2O$). Some modern pigments such as zinc white (ZnO), chrome green (Cr_2O_3) or cadmium yellow (CdS) were also identified; moreover, it may be deduced that Bilbao often used cobalt blue ($CoAl_2O_4$) which was one of his favourite pigments through his entire artistic life. On the other hand, copper based green was identified only in his earliest paintings, while it was completely substituted by chrome green since the beginning of the 20th century. This could have been a conscious decision when knowing that cadmium pigments are not compatible with copper ones, yet they turn black (Montagna 1993, West Fitzhugh et al., 1987–2007, Estaugh et al., 2008).

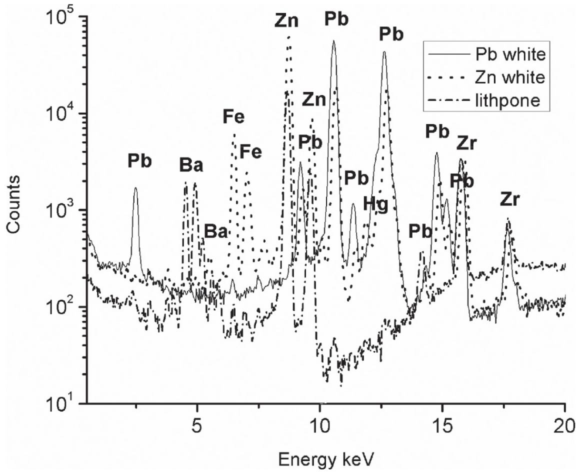

Figure 2. XRF spectra of three different priming layers.

Table 1. Pigments identified on selected paintings by Gonzalo Bilbao from different artistic periods; more (***) or less (*) present on his palette and sometimes difficult to confirm (?).

	M.L. Ramos (1891)	Madrecita (1899)	Patio Bojes (1905)	M. Roy (ca.1910)	Bordadoras (ca.1910)	Pl. Zocodov (1910)	La Gitana (1910)	Susana (ca. 1914)	Cigarreras (1911)	Cigarreras (1915)	T. de Igual (1918)	Cl. Mayor (1920)	F.R. Marín (1934)
Pb white	***	***	***	***	**	**	***	***	***	***	*	**	*
Ochres (Fe)	**	***	**	***	**	***	***	***	***	***	**	**	**
Vermilion (Hg)	***	***	***	***	*	*	***	***	**	***	**	**	
Cu based green	***												
Umber (Mn, Fe)	*	**	*		**	*		*	*		*		
Bone black (Ca)	***	**	*	**	***	*	**	**	**	**	**	*	**
Zn white	*	*	**	**	**	***	*	**	**	**	***	***	***
Lithopne (Ba, Zn)											**	*	**
Sr yellow (Cr, Sr)			**?			**	**	**	**?	**	*?	**	
Cd yellow	*	**	*	***	**	**	**	***	*	***	***	**	*
Cd orange						**	**	**	*	***	**	*	
Cd red (Cd, Se)												***	***
Co blue	***	*	**	***	**	***		**	*	**	**	***	**
Cerul. blue (Co, Sn)	*?	*?	*?		*	*			*				
Co violet (Co, As)			**	*		***		**		**	**	***	***
Cr green	*	**	*	*	**	**	**	***	**	***		**	*

3.2.2 *Around 1900–1910*

Around 1900 Bilbao introduced a new pigment, strontium yellow ($SrCrO_4$), which appears in very bright yellow areas and may be identified by high Cr and Sr peaks. In the first decade his palette still contains principally traditional pigments, but modern pigments as zinc white, cadmium yellow, chrome green and cobalt blue are gaining their importance. A new pigment was also introduced, cobalt violet ($Co_3(AsO_4)_2$), of a very intense violet colour, which later on became one of his favourites. In this period, Bilbao experiments with some other pigments which disappeared after 1910, like the intense copper and arsenic green that could be Scheele's ($CuHAsO_3$) or Schweinfurt/Emerald ($Cu(CH_3COO)_2 \cdot 3Cu(AsO_2)_2$ green. With XRF it is not possible to distinguish between them due to the same characteristic chemical elements.

3.2.3 *After 1910*

In the case of the paintings carried out after 1910 it is sometimes difficult or even impossible to identify the pigments, as they cannot be unequivocally identified on the basis of the corresponding XRF spectra. Nevertheless, it is possible to confirm the introduction of cadmium orange (CdS) and cerulean blue ($CoO \cdot nSnO_2$). Moreover, an important change in the basic palette has also been unveiled: lead white and zinc white are indifferently used by the painter.

3.2.4 *After 1920*

Further changes were revealed in the selection of Bilbao's pigments in his late artistic period, from around 1920. The painter introduced lithopone ($ZnS + BaSO_4$), zinc white became his principal white pigment, while lead white almost disappeared. He still applied ochre and vermilion, but their use was less frequent. He continued experimenting with new pigments, possibly including phthalocyanine green ($C_{32}H_4N_8Br_4Cl_8Cu$), a recently discovered organic pigment of greenish-bluish tonality, whose identification by XRF is not univocal. In his latest period he introduced a new pigment, cadmium red (CdSe), traded since 1910 and identified by Cd and Se peaks, not visible in any earlier works. Bilbao started to use it also in flesh tones, with the consequent elimination of vermilion from his palette.

4 CONCLUSIONS

The analysis of selected paintings by Gonzalo Bilbao revealed important changes in the preparation of his canvases and in the selection of pigments. The painter lived in a period of transition and innovation, in which many new pigments appeared on the market and were introduced into his work. On the other hand, traditional ones, commonly used during his early artistic stage, were gradually disappearing from his palette. As an example, the lead white priming was substituted first by zinc white and at the end by lithopone. Traditional pigments as lead white, ochre, vermilion or copper based green were substituted by zinc white, cadmium yellow, orange and red, chrome green. At the same time, new ones such as cobalt blue, cerulean blue, cobalt violet, strontium yellow and probably emerald or Scheele's green were gradually introduced. These results were also useful to help confirm dating of paintings, accordingly to the applied pigments. In particular, the *Portrait of Maria Roy* could be dated in 1910 instead of 1890, as previously proposed.

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

A novel approach for micro FTIR reflection absorption analysis of artworks' surface

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ABSTRACT: Non invasive reflection FTIR measurements provide valuable information about the chemical composition and degradation processes taking place at the surface of works of art. However, band assignments and the identification of components can often be complicated by the fact that the IR reflection response of artworks' surface is rather complex. In order to overcome this problem, a novel approach of μ-transflection analysis of artworks' surface is proposed. The obtained transflection spectra are very similar to the transmission ones, offering an easier interpretation. Although micro sampling is required, the sample removal leaves barely visible traces. In addition to the identification of the components present at the surface of the work of art, the technique can also be applied for monitoring of the chemical cleaning. Some examples of the identification of the surface of a Baroque easel painting are presented.

1 INTRODUCTION

The priceless value of cultural heritage objects has been dictating the development of non-invasive methods for artworks characterization in the last decade. By utilization of these novel methods many works of art have been characterized (Rosi et al. 2007, Miliani et al. 2009, Van der Snickt et al., 2011). Additionally, two projects, namely Eu-artech and Charisma, recently founded within the 6th and the 7th Framework Programmes of the European Union, promoted the transnational access to the mobile facilities for in situ non-invasive measurements (MOLAB), which investigated many interesting pieces all over Europe. Instruments like portable XRF, Raman, FTIR, XRD were found to be very useful for the characterization of artworks' surface as well as the bulk.

Apart from identification, fiber optic FTIR can additionally be very helpful in following the chemical cleaning of the artworks' surface, especially when organic components (like old varnish layers) need to be removed (Ropret et al., 2012). However, the interpretation of fiber optic FTIR spectra can often be complicated due to the fact that the reflection present at the artworks surface is usually a complex process. The morphology of the paint layers as well as their thickness give rise to both diffuse and specular reflection phenomenon that may result in band shifts and changes in the shape of the IR peaks. In the last few years several papers including reflection spectra of both pure materials as well as original artworks have been published (Miliani et al., 2012, Vagnini et al., 2009, Rosi et al. 2007), nevertheless, the interpretation of reflection spectra is still the main limitation of this technique.

The aim of this work was to design a new analytical approach that would give the result on the chemical composition at the artwork surface, and offer a relatively easy interpretation by using transmission spectra as a help in the interpretation.

2 EXPERIMENTAL

A diamond holder (supplied by PerkinElmer), otherwise designed as a DRIFT accessory, was used to remove the samples from the artwork surface. The size of the sample was at the micrometer scale, and showed visible traces at the surface at the microscopic level (see Fig. 1a, b). The macro-image of the detail (Fig. 1c) where the sampling was preformed (inside the white rectangle) shows that the traces of sampling cannot be noticed by the naked eye. Figure 1d shows locations of sample removal from the surface of the Baroque painting entitled "*Worship of the holy cross*" attributed to Matteo Ingoli. The diamond holder was then put under the FTIR microscope to perform the measurements. Two locations (MIK-T1 and MIK-T2, see Fig. 1d) were selected on blue areas for the identification purposes, while one location (MIK-T3, see Fig. 1d) was selected for following the chemical cleaning. The solvent used for the cleaning purposes was white spirit (supplied by SIGMA-ALDRICH).

FTIR analysis of samples was carried out with a Perkin Elmer Spectrum 100 FTIR spectrophotometer coupled to a Spotlight FTIR microscope (Cassegrain objective 16x) equipped with nitrogen cooled MCT detector. The spectra were collected in a reflectance mode between 7000 and 650 cm^{-1}, at 4 cm^{-1} spectral resolution.

3 RESULTS AND DISCUSSION

The results of the measurements on the removed micro-samples are presented in Figures 2 and 3. The spectra of the two blue areas (Fig. 2) clearly show the presence of ultramarine (MIK-T1) and Prussian blue (MIK-T2). In addition to the characteristic Si-O-Si asymmetric stretch of ultramarine at ca. 1010 cm^{-1} it was also possible to identify the presence of CO_2 entrapment in the matrix on the basis of the band at 2340 cm^{-1} confirming the presence of natural ultramarine (Miliani et al., 2008). Prussian blue was identified on the basis of the band at 2090 cm^{-1}, characteristic for the CN stretch (Silva et al., 2006). In addition to the blue pigments present it was also possible to identify calcium carbonate ($\nu_2(CO_3^{2-})$ at 876 cm^{-1}), and protein (amide bands at 1652, 1549, and 1460 cm^{-1}).

The technique can also successfully be applied for following the chemical cleaning, as shown in Figure 3. The spectrum of the un-cleaned area shows modes characteristic for

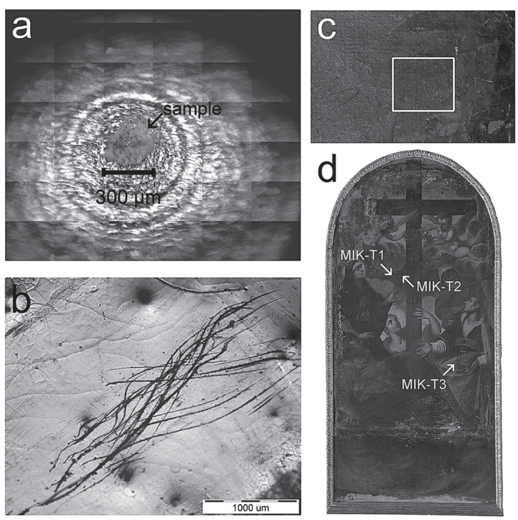

Figure 1. Photomicrograph of a sample on a diamond holder recorded with FTIR microscope (a), microscopic image of the surface of a model painting after sample removal (b), macro-image of a detail where the sampling was performed (c), and sampling locations (MIK-T1 to MIK-T3) (d).

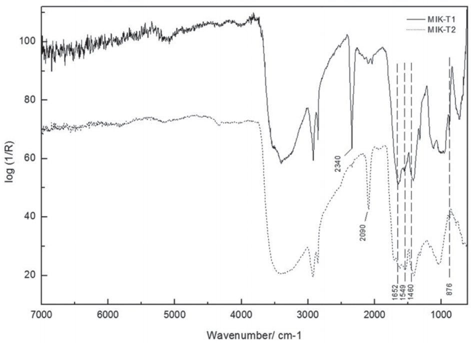

Figure 2. Micro transflection spectra of two blue areas (MIK-T1, and MIK-T2).

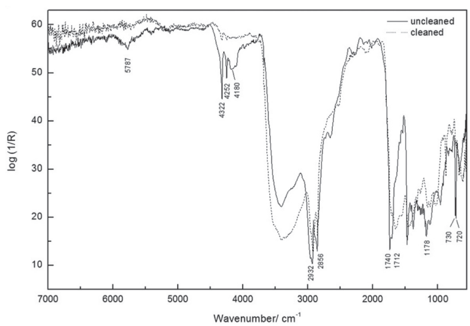

Figure 3. Micro transflection spectra of cleaned and un-cleaned area (MIK-T3).

beeswax. In the spectrum of the cleaned area there is an obvious decrease of intensity of the two marker bands at 730 and 720 cm^{-1}, significant for in-plane rotation of linear carbon chains ($\delta(CH_2)_n$), as well as the decrease of intensity of asymmetric C=O stretch of ester groups at 1740 and 1712 cm^{-1} (Brambilla et al. 2011). Additionally, also the NIR region can be used for following the cleaning: see for example the first overtone of ν(CH) at 5787 cm^{-1} (Siesler et al., 2008, Vagnini 2009) and combination bands as the CH combination mode at 4322 cm^{-1}, which show a significant decrease of intensity.

Albeit, the reflectance mode was used, the spectra are quite comparable to the transmission spectra due to the μ-transflection process that occurs when the IR beam passes through the sample and reflects back from the rough diamond surface.

4 CONCLUSIONS

The presented μ-transflection FTIR method shows a promising application for the characterization of the artworks surface since the resulting spectra are easily comparable to the transmission spectra thus offering an easier interpretation with respect to reflection IR spectra. Furthermore, although the technique should be considered invasive, the sampling procedure leaves barely visible traces. Additionally, no sample manipulation, such as cross sections preparation, is needed therefore no information from the surface is lost.

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

Methodology for the study of the walls of the Patio de Santo Tomás, University of Alcalá

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ABSTRACT: The main courtyard of the University of Alcalá, Patio de Santo Tomas, has undergone many transformations and changes of use since it was built in the 16th century. During the restoration works of the building, the wall renderings were removed, showing the building materials of the walls. It was observed that the historical building works were overlapped on the same plane of the wall. This exceptional event allowed a direct study of the historical evolution occurred on the building, through an analysis of the materials and the construction techniques.

The aims of the study were: first, finding out the shape and size, building techniques and materials of the original Patio; second, identifying the main elements and construction techniques of the different historical stages of the building; and third, surveying the successive building works undertaken in the building over the past five centuries. In order to achieve these goals, the methodology used combined historic and graphic documentation, stratigraphy, morphology and metric analysis and materials characterization.

1 INTRODUCTION

The University of Alcalá de Henares was founded by Cardinal Cisneros in 1495 and was declared World Heritage Site by UNESCO in 1998. The first stone of the Main College of San Ildefonso was placed by Cisneros in 1499 and his servant Gonzalo Fernández el Zegrí (Torre 1946), a formerly noble Nasrid baptised by Cisneros, was present in the event (Hefele 1869). The construction begins in 1501 under the direction of the architect Pedro Gumiel. The building was constructed using rammed earth, the cheaper and faster technique available in that moment. Cisneros referred to it with a famous sentence said to Ferdinand the Catholic: "Others will build with marble and stone what I have done with mud". In 1670 the new cloister of the building, nowadays known as Patio de Santo Tomás de Villanueva, was crowned with this sentence in the inscription in Latin: "en luteam olim celebra a marmoream" (first in mud, now in stone).

In 1537 the main Façade of the building was substituted by the nowadays façade, designed by Gil de Hontañón. In 1599 a Clock tower located at the south wall of the patio is ordered to Juan de Ballesteros. The tower construction was involved in several building problems and finally was substituted by a smaller tower, designed by Fray Alberto de la Madre de Dios and constructed in 1615, under the supervision of Juan García Atienza. The cloister of granite that can be seen nowadays was designed by José de Sopeña and built up between 1656 and 1670.

The decline in the late XVIII century led to the relocation of the University to Madrid in 1836. The existing buildings were useless and abandoned until 1850 when was occupied by the army and later was transformed into a religious school (Priarist Fathers) that ran until 1931. At last, the university returned to Alcalá de Henares in 1977 and the main College returned to be the central piece of the renewed university.

During 2010–2011 new rehabilitation works were undertaken on the main foundational buildings, removing all the renderings of the walls. All of the constituent materials of the walls could be seen together for the first time. In order to study the history of the building through the materials and building techniques, a set of high quality photographs of all the four walls and several materials samples were taken. It was observed that the historical building works were overlapped on the same plane of the wall. From these new data, a research program was conducted, combining different techniques.

The main objectives of the study were: first, finding out the shape and size, building techniques and materials of the original Patio; second, identifying the main elements and construction techniques of the different historical stages of the building; and third, surveying the successive building works undertaken in the building over the past five centuries.

This study is part of the Program "Geomateriales. Durabilidad y conservación de geomateriales del patrimonio construido" (S2009/MAT-1629) funded by the Comunidad de Madrid.

2 METHODOLOGY

The study combined the study of historic and graphic documentation of the Patio, a planimetric survey (Undurraga 2012) of the walls (Fig. 1) and wall stratigraphy, a morphological analysis of the masonry and other building techniques, a materials characterization of samples extracted from the walls (Barluenga et al. 2010), a classification of the materials and building techniques and a metric analysis using Castilian foot and vara, according to those used in the XV century in Spain (3 Castilian feet = 1 Castilian vara = 83.59 cm). The aim of this multiple approach was to obtain results which can support feasible hypothesis on the original Patio and to identify a temporal sequence of the main events occurred during the last 500 years.

3 RESULTS AND DISCUSSION

Four chronological and constructive stages of the evolution of the Patio were identified:

3.1 *Stage 1: Foundation of the University (1499) and construction of the main Façade (1553)*

The original Patio was two stories high and was built with rammed earth (*tapial boxes*) placed between brick-work piles. The new façade was three stories high and the north side of the Patio was elevated one story more, as it can be observed in Figure 1.

The constructive techniques and materials identified which correspond to the original Patio were: 3 feet limestone baseboard, tapial boxes (rammed earth) of 3½ by 9 feet, with 3 to 4 putlog holes horizontally distributed, placed between brick-work piles of 4 to 6 feet width. The brick-work used bricks of 4 × 16–18 × 8–10 cm and limestone mortar. The walls were

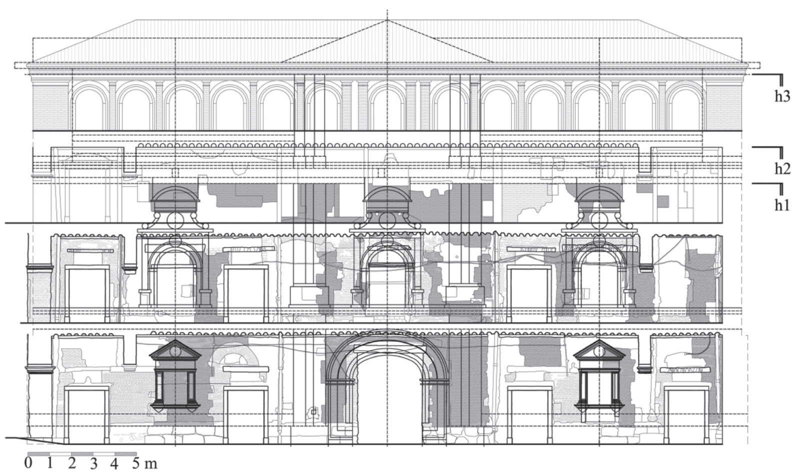

Figure 1. North wall of the Patio. The main façade of the building has been superimposed. It can be observed the coincidence of some of the present voids of the Patio with the windows of the façade. h1: original height: 43 feet (1508); h2: cloister height: 49 feet (1670); h3: façade height: 61 feet (1553).

covered with a thin layer of limestone mortar which hid the putlog holes. The dimensions of the original windows were 4 ½ × 12 feet.

The lack of horizontal rows of bricks between the rammed earth boxes is not a usual *tapial* solution in the area of Madrid (Maldonado et al. 1997). However, this type of construction can be found in the south of Spain, as it has been described in the literature (Graciani & Tabales 2008, Jaquin et al. 2007). In fact, the walls of rammed-earth boxes between brick-work piles and without horizontal rows of bricks between the boxes are typical in the Spanish-Muslim architecture (Pavón 1999). The use of this technique in the building can be explained based on the active involvement of Cardinal Cisneros in the conquest of the kingdom of Granada in 1492 and the subsequent baptism of the converse Muslims. It can be highlighted the presence of his right-hand man, a formerly noble Nasrid, in the placement of the first stone of the university.

With regard to the original building shape and size, the results point out that originally the four sides of the Patio were not of the same height, even before the new façade was built up. The original north side of the Patio reached 43 feet (Fig. 1), while the other three sides barely reached 31½ feet of height. Furthermore, the first floor of the north side was, at least, 1 vara (3 feet) above the others (20 feet above the Patio). This different position of the floors makes us to think that the original corridor of the Patio did not run uniformly along the four sides of the Patio. Actually, it is very probably that there was no gallery on the north side of the Patio, because the first floor was quite surely the main Library of the College and the access was through a staircase inside the building.

3.2 *Stage 2: Improvements in the XVII century—Clock tower (1599) & granite cloister (1670)*

The cloister reached the height of the side parts of the main façade and the other three walls of the Patio were elevated to three stories. The clock tower emphasized the north-south axis and the cloister provided an internal façade and a centre to the Patio.

To raise the walls of the Patio a different type of bricks were used. The dimensions of the bricks were 4 × 26 × 14 cm and the thickness of the mortar layers also increases, reaching 4 cm. However, the composition of both was very similar to the former of the XVI century.

In contrast, the materials used for the Clock tower largely differ from the others. It has been observed that, although the size and shape was the same as the former brickwork, the composition of the bricks and the mortars were different. The manufacturing temperature has been measured to be clearly higher than on the other bricks and the type of sand of the mortar had a different chemical composition (Barluenga 2012). This fact could be explained considering the troubles reported to occur during the tower construction. According to the historic documents, the tower was planned to be very high (133 feet) and during the construction structural problems emerged. As a consequence, the architect was dismissed, the tower design was changed (96 feet) and the brick-work was demolished and reconstructed, probably with another contractor.

3.3 *Stage 3: Rehabilitation works in the XIX century (Army & Priarist Fathers School)*

Many new voids were opened in the four walls of the Patio, accordingly to the new uses of the spaces (bedrooms, classrooms, canteen, kitchens, stores and stables) (Iglesia 1844).

The brickwork was constructed using thicker bricks 5 × 24 × 12 cm and mortar layers of 1.5 cm. The chemical composition and heating temperature greatly differ from the previous. The works are located mainly on the sides of the voids and new timber lintels were used to raise the doors in order to reach the high of the former windows. The some brickwork can be found closing several former voids and strengthen the eats wall. The preserved voids and the new ones follow the rhythm of the archery of the granite cloister, unifying the architectural composition.

3.4 *Stage 4: Restoration and refurbishment works in the XX century*

Several interventions of restoration were accomplished and the Clock tower was demolished.

The height of the voids was drastically reduced including first a false arch and, afterwards, lowering the lintels. The width of the voids was enlarged in all of them, but the two main entrances of the Patio, some voids were closed and a new granite band is placed as a skirting board and framing the voids. In this stage, reinforced concrete elements were integrated in the walls in some specific areas, and the remaining rammed-earth walls were covered with hollow brick masonry in order to provide a support for a continuous rendering.

4 CONCLUSIONS

In this study, the different stages of the evolution during the last 500 years of the Main courtyard (Patio de Santo Tomás de Villanueva) of the original building of the Alcalá University (College of San Ildefonso) have been identified through the study of the original materials, metric and constructive techniques of the walls of the Patio.

A multiple researching approach, combining historical documentation and planimetric survey of the walls, materials characterization, a morphological and a metric analysis, allows a scientific interpretation of the data obtained directly from the nowadays walls' constitution. This methodology has proved to be a very useful tool to study historical buildings and can be a practical method to analyse other examples of the architectural heritage.

The morphological and metric analysis indicates that the north side of the College was from the beginning higher than the other three sides and it could even have an independent functionality. The original Patio was organised according to an east–west sequence and the nowadays north–south axis was defined later through the refurbishment works during the XVI and the XVII centuries. The constructive techniques used in the original Patio corresponded to Spanish-Muslim architecture: walls of rammed-earth boxes between brick-work piles and without horizontal rows of bricks between the boxes. Although, as far as the available data can reach, the Patio was not built in the Cisneros-style (Spanish-Muslim decoration) as some of other parts of the College were, as the San Ildefonso Chapel or the Trilingual Auditorium.

The successive interventions on the Patio shown a relationship among them, as far as the general dimensions of the Patio remained constant over time. The main façade built in the XVI century fixed the height of the granite cloister constructed a century later and the height, size and location of the main voids. Some important differences in the materials and brickwork techniques have been also identified.

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The altarpiece of the church of Freixo de Espada-à-Cinta: A study on its artistic materiality

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ABSTRACT: The Altarpiece from the Church of Freixo de Espada-à-Cinta, in Portugal, is a remarkable work from the 16th century attributed to workshop of Viseu and its master, the great Portuguese renascence painter Vasco Fernandes. However, some questions have been raised about the true attribution of the altarpiece, and art historians have pointed out different hypotheses about the painters and the workshops involved in its production.

This work presents the study of the 16 paintings that constitute the Altarpiece, using a multi-analytical approach for the characterization of the painting technique and materials applied in the paintings, with the purpose to answer to some of the problematic questions. Several micro-samples were collected from each painting and then analysed by optical microscopy, FTIR, and SEM-EDX. Data obtained through the combination of these analytical techniques, along with infrared reflectography, bring to the light new evidences that contribute to the problematic questions on the altarpiece's attribution.

1 INTRODUCTION

One of the main Portuguese painters from the 16th century, Vasco Fernandes lived and worked in Viseu for at least forty years, since 1501. Popularized as "*Grão Vasco*", Vasco Fernandes has being associated to the nucleus of paintings of Freixo de Espada-à-Cinta, which has sixteen panel paintings—with average dimension of 77.5 cm (height) by 75.7 cm (width)—initially inserted in an altarpiece and nowadays at the side walls of the main chapel of Freixo de Espada-à-Cinta's Church.

Reis-Santos has pointed out Vasco Fernandes as the author of this polyptych, with the possible collaboration of one of his disciples, António Vaz, supporting his hypothesis on a monogram with the initials "AVF" painted on the panel of the "Three Wise Men" (Reis-Santos 1946: 24) as a signature of the workmanship is treated. Such line of aesthetic thought was followed by Jorge Henrique Pais da Silva. The attribution of the masterpieces to the Master was done again by

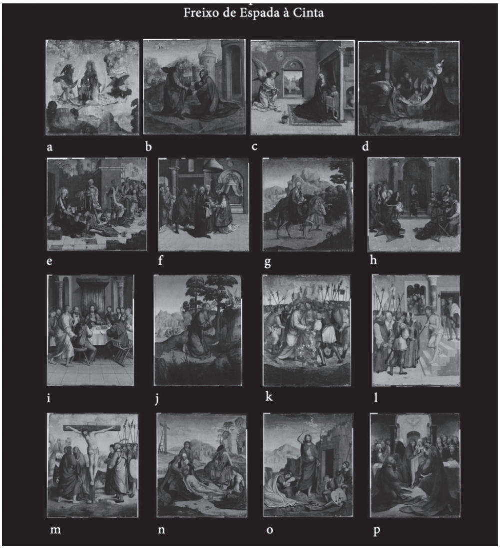

Figure 1. a) *Assunção da Virgem*; b) *Santa Ana e São Joaquim*; c) *Anunciação*; d) *Natividade*; e) *Adoração*; f) *Apresentação*; g) *Fuga Egipto*; h) *Jesus entre os Doutores*; i) *Última Ceia*; j) *Cristo no Horto*; k) *Prisão de Cristo*; l) *Ecce Homo*; m) *Calvário*; n) *Descida da Cruz*; o) *Cristo em Ressurreição*; p) *Pentecostes*.

Reynaldo dos Santos and Adriano de Gusmão (Rodrigues 2000: 464). However, more recently, Dalila Rodrigues considers the pictorial language of Freixo "much more simplified, the copy, the decal, the interpretation and recreation of the Master language" (Rodrigues 2000: 468).

So, has the Master of the Viseu's workshop, Grão Vasco, to whom these painting were attributed, been actually present on its execution? There's no doubt that he deeply influenced the painters that worked with him, originating an important centre of production in the second decade of the 16th century (Rodrigues 2000). Thus it is essential to materially investigate the 16 panel paintings in order to try to identify the authors of the polyptych.

In this paper we present the study of the 16 paintings that constitute the Altarpiece of the Church of Freixo de Espada-à-Cinta, using a multi-analytical approach for the characterization of the painting technique and materials applied in the paintings. This work gives continuity to another study, carried out by the Universidade Católica do Porto, where samples from some panels were analysed by Fourier transform infrared spectroscopy (FTIR). In that previous study, oil was identified in the chromatic layers and a protein based binder in the ground layers.

In the present work, all paintings were submitted to infrared reflectography examinations, and a systematic sampling was carried on. Samples were analysed by optical microscopy (OM) and scanning electron microscopy-energy dispersive x-ray spectrometry (SEM-EDX). Data obtained through the combination of these techniques bring to the light new evidences that give an important contribution to the problematic questions of the panels' attribution.

2 EXPERIMENTAL

Infrared reflectography was carried out using an Osiris high resolution IR reflectography equipment with a InGaAs array detector, which has a spectral resolution the ranges from 0.9 mm to 1.7 mm.

Sampling was done in order to cover the broadest possible chromatic tones in the panels. So, samples were collected mainly from blue, red, green and carnation areas. Cross-sections from the samples were prepared for OM and SEM-EDX examinations. OM observation of the cross-sections was carried out under visible light using a Leitz Wetzlar optical microscope coupled to a Leica DC500 digital camera.

SEM was performed on a scanning electron microscope Hitachi 3700 N coupled with a Bruker energy dispersive x-ray spectrometer. A maximum accelerating voltage of 20 kV was applied. Prior to analysis, cross-sections were coated with a thin film of carbon by a sputtering system. Cross-sections examination by SEM-EDX allowed the detailed visualization of the multi-layered structure of samples and to perform point and 2D elemental analysis.

3 RESULTS

The infrared reflectographs acquired from all paintings reveal little preparatory underdrawing. In general, only the some outlines are well defined, especially those of the hands, clothes, and faces. Also some sketching of the areas to be painted with dark colours, that is, shadow zones, although not very detailed in their majority, is visible. So, the underdrawing is very simple in almost every painting, apart from the "Last Supper" that reveals greater detail, and can be assumed as an exception. While most paintings show the contours of the various elements simply outlined, the "Last Supper" reveals well-defined outlines and very detailed demarcation of the shadow areas in all the elements depicted (Fig. 2).

In the blue areas—skies and garments—the construction of colour is very similar. This first layer is the ground layer, which followed by a white or greyish layer—*imprimitura*—and one or two blue layers. In the SEM-EDX analyses it was detected mainly lead and carbon in the *imprimitura*, and copper and lead in the blue layers, as it can be observed in the elemental distribution maps. In the particular case of the Three Wise Men painting, the cross-section taken from the Virgin's mantle suggests a more elaborate work of the colour. In the first blue layer the pigment has a thinner grain than in the second one. This kind of cross-section structure in samples from blue areas is relatively common in 15th century Flemish painting (Escobar & Campelo 2010), being the blue pigment in the two layers azurite, as suggested by the detection of copper by SEM-EDX.

With regard to the green colours, cross-sections show complex structures. In the foliage, two green layers above the *imprimitura* are found, being the last one composed by somewhat translucent green material, which suggests the use of cooper resinate. Nevertheless, in the samples from the garments cross-sections reveal one, two or more green layers. In the case of the sample cross-section depicted, we can see three layers above the *imprimitura*. In SEM-EDX analysis of this sample it was detected lead, tin, copper and iron in the first green layer; the second, which appears to be composed by an organic material, only cooper and carbon was detected; and in the last layer, which in lighter in colour, it was detected tin, lead,

Figure 2. "*Last Supper*", Photography and IR Reflectography, reveals well-defined outlines and very detailed demarcation of the shadow areas in all the elements depicted. Can be assumed as an exception.

and cooper. These results indicate that the green pigment in the first and third layers above *imprimitura* is a copper based pigment such as verdigris or malachite. The presence of tin and lead suggest the use of lead and tin yellow. The second layer is a translucent green brownish layer and the detection of copper suggests the use of copper resinate.

All red areas were painted in the same manner. Two red layers are found above the ground layer: the first is composed of mainly by a red pigment, and sometimes black pigment was added; the second one is an organic translucent layer, a red lake. SEM micrograph, in Figure 5, shows that this last layer is essentially constituted by a material composed of light elements, suggesting the use of a red dye mixed with an organic binder. The presence of sulphur and mercury in the first red layer indicates that it is constituted mostly by the pigment vermillion (b-HgS). It is worth mentioning the fact that only four paintings present *imprimitura* between the ground and chromatic layers, namely "The Annunciation", "Calvary", "The Prison of Christ" and "Resurrection".

Carnations are made very much the same way. Cross-sections reveal one or two pink layers above the *imprimitura*. This variation in the number of pink layers is related to the light and shadow modulation. Pink layers are constituted by a white pigment and a little quantity of a red pigment—white lead and vermillion, considering SEM-EDX analyses. In some cases, a black pigment is present in these layers. Besides carbon no other elements were detected in the analyses of those black pigments, indicating that it has a vegetable origin. The analyses by SEM-EDX of the ground layers of all paintings allowed identifying these layers as being constituted mainly by calcite ($CaCO_3$), as the most abundant element detected was calcium. No sulphur was detected, what would indicate the presence of gypsum.

4 CONCLUSIONS

The infrared reflectographs and the analysis of the cross-sections by MO and SEM-EDX allowed a perception of the execution tecnique of the paintings that constitute the polyptych of Freixo de Espada-à-Cinta. The detection of Calcite ($CaCO_3$) in the ground layers, and the structures presented by the cross-sections suggests a Northern influence, possibly Flemish. In spite of small variations in the construction of colours, there is a consistency in the way the elements studied were executed—skies, vegetation, garments and carnations. Although there is a great coherence in the execution of all the paintings, some unevenness is notorious in how some colours are achieved, particularly the reds, as well as in the care the underdrawing was made. A personal imprint can be not assigned to the underdrawing revealed by the paintings. So the attribution to one or more authors will have to rely in the crossing of the obtained data until now with other yet to accomplish. Many issues regarding this polyptych still remain unanswered. Nevertheless, the information gathered is assumed, from now on, as an important input for future comparative studies, so that even small singularities may find a larger expression.

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Optically Stimulated Luminescence dating of Roman mortars in Braga (Portugal)

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ABSTRACT: Optically Stimulated Luminescence (OSL) dating of ancient mortars from a Roman monument of Braga (NW Portugal) is proposed in this work, using the single aliquot regenerative dose (SAR) protocol to estimate the equivalent dose on quartz grains of the mortar aggregate. The OSL signals of the quartz grains of the mortars indicate reliable signals for dating. The obtained age results fall within the Roman period (considering the error range) but there are considerable differences among samples. As OSL dating is based on changes induced in minerals by ionizing radiation, further research on the estimation dose rate of ionizing radiation of materials surrounding the samples and on the heterogeneity of the beta dose are needed to calculate more accurately the dose received by the grains and achieve a more accurate age.

1 INTRODUCTION

Historical documents are the most suitable dating method for ancient buildings, but in most cases they might be scarce or have been lost. Absolute dating methods provide ages for archaeological objects, including building materials. However, some problems usually hinder the use of such techniques: man-made modifications on buildings can distort their properties and reused materials provide the age of the first use. Mortars are aggregate structures typically composed of mixture of an aggregate (sand or gravel) and a binder agent. They are ideal materials for dating, as they cannot be reused. Lime mortars are formed by the reaction of quicklime (CaO obtained from crushed and burned limestone) with atmospheric CO_2 in the presence of water to give the putty that will result in the binder. Although different procedures of radiocarbon dating of the lime binder has been recently proposed, e.g. by Heinemeier et al. (2010, 2011) and Marzaioli et al. (2011), they are not routinely applied for being expensive and time consuming.

Luminescence is the emission of light from crystalline materials. Naturally radioactivity causes the excitation of atoms within a crystal lattice and as a consequence electrons are activated at higher energy states. Some of them are captured at levels called ‘electron traps’. With increased time, electrons will be captured at a constant rate. The release of trapped electrons occurs in the form of light (luminescence) and requires a stimulus (usually light or heat), causing the zeroing of the luminescence signal. The intensity of light emitted is proportional to the amount of electrons trapped, and to the energy received by the mineral due to ionizing radiation since zeroing for last time. The ratio of the accumulated charge and the rate environmental radiation provides the luminescence age. The accumulated charge can be estimated as the Equivalent Dose (ED) by stimulating the mineral grains with heat (Thermoluminescence or TL) or light (Optically Stimulated Luminescence or OSL). The rate of environmental radiation can be estimated as the Dose Rate (DR) by assessing the U, Th and K content on the dated and surrounding materials or the environmental dose rate with dosimeters (TLDs) (Aitken 1985).

Luminescence dating of lime mortars has been tested on the mortar quartz of the aggregate sand providing promising results. This requires the exposure to daylight of quartz grains during the mortar manufacture (before the mortar setting) enough time (or under enough light intensity) to zero the OSL signal. This occurs during the extraction and transport of the sand, and the mortar manufacture (Botter-Jensen et al. 2000, Goedicke 2003). First OSL dating of an ancient lime mortar was successfully performed on such quartz grains (Zaccharias et al. 2002). However, some other problems have just been partially resolved. Incomplete zeroing has been regarded as particularly problematic as it causes age overestimation. The OSL signal is derived from a number of grains that form the sub-sample (aliquot). Wallinga (2000) suggested that the best method to check whether the ED of a sample might be overestimated as a consequence of incomplete zeroing is to use small aliquots (~100 grains) and to look at both the spread in the ED and the symmetry of the ED distribution. Symmetrical ED distributions are indicative of homogeneous bleaching. Jain et al (2004) investigated the OSL of mortar samples and found that quartz sand were poorly bleached and weakly sensitive. Poor precision resulted from their ED calculations. However, in a previous study they found accurate dose-depth curve in the walls of the building (Jain et al. 2002). Goedicke (2011) assessed the level of bleaching of quartz for 14 mortar samples He found that 7 of 14 samples were datable by standard OSL, other 5 with other procedures and 2 samples were not datable.

Calculating the dose-rate of ionizing radiation in building materials also involves problems, as the mortars are heterogeneous materials. Problems derived from the gamma dose must be considered, as building walls are heterogeneous environments. It is therefore necessary to measure the in situ dosimetry or to consider a geometric approach from the content of radioactive elements in each of the materials of the wall (Guibert et al. 1988, Feathers et al., 2008). In this study we show the first results of OSL tests to date ancient Roman lime mortars. Three mortar samples from a Roman monument of Bracara Augusta (Braga, NW Portugal) were taken and analysed in the Luminescence Lab of the University of A Coruña.

2 EXPERIMENTAL

Quartz is considered as the most adequate mineral for luminescence dating. The 2 mm outer layer of each sample was removed under subdued red light, and the central part was used for luminescence. The samples were carefully crushed in a vice (taking care to do not crush sand grains) dried and sieved. Sand grains within the range 90–180 µm were separated with the quartz inclusion technique typically used for pottery (Aitken 1985). Small aliquots (~100 grains) were mounted on stainless steel discs for OSL analysis. The equivalent dose was measured on a Riso DA-15 automated TL/OSL reader system equipped with a 0.130 ± 0.003 Gy · s^{-1} $^{90}Sr/^{90}Y$ beta-sources and a 9235QA photomultiplier tube (PMT). An optical Hoya U-340 filter was used to measure the UV range emission after optical stimulation with blue diodes.

The single aliquot regenerative dose (SAR) protocol (Murray & Wintle 2000) was used to estimate the ED. Such protocol permits the generation of a growth curve (OSL signal vs. absorbed dose) by making repeated measurements after the signal has been erased and regenerated. The growth curve is fitted by integrating the first second of the OSL decay curve, minus the average signal during the last four seconds of stimulation. After each OSL, the OSL response to a test dose is measured and used to correct for any sensitivity changes occurred during repeated cycles of irradiation, preheating and OSL stimulation. Measurements were performed at 125ºC for 40 s after preheat at 180ºC for 10 s (preheat temperatures were chosen after performing tests for all samples).

To calculate the annual dose-rate, the U and Th were measured by ICP-MS, and the K_2O content by X-Ray Fluorescence on bulk samples. Conversion factors were used to calculate the beta and gamma contribution (Adamiec & Aitken 1998). The porosity and water saturation were measured to correct the effect of water content. We used a geometric approach to calculate the dose-rate.

3 RESULTS AND DISCUSSION

The EDs of the samples were calculated after measurement of between 35 and 46 aliquots (Table 1). The distribution of the EDs is similar in all the samples. Histograms show asymmetric and skewed distribution with two or three probable groups of aliquots (Fig. 1). This is typically found when the OSL signal was incompletely zeroed before burial (in this case before the mortar setting). Radial plots (proposed by Galbraith et al. 1999) are also used to assess the weight of each sample on the final ED due to the error of each measured aliquot. They show similar ED distributions (Fig. 1 corresponds to T-3). Thus, incomplete zeroing is suspected in all the samples. Further work should consider measuring smaller aliquots (containing fewer grains) or single grains to assess a reliable ED and age.

The dose-rates of the samples were estimated from the U, Th and K content of the mortars. Thus, information in the external gamma dose is missing for these first results. This lack of information involves a typical error of 20–30% in the age estimate (Aitken 1985). We have not included such error in this first estimate, but this consideration must be taken into account. We have tentatively calculated an age with our data, and results are provided in Table 1. The ages fall in the time ranges 278–815 AD, 153 BC–427 AD and 422–907 AD, for samples T-1, T-2 and T-3, respectively. All ages fall in the Roman period (within errors) as it has been expected, but considerable differences exist. Therefore, the definitive assessment of the DR, considering surrounding materials to calculate the gamma dose probably will provide a reliable age.

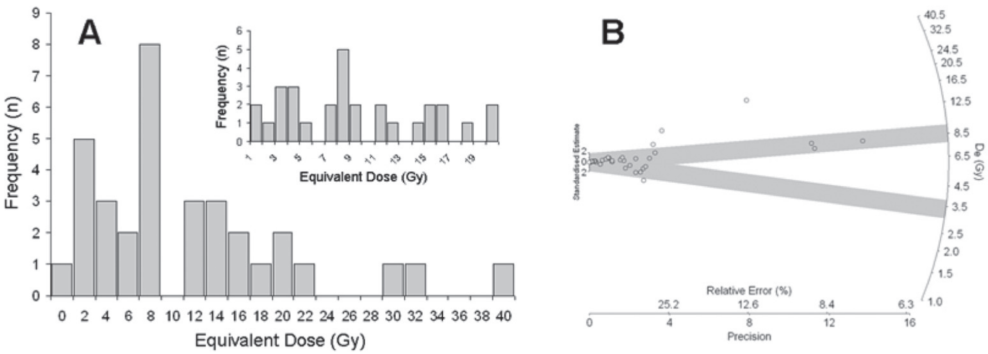

Figure 1. Complete and detailed (inset) histogram (A) and radial plot (B) of the ED distribution for the sample T-3.

Table 1. U, Th and K content of the dated samples, calculated dose rate (DR), number of measured aliquots (n), calculated Equivalent Dose (ED) and age (in ka).

Sample	U (ppm)	Th (ppm)	K (%)	DR (mGy/a)	n	ED (Gy)	Age (ka)
T-1	8.88 ± 0.44	58.0 ± 2.90	3.22 ± 0.03	5.80 ± 0.29	37	8.50 ± 1.50	1.46 ± 0.27
T-2	9.93 ± 0.50	53.7 ± 2.69	3.09 ± 0.03	5.44 ± 0.39	46	10.20 ± 1.39	1.87 ± 0.29
T-3	11.10 ± 0.56	59.8 ± 2.99	3.09 ± 0.03	5.94 ± 0.40	35	8.00 ± 1.34	1.35 ± 0.24

4 CONCLUSIONS

OSL is theoretically a reliable technique to assess the age of a mortar based on the analysis of the luminescence signal of the sand grains in the mortars. Our study on quartz grains of Roman lime mortars indicates that incomplete zeroing is probable common, but reliable EDs can be obtained from the distribution of EDs of the measured aliquots. Thus, measuring the EDs from small aliquots (containing small grains) or single grains, measurements of the surrounding gamma dose rate and research on the beta dose heterogeneity will probably provide a more accurate estimation for the age of the mortars.

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Acknowledgements to the Archeology Unit of the University of Minho and Prof. Manuela Martins for allowing access to the samples. To the Portuguese-Spanish collaboration Project “Ação Integrada E-141/10” (Fundação das Universidades Portuguesas) and “Acción Integrada PT2009-0077” (Ministerio de Ciencia e Innovación), to the project PUDC10N04 funded by the University of A Coruña, and to the Fundação para a Ciência e Tecnologia that support the (pluriannual funding program for research units, PEst-OE/CTE/UI0697/2011, Portuguese funds).

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Analytical studies of 19th century photographs by non-destructive techniques

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ABSTRACT: The late 19th century photographs are chemically a multilayer material of inorganic and organic compounds. A wide variety of chemical composition can be observed as consequence of the large number of photographic processes and products that were used as well as due to the ageing effects. The knowledge of the chemical composition of a photographic print can be very useful in determining its age and authenticity and the adequate restoring techniques or storage protocols. Most of the conservation work was done based on artistic evaluation; nevertheless, during the last decade, non-destructive analytical techniques have been associated with microscopic and visual methods for the identification and conservation of photographs and photographic emulsions. This work presents the analytical studies performed on two selected 19th century photographs; a non-destructive multi-technique approach was used to determine the composition and degradation status of the selected photographic samples.

1 INTRODUCTION

The aim of the present work was to study the photographic process used by a well-known Portuguese photographer, A. Solas, who worked in Lisbon in the late 19th century. Two *carte-de-visite*, G1 and G2 (Fig. 1), of this photographer were studied by several analytical techniques in order to determine the photographic process and the possible degradation agent of the prints. The surface morphology of the prints was analyzed following a non-destructive methodology which included variable pressure Scanning Electron Microscopy coupled with X-Ray Energy Dispersive Spectroscopy (VP-SEM-EDS). X-Ray Fluorescence Spectroscopy (EDXRF) was also used for the analysis of the samples. In-situ Reflectance Fourier Transform Infrared (FT-IR) Spectroscopy allowed the identification of a protein based material. Preliminary visual and microscopic analyses of the selected photos were done.

2 EXPERIMENTAL

Samples G1 and G2 were analyzed in several points of the highlight and shadow areas. The microscopic examination was done with a Stereoscopic Zoom Microscope NIKON SMZ 1500 with a high resolution digital camera and magnifications of 10x and 70x for all the samples with a 45° illumination beam and a constant exposure and gain for each magnification.

Figure 1. Photographic samples: G1 and G2 (A. Solas, c. 1896—collection M. Peres).

The experimental set-up for EDXRF analysis consists of a commercial X-ray tube (PW 1140; 100 kV, 80 mA) equipped with a molybdenum secondary target and a Si (Li) detector, with a 30 mm^2 active area and 8 μm beryllium window. The analyzed areas (Fig. 1A, B) were ellipses with the axes dimensions of 1.0 cm and 1.4 cm.

The SEM-EDS analyses were carried out in a HITACHI S-3700 N variable pressure Scanning Electron Microscope coupled with a Brüker Xflash 5010 X-ray Energy Dispersive Spectrometer. Acceleration voltage of 20.0 kV and a pressure of 50 Pa in the chamber were used for chemical analyses. Backscattered imaging mode was used for the analyses. A large specimen chamber and stage that allows observation of specimens at diameters up to 150 mm allowed the analysis of the entire photograph, thus avoiding micro sampling. Eight different analyses were done in A zone (Fig. 1, G1).

The Reflectance FTIR analyses were performed on the marked three points shown on Figure 1 (1, 2 and 3) using a Brüker ALPHA spectrometer coupled with an A241/DV QuickSnap reflectance module equipped with a video camera. Spectra were collected in the reflection mode, as sum of 64 scans at 4 cm^{-1} resolution, between 3500 and 500 cm^{-1}, and transformed in absorbance mode by the Kramers–Kronig algorithm. The beam diameter was about 5 mm.

3 RESULTS AND DISCUSSION

Visual observation of both prints revealed a shining surface with a warm brown colour, no fading and little deterioration. The microscopic analysis of the prints G1 and G2 was inconclusive because the protective layer hides papers fibers.

Figure 2 shows the spectra obtained by EDXRF analysis of both prints G1 and G2 in the marked zones A and B, respectively, and Figure 3 presents the EDS spectrum for one of the analyzed points (P5). A significant amount of lead is confirmed by both techniques while the presence of silver was only observed by the EDS examination. The use of lead indicates an enameled print. This enamel protection was achieved by scattering metallic pigments on the collodion surface. Usually the most common pigments used were lead oxide or zinc oxide. A final treatment was done with a warmed polishing cylinder (Woodbury 1896). No gold was found, confirming a photographic process with silver salts, without gold toning.

The overall detection of barium suggests a baryta layer. Although sulfur was detected by XRF, due the large amount of lead (the $K\alpha$ and $K\beta$ lines of sulfur are superimposed with the $M\alpha$ line of lead) it is not possible to evaluate by EDS the atomic proportion of both elements in the print. Strontium and manganese are typical of the silver halide technology of black-and-white photographs (Cattaneo et al., 2008). The detection of other elements in the emulsion probably indicates the low purity of commercial chemicals used in these historical photographic processes.

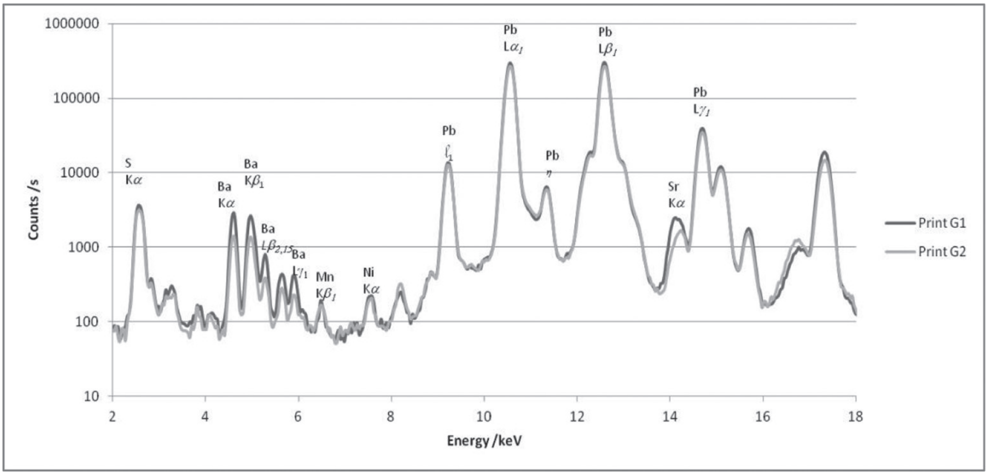

Figure 2. EDXRF spectra (print G1, zone A and print G2, zone B).

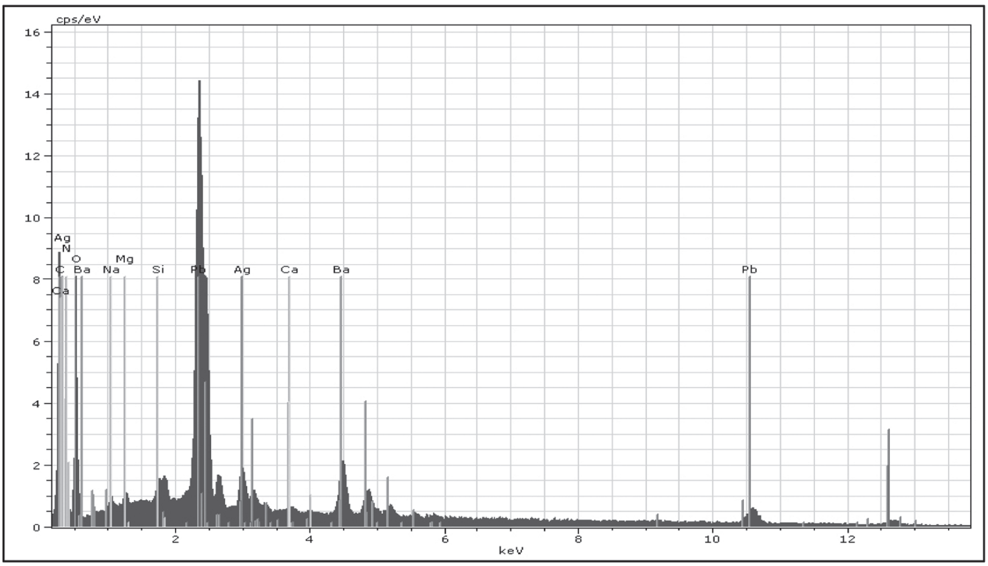

Figure 3. EDS spectrum obtained at the P5 (Fig. 1, G1).

With the experimental setting of the Reflectance FT-IR Spectroscopy a high contribution of specular reflectance is obtained and the spectrum is then subjected to Kramers-Kronig transformation. The analytical signal is therefore fundamentally due to the surface layer, which is the protective layer used in the prints.

All the spectra are very similar with good reproducibility for each zone. Figure 4 presents the average spectra of the 3 points and for comparison a spectrum obtained with a collodion photographic emulsion test (E2).

The spectrum of the print G1 shows that there is some evidence for collodion (cellulose nitrate) considering the characteristic bands: stretching band N-O in the ranges 1660 to 1625 cm^{-1} and 1285 to 1270 cm^{-1}; the C-O bending band at 1300 to 900 cm^{-1} and the N-O bending band at 890 to 800 cm^{-1} (Cattaneo et al., 2008). The bands occurring at 2922 and 2853 cm^{-1} are attributed to the baryta layer (barium sulfate) (Derrick et al., 1999). The band occurring at 1741 cm^{-1} can be attributed to castor oil, a plasticizer used in the preparation of the collodion emulsion (Cattaneo et al., 2008).

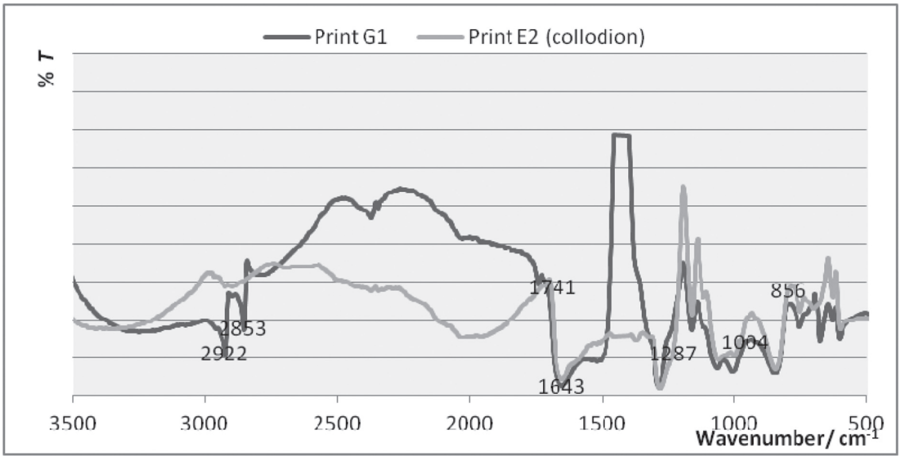

Figure 4. FT-IR reflexion spectra of G1 and E2 prints.

4 CONCLUSIONS

The multi-technique analyses allow us to conclude that these photographs are collodion positives prints with a baryta layer without gold toning; they have also been submitted to a final enamel protection treatment.

It should be emphasized that SEM-EDS analysis at a low vacuum (50 Pa) observation method gave good reproducible results and enabled the observation of non-conductive samples, such as the photographic prints, avoiding sample preparation or micro sampling procedures.

Additionally, in-situ reflectance FTIR spectroscopy revealed itself to be extremely useful in probing the nature of the protective layer.

The surface analyses didn't detect degradation products which can be attributed to the type of enamel protection that has helped to preserve the prints.

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This work has been done within the scope of the research project PTDC/HIS-HCT/102497/2008 which is financed by FCT (Fundação para a Ciência e Tecnologia). We are especially grateful to José C. Frade from Laboratório de Conservação e Restauro José de Figueiredo.

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*Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)*

Rheological analysis of some historical and commercial binders labelled as thixotropic in oil painting references

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ABSTRACT: Some binders used in oil painting are supposed to have special properties and advantages because of their "thixotropic" behaviour: they would flow easily in contact with the brush, but they would be like a gel at rest. Time factor is not clearly established and results in confusion between shear thinning and thixotropy when describing them. In this work we have analysed rheological properties of 8 different binders: 2 historical artisan recipes and eight nowadays commercial media. The results revealed that handmade *Rubens according Mytens* turned to be a Newtonian fluid (viscosity is independent of shear rate), while the rest of binders were highly shear thinning. These seven non-Newtonian systems had also a viscosity decreasing with shear time, but only the handmade *Van Eyck according Mayer* recovered part of its initial viscosity after resting. Therefore, most of binders analysed do follow the behaviour that is described in painting manuals and handbooks.

1 INTRODUCTION

Oil painting manuals and handbooks show lots of medium recipes that are labelled as thixotropic. These binders are supposed to have special properties: they would flow easily in contact with the brush, but they would be like a gel at rest (Van de Wetering 2006). All of them present a common composition based on: drying oil (linseed or walnut), stiffness elements (dammar resin, mastic, sandarac or gum arabic), plasticisers (beeswax and/or egg), solvent (turpentine or lavender), and optionally dryers (litharge or lead white, now replaced by cobalt and zirconium dryers). Their use has been attributed to great masters of painting (Viguerie et al., 2009). The legend of thixotropy in oil painting thought Rubens was its beginner and this idea was supported by XIXth century painters and writers like Jacques Maroger (Manguta 2010). Current commercial brands try to recover these ancient medium recipes. They sell their products as the inheritors of the tradition of thixotropy in oil painting but with improved recipes and different components that are characteristic of our century.

The phenomenon of "thixotropy" was discovered during the emergence of rheology, in 1930s, so it coincided with the recovery of thixotropic binders' recipes. The term was referred to materials with a consistency altered by flow, but the time factor was not clearly established and confusion between time-dependence an shear rate dependence (shear thinning) appeared, and still persists (Mewis & Wagner 2009). Nowadays, in rheology thixotropy is considered to be a decrease of viscosity with time, which must be reversible when the flow is stopped.

The aim of this work was to analyse thixotropy, shear thinning behaviour and viscoelasticity in 8 different binders: 2 historical artisan recipes (*Rubens medium* and *Van Eyck medium*) and 6 nowadays commercial media manufactured by Lefranc et Bourgeois and Winsor and Newton.

2 MATERIALS AND METHODS

2.1 *Products*

2.1.1 *Handmade media*

Rubens medium according Daniel Mytens. It is made of one portion of raw linseed oil cooked, one portion of mastic resin dissolved in the boiled linseed oil and two parts of Venice Turpentine.

Van Eyck medium according Ralph Mayer. (Mayer 1993) A thick medium made of one portion of raw linseed oil cooked and one portion of dammar resin that was dissolved in the boiled linseed oil. 1/2 part of egg and five portions of gum arabic were mixed together and the mixture of gum and egg was added in the resinous oil.

2.1.2 *Commercial media*

2.1.2.1 *Winsor and Newton*

Liquin Original. It is a semi gloss medium made of alkyd resin, linseed oil and dryers.

Liquin Light Gel. A quick drying, semi-gloss medium made of alkyd resin, linseed oil and dryers.

Liquin Impasto. A semimatte, quick drying impasto medium made of alkyd resin, linseed oil and dryers.

2.1.2.2 *Lefranc et Bourgeois*

Venetian medium. It is made of linseed oil, beeswax, pine essence and dryers. Its composition is very close to Rubens medium according to Maroger.

Flemish medium. It is made of gum mastic, linseed oil, essence of spike lavender and cobalt-zirconium siccative.

Crystal medium. It is made of poppy oil and silica based medium.

2.2 *Rheological measurements*

A controlled stress RS1 Rheometer (Haake) with a DC30 thermostatic bath was used. After loading, the samples were allowed to relax for 900 sec. To avoid slippage serrated parallel plates were employed. Three types of measurements were performed (by duplicate at 25º C):

Shear thinning behaviour: Step flow curves (viscosity as a function of shear rate) from 10^{-4} s^{-1} to 100 s^{-1} aprox. were recorded.

Thixotropy: viscosity at a constant shear rate of 10 s^{-1} was measured during 300 s and afterwards the binders were kept resting between sensors for 45 min and measurements were repeated in order to check reversibility.

Viscoelasticity: frequency sweeps between 0.01 and 10 Hz were performed in linear viscoelastic region, previously determined by stress sweeps.

3 RESULTS AND DISCUSSION

Rubens medium according to Mytens turned to be a Newtonian fluid with a viscosity of about 3 Pa s, which corresponded to 100 times the viscosity of the linseed oil used to prepare it, for that reason thixotropy can not be shown. The handmade binder *Van Eyck according Ralph Mayer* was clearly a shear thinning fluid, with a plateau region of constant viscosity, η_0, for very low shear rates (practically at rest), and highly decreasing viscosities when increasing shear rate for shear rates higher than a critical value, $\dot{\gamma}_c$. The same behaviour is observed for the six commercial binders (Fig. 1b and c), so all of them fitted well (continuous lines in fig. 1) to Carreau model (equation 1, Rao 1999).

$$\eta = \frac{\eta_0}{\left[1+\left(\frac{\dot{\gamma}}{\dot{\gamma}_c}\right)\right]^s} \quad (1)$$

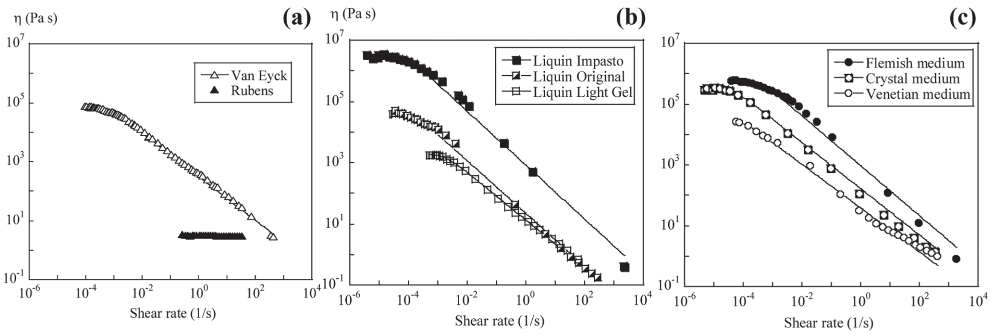

Figure 1. Flow curves for homemade media (a), Winsor and Newton media (b) and Lefranc et Bourgeois media (c).

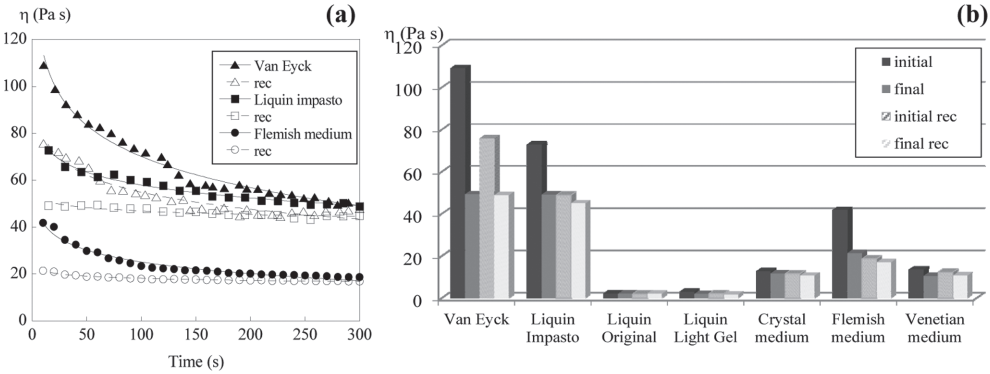

Figure 2. Viscosity at 10 s^{-1} as a function of time, fitted to Weltmann model for some binders (a). Initial (t = 0 s) and final viscosities (t = 300 s), for the first measurement and repetition after 45 min resting (b).

The highest viscosity at rest corresponds to *Liquin Impasto* (about $3 \cdot 10^6$ Pa s) and the lowest to *Liquin Light Gel* (about $2 \cdot 10^3$ Pa s). For high velocities, of about 50 rpm (100 s^{-1}) viscosities decay up to 0.3–15 Pa s. This is the typical behaviour described in manuals and handbooks.

It is interesting to point out that the different products of each brand deal to three levels of viscosity in the whole range (Fig. 1b and c). On the other hand, the shear thinning homemade medium has an intermediate behaviour between *Crystal medium* and *Flemish medium* by Lefranc and Bourgeois.

When measuring viscosity at a constant shear rate of 10 s^{-1} (about 5 rpm), a logarithmic decrease of viscosity with time was observed (Fig. 2a), thus suggesting a thixotropic behaviour. All curves were successfully fitted to Weltmann model, $\eta = A - B \ln t$ (Rao 1999).

As in order to have real thixotropy, initial viscosity must be recovered after stopping flow, we compared values obtained after 45 min resting. In Figure 2b it is clear the artisan medium *Van Eyck according to Mayer* recovered part of its initial viscosity. However, none of the six commercial media seems to recover its structure, at least along this resting period.

Oscillatory measurements for different frequencies gave us information about viscoelastic properties of the binders. In all cases storage modulus, G' (or elastic modulus) is higher than loss modulus, G" (or viscous modulus), what indicates that elastic behaviour is predominant. In all the commercial binders the elastic modulus G' is rather constant over the range of frequencies investigated. However, for the Winsor media, the viscous modulus, G", is more dependent on frequency than for Lefranc media (examples in Fig. 3). This indicates that all

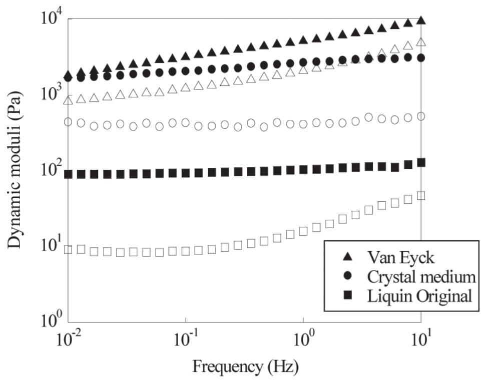

Figure 3. Dynamic spectra of some binders. Full symbols: storage modulus, G', and open symbols: loss modulus, G", as a function of frequency.

of them are structured systems, with all Liquin systems being weak gels, while Lefranc media could be considered as true gels (Rao 1999).

4 CONCLUSIONS

The results showed that except for the handmade *Rubens according Mytens*, which turned to be a Newtonian fluid (viscosity is independent of shear rate), the rest of binders certainly presented the behaviour indicated in manuals, as their resistance to flow (viscosity) decreased when stirring. They were highly shear thinning, as viscosity decreased a lot when increasing velocity of stirring and also when stirring for a period of time (thixotropy), although only the handmade *Van Eyck according Mayer* recovered part of its initial viscosity after resting. On the other hand, the viscoelastic behaviour of all commercial binders may indicate that they are structured systems, containing a three-dimensional gel network.

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Bricks and mortars from the "Patio de Santo Tomás", Alcalá University (Madrid, Spain): A combined study of fabric characterization and building morphology

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ABSTRACT: A combined study of fabric characterization and building geometry and morphology has been undertaken at the "Patio de Santo Tomás, Colegio Mayor de San Ildefonso" from the Alcalá University (Madrid, Spain). A set of bricks and their associated mortars from different chronology and locations has been selected to carry out fabric characterization, which were accomplished by using observation and analytical conventional techniques, such as thin section polarized light microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDS), and thermogravimetric-differential thermal analysis (TG-DTA). Resulting data have enabled the recognition of three groups of bricks with their associated mortars in the five constructive phases of the building. Each group showed compositional and technological differences which can be correlated with their chronology and location in the building. This combined study has provided outstanding data which can be useful for future conservation and restoration strategies.

1 INTRODUCTION

Cardinal Cisneros founded the University of Alcalá in 1495 whose main building was the "Colegio Mayor de San Ildefonso". This building has undergone many transformations and changes throughout the history since its construction in early sixteenth century. A recent restoration of the building has allowed the identification of up to five constructive phases (Barluenga et al. 2012). The first one begins with the construction of the "Colegio Mayor de San Ildefonso" between 1501 and 1508 under the direction of the architect Pedro de Gumiel. The second phase refers to the construction of the main façade of the building, between 1537 and 1553, whose works were undertaken by the master Rodrigo Gil de Ontañón. A clock tower was later added to the south wall between 1599 and 1615 which is the third constructive phase. At the beginning the clock tower was ordered to Juan de Ballesteros. However, several building troubles make Juan de Ballesteros left the work, which was finally ended by Juan García Atienza.

An important element of the building is the courtyard known as "Patio de Santo Tomás" which was originally made of bricks, even though bricks were later covered with granite during the construction of the cloister that can be nowadays seen. The cloister was built between 1656 and 1670 by José de Sopeña and constitutes the fourth constructive phase.

At late eighteenth century the University of Alcalá entered a period of decadence which ended with its move to Madrid in 1836. After some years, the building was occupied from 1850 by the army. The late phase identified is the period comprised from 1865 to 1868 in which the "Patio de Santo Tomás" was reconditioned. The modern University of Alcalá was created in 1977 and, from then, the "Colegio Mayor de San Ildefonso" was recovered for academic use.

Table 1. Classification of the samples analyzed.

Sample	Constructive phase	Type of brick (high × length × width in cm)
A	4	ii (4 × 24–26 × 12–14)
B	4	ii (4 × 24–26 × 12–14)
C	2	ii (4 × 24–26 × 12–14)
D	1	i (4 × 16–18 × 8–10)
E	5	iii (5 × 24 × 12)
F	5	iii (5 × 24 × 12)
G	3	i (4 × 16–18 × 8–10)
H	1	i (4 × 16–18 × 8–10)

The building is a masterpiece of the Spanish Renaissance. Along with the rest of the historic city of Alcalá de Henares, in 1998 it was declared World Heritage Site by the UNESCO.

Due to recent rehabilitation of the building, accomplished during 2010 and 2011, a research program combining historic, graphic, morphological, geometrical, and materials characterization was started. This contribution presents the results derived from the combined study of fabric characterization and building geometry and morphology. The study was carried out when wall sections were exposed, for the first time, during rehabilitation works. The main goal of the study was the characterization of some building materials, such as bricks and mortars, to look for differences or similarities in the five constructive phases of the "Patio de Santo Tomás".

2 EXPERIMENTAL

To undertake fabric characterization a set of bricks and their associated mortars was selected. These samples were taken in different locations of the building and encompassed either the four façades of the "Patio de Santo Tomás" or the five constructive phases. Table 1 shows the classification of the eight samples selected, as well as the types of bricks employed.

The following observation and analytical conventional techniques were used to carry out fabric characterization: thin section polarized light microscopy, scanning electron microscopy (SEM), X-ray diffraction (XRD), energy dispersive X-ray spectrometry (EDS), and thermogravimetric-differential thermal analysis (TG-DTA).

Polarized light microscopy was undertaken through examinations of thin sections by means of a Kyowa Bio-Pol 2 microscope. Micrographs from thin sections were recorded with a Moticam 2500 camera. SEM observations were accomplished by a Philips XL30 equipment, using acceleration voltages of 20 kV. Powder XRD analyses were carried out with a PANalytical X'Pert-MPD unit using Kα of copper radiation (1.54056 Å), under set conditions of 45 kV and 40 mA. Diffractograms were obtained between $2\theta = 5–60°$. Powder samples for XRD analyses were prepared by grinding the body of bricks and mortars selected in an agate mortar. The EDS equipment used was a DX4i spectrometer attached to the SEM microscope already mentioned. Finally, TG-DTA recordings were undertaken by a SDT Q600 equipment using a platinum cell holder under air atmosphere, at a heating rate of 10 °C/min ranging from room temperature up to 1200 °C.

3 RESULTS AND DISCUSSION

Fabric characterization determined three groups of bricks. Group 1 is formed by the following five samples: A, B, C, D, and H, which correspond to constructive phases 1, 2, and 4, from sixteenth and seventeenth century. Thin sections of this group (Fig. 1a) show a fine textured calcareous clay with a high degree of birefringence. Inclusions composed of quartz, feldspar, and mica appear disseminated throughout the clay matrix. Quartz and feldspar inclusions are rounded to sub-angular in shape and not higher than 500 μm in size, while mica is in general small needle-shape and between 500 and 600 μm in length. The most outstanding feature of this group is the presence of relatively abundant inclusions of grog or chamotte (crushed fragments of ceramic) which was, in all probability, deliberately added to the clay matrix to improve mechanical properties of these bricks (Rice 1987). The size of grog fragments reach up to 1 mm in length.

XRD data (Fig. 1b) confirm the presence of quartz and two kinds of feldspars: plagioclase (Na-rich feldspar) and microcline (K-rich feldspar). In addition, they also determine reflections corresponding to illite, calcite, hematite, and gehlenite. Illite decomposes from 850 to 900 °C and calcite from approximately 750 °C, while hematite is usually neo-formed from 700–750 °C and gehlenite from 800 °C (García-Heras et al. 2006). Based on the joint presence of these four phases a low firing temperature of 800–850 °C can be estimated. A shrunken microstruture of non-vitrification is observed by SEM, while TG-DTA curves, not included due to space constrains, agree with the firing temperature estimated by diffractograms. Group 2 consists only in sample G, which corresponds to the constructive phase 3 from seventeenth century. The petrographic thin section (Fig. 1c) shows a very sorted calcareous clay with low birefringence and signs of vitrification. Small mainly rounded inclusions not higher than 300 μm of quartz and feldspars appear disseminated throughout the clay matrix. Apart from quartz and two kinds of feldspars: plagioclase (Na-rich feldspar) and microcline (K-rich feldspar), the X-ray diffraction (Fig. 1d) determines reflections of hematite, gehlenite, and diopside. Due to the presence of both gehlenite and diopside, which approximately crystallize from 800 °C; and the absence of illite, whose full dehydroxilation occurs nearly 900 °C (Rice 1987), it can be estimated a relatively high firing temperature, between 900 and nearly 950 °C, for this brick sample. The starting of a vitrification microstructure is observed by SEM, while TG-DTA curves display neither endothermic nor exothermic effects as a result of the high firing temperature. Group 3 is formed by samples E and F, which correspond to the last con-

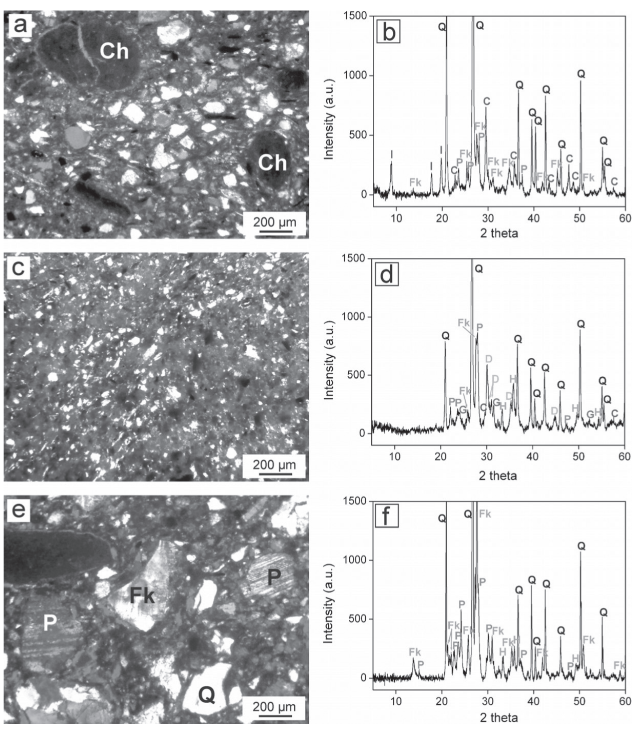

Figure 1. Thin section micrographs and diffractograms from representative brick samples of the three groups. a) Sample B. b) Sample A. c–d) Sample G. e–f) Sample F. Inclusions and phases: C calcite, Ch chamotte, D diopside, Fk K-feldspar, G gehlenite, H hematite, I illite, P Na-feldspar, Q quartz.

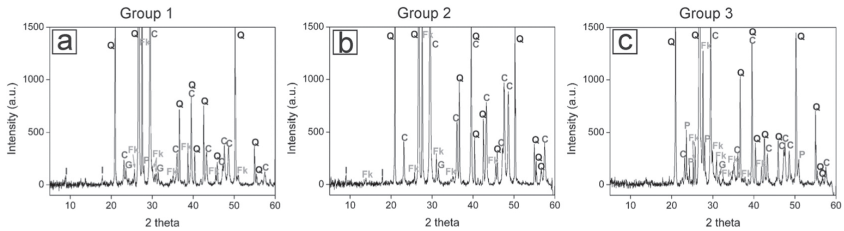

Figure 2. Diffractograms from representative mortar samples of the three groups. a) Sample A. b) Sample G. c) Sample E. Phases: C calcite, Fk K-feldspar, G gehlenite, I illite, P Na-feldspar, Q quartz.

structive phase dated at mid nineteenth century. Thin sections of this group (Fig. 1e) show a poor sorted and birefringent non-calcareous clay in which a feldspathic sand, characterized by highly angular and sub-angular grains of quartz and feldspars, was added.

X-ray diffractograms (Fig. 1f) confirm the presence of quartz and both feldspars. They also display reflections assigned to hematite. However, those reflections corresponding to illite and calcite are not present, which indicate an intermediate firing temperature that can be estimated roughly from 850 to 900 °C. As far as the associated mortars are concerned, fabric characterization mainly undertaken by XRD data also determined three groups of mortars (Fig. 2), which are in conjunction with the three groups of bricks. All the groups are formed by lime mortars (reflections of calcite and gehlenite) with show small differences probably due to the raw materials employed. In all cases a feldspathic sand was used as aggregate. Such differences are as follows. Group 1 (Fig. 2a): Na-K feldspar sand with traces of illite. Group 2 (Fig. 2b): K-feldspar sand also with traces of illite. And Group 3 (Fig. 2c): Na-K feldspar sand without traces of illite.

4 CONCLUSIONS

The combined study of fabric characterization and building geometry and morphology has enabled the recognition of three groups of bricks and their associated mortars in the five constructive phases of the "Colegio Mayor de San Ildefonso". Each of the three groups displayed compositional and technological differences, which can be correlated with their chronology and location in the building. Construction materials from sixteenth and seventeenth century can be easily distinguished to those from nineteenth century. In this sense, it must be noted the high quality of the brick (sample G) from the clock tower, which was probably made in the period of Juan García Atienza after the building troubles occurred during the work directed by Juan de Ballesteros.

This exploratory study has thus provided, for the first time, outstanding data on bricks and mortars employed in the different historic constructive phases of the "Patio de Santo Tomás".

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Study of alterations on Roman masonry in the Tower of Hercules

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ABSTRACT: The Tower of Hercules is the only Roman lighthouse still in use today. It is located on a headland in the city of A Coruña in Galicia (north-western Spain) and it was declared a World Heritage site in 2009. From the original Roman build, the helicoidal access ramp, the external wall and the rotunda that held the beacon, were lost, but the internal core of the lighthouse building, of quadrangular plan, divided in four chambers and three floors, remains. Given its age and continued use, the state of conservation is very good. Nevertheless, the masonry suffers from alterations, originated for the most part in past times. The study of alterations on the Roman masonry aims to evaluate the actual state of conservation as to be able to establish the adequate protocol for its preservation.

1 INTRODUCTION

Nowadays it has a height of 55 m, from which 34 m belong to the Roman build and 21 m to the renovation by naval engineer Eustaquio Giannini, who added to the Roman core the two octagonal bodies the beacon was placed on (Goy Diz 2008).

The external structure of the Roman lighthouse was gradually lost along its history, due to collapse of the masonry and pillaging of the stone ashlars. What we see today is the outcome of the 18th century restoration. Giannini respected the Roman body and raised an extraordinarily sober façade, built entirely of stone ashlar, resembling the twin pairs of windows and the access ramp with a helicoidal impost (fascia).

The Roman masonry remains, although with modifications, from the foundations to the room the beacon sits on. The visible façades (interior walls of the lighthouse) are built in opus vittatum, of local leucogranite stone (aplite), that serve at the same time as façade and formwork for the opus caementicium that constitutes the walls' core. The frames (bays) of the doors, which communicate on each floor the chambers in pairs, and the windows, which originally gave access to the exterior ramp, are built of cyclopean stone ashlars from local granite (late granodiorite). Given the heterogeneity of the walls' surfaces, mainly due to the different levels and types of alteration, it is difficult to determine the original finishing. The putlog holes, used to hold the scaffolding and the support structure for the falsework, have been documented for all chambers.

2 STUDY

Even though the tower was subject to an integral restoration in 1992, under the direction of Pablo Latorre (Latorre et al. 1991), there has been no study, to date, of the state of conservation of the monument. The aim of this initial phase of research, carried out in 2010, was to determine the actual state of conservation of the Roman masonry and to establish guidelines for the preventive conservation and restoration, and to examine in depth the specialized studies related to the materials as well as to the conservation environment.

2.1 *In situ data collection and representation*

We gathered data that allowed us to elaborate cartographies representing the lesions on the stone and the superficial salts contained in the walls, as well as samples of altered material to analyse the saline content and the porous system of the stone.

We represented the lesions, differentiating between those which take place superficially or that do not imply loss of material, and those that come with losses. The graphic representation was assembled on image editing computer software, based on the sketches drawn in situ. Each type of lesion is drawn in a separate layer, allowing to display them individually or in groups. The detected forms of alteration were classified, almost entirely, according to the descriptions used on the *Illustrated glossary on Stone deterioration patterns* from ICOMOS-ISCS (VV. AA., 2008): discoloration, salt crust, undetermined crust, biological colonization, deposit, efflorescence, graffiti, liming residue, staining, erosion, rounding, alveolization (pitting and coving), mechanical damage, scaling, spalling, crack, fracture and fragmentation, missing part.

The data relative to humidity and superficial salts were obtained in situ with electronic detectors, and the graphic representation was created through computer processing of the analytical data; starting from these data, contour lines were calculated by means of spline interpolation on data analysis software.

The scaffolding installed for the data collection, allowed us to document other interesting aspects of the building. We documented, among others, all the putlog holes, used for the installation of scaffoldings during the construction; the tiny remains of red coloration, which may have constituted a surface finishing of this colour, although given to its location almost exclusively on the higher areas of the chambers it is more likely that only the vaults were coloured; and the differentiating element used by Eustaquio Giannini to differentiate his intervention.

2.2 *Analysis*

Having a very limited budget for specialized laboratory analysis, only a representative sample, dislodged from leucogranite affected by spalling, was analysed. An aliquot of the salt content was analysed by DRX. It is a mixture with a considerable proportion of gypsum and smaller proportions of halite and quartz dust, sodium anorthite and magnesium muscovite, coming from the stone. The ATD-ATG-FTIR shows a high hydration, the presence on small proportions of calcite, and a mineral mixture, that can be related to the gypsum and halite. These kinds of salts can be attributed to the sulphation of lime and sand mortars, and dissolution of the generated calcium sulphate that penetrates the stone. At the same time, halite precipitates, which makes this sulphation very likely to be produced by the effect of the air and marine spray. Through an affordable method, qualitative and semi-quantitative, (Sulfate Test (range: 200–1600 mg/l SO_4^{2-}) and Nitrate Test. (range: 10–500 mg/l NO_3^{-}). Method: colorimetric with test strips, Merck Chemicals. Chloride Test (range: 0–1000 mg/l). Method: titration, Hanna Instruments), 357 samples of disaggregated material (stone and mortar) were analysed.

2.2.1 *Porous system*

The analysis of the porous system of the granite from the Roman masonry shows that these stones are not too altered despite their appearance. The aplite is partially altered from origin; however, its high interparticular porosity, and the fact that the pore groups are very well connected, helps to confer a higher response to the alterability derived from freezing and salt damage. (Total porosity: 4,88%. Interparticular porosity: 3,57%. Intraparticular porosity: 1,30%). The granodiorite came also partially altered from the quarry. Inter and intraparticular porosities are very similar, and the stone has good transpiration qualities. (Total porosity: 3,68%. Interparticular porosity: 1,76%. Intraparticular porosity: 1,91%).

2.2.2 *Characterization and dating of mortars*

Although indirectly related to the conservation of the monument, there is a great interest from the editing team of the Director Plan, whose responsible is Ana Goy Diz, in dating the

Table 1. Paleodoses measured by OSL and final ages.

Chamber	Sample	Annual dose (mGy/year)	Paleodose (Gy)	Aliquots (n)	Age (years)	Year AD	Year range AD
2A_	TH_079	5.85 ± 0.40	2.21 ± 0.26	15	378 ± 51	1633 ± 51	1582–1684
2D_	TH_147	4.39 ± 0.32	0.76 ± 0.19	7	163 ± 46	1848 ± 46	1802–1894
1A_	TH_209	6.97 ± 0.34	2.35 ± 0.24	18	337 ± 38	1674 ± 38	1636–1713
0B_	TH_298	5.73 ± 0.34	7.48 ± 1.24	12	1306 ± 229	705 ± 229	475–934

original masonry and the later renovations of the lighthouse. For this reason, some samples of mortar, selected for their location on the walls, where characterized and dated by Optically Stimulated Luminiscence (OSL).

The granulometric study allowed us to differentiate the aggregate part from the binder, making it possible to perceive small differences between mortars in the aggregate's granulometry. The binder is always lime, and the proportions in the arids' granulometry make it possible to differentiate three different types of mortar. Despite the coincidence of their chemical composition, they differ in age.

The mortar that stands apart chronologically belongs to the vault of chamber 0B, since it is, by far, the oldest of the studied mortars, and it was collected thinking it could be the original one. The dating brings it to a late-Roman or high-medieval period. There is possibly an error in the dating due to contamination of the sample by the use of Portland cement on the restoration that took place at the beginning of the 20th century, since it seems unlikely to come from a restoration during a period thought to be of decadence of the building. The sample from chamber 2 A presents a substantial difference in age, since it takes us to the 16th or 17th century. It is a filling mortar from the vault with brick, which was thought to correspond to Giannini's restoration; but the chronology points to the moment in which A Coruña City Council began to be concerned about the recovery of the lighthouse and the dismantling of the vaults, commissioned by the Duke of Uceda to install the wood staircases in 1684. The sample taken from chamber 1 A, which was dislodged from the surroundings of the centre hole of the vault already restored with brick or tile, could have originated in that date. The youngest sample is that collected from the interior of a putlog hole in chamber 2D, which either belongs to Giannini's intervention or to the "embellishment" carried out with the occasion of the visit of Queen Isabel II (Goy Diz, 2008).

2.3 *Results*

The vast majority of the stone from the Roman masonry is altered from old natural erosion, with special incidence in areas exposed to the wind in the period of abandonment of the lighthouse, and especially by salt formation from the marine aerosols and the Portland cement used in the 20th century interventions. Porosity, although high for healthy granite, is much lower than that documented in other monuments from A Coruña, built of the same material in much more recent dates (12th to 18th century).

Alteration is much greater in the joint mortars. Joints are the natural path for evaporation, and thus salts crystallise on these areas, but the most devastating effect is without doubt due to the cement, which not only generated harmful salts but also impeded the "breathing" of the masonry through the lime joints, forcing it to do so through the stone face itself, thus promoting its deterioration.

Apart from the numerous spots of mechanical damage produced by the multiple installations held by the tower over the time, other generalised lesions with loss of material can be seen, as well as many remains from the cement mortars used in the joints of all chambers. Perhaps related to the latter, there is a remarkable formation of a whitish veil, formed by saline efflorescences and in some cases by liming residue. These efflorescences have a lower incidence on the large ashlars around the holes, perhaps because they were never whitewashed.

Another on-going pathology is algae colonisation, which was thought to be caused by the continuous and condensation due to lack of ventilation. However, comparing the cartographies of humidity and colonisations, it was seen that in most cases the amount of light hitting the colonised wall is more relevant than the level of humidity in the stone.

In some of the chambers from the first and second floors there is a reddening on the stone, on the lower part of the corners, which can be due to the existence of fireplaces (this phenomenon is prior to the cutting off of the vault). There is also staining, produced by rust from the old iron tubing used for electrical cabling.

In general terms, superficial humidity is higher than the internal one, and in both cases it is more relevant on the highest parts of the chambers, no matter the floor. This makes us believe that, except for exceptional cases, humidity in the tower is driven by condensation phenomena, difficult to eradicate. Salt concentration seems to be related to humidity. Where humidity is high, salts are dissolved, unseen to the naked eye but detectable by electronic measurement tools. Crystallisation occurs primarily on the driest areas. Sulphate content is very high on the granite samples, though they also contain chlorides and nitrates. Nitrates and chlorides content is usually higher in mortars, some of which also contain high quantities of sulphates, whose origin can be attributed to the Portland mortars, since in all samples characterised lime is the only binder, without added gypsum. The pattern is repeated throughout all chambers and heights.

3 CONCLUSIONS

From the study, the conclusion was reached that the most urgent action is the elimination of the remaining cement and the re-joining of the masonry with lime mortar, which will not only help to preserve the remaining old mortars, but also to re-establish the system of evaporation and salt elimination through the joints.

It was possible, within the Director Plan, to establish a protocol of maintenance, conservation, restoration and research interventions.

We also proposed a climate monitoring system (5 dataloggers, situated at different levels of the building's interior) that will help determine whether changes in humidity and temperature are having an influence on the deterioration of materials.

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The application of non invasive geophysical techniques for the diagnosis and conservation of stone cultural heritage: The case of a Portuguese fifteenth century tomb

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ABSTRACT: Results of self-potential, seismic reflection and refraction, Infrared spectroscopy, ion chromatography and IR thermography survey performed over a Portuguese artistic tomb made of a porous limestone are presented. The tomb presents nowadays severe decay phenomena. The decay products associated to the decay patterns observed are mainly related with the presence of salts, namely nitrates and secondarily of chlorides. The self-potential and the thermography survey allowed verifying that moisture degrees change in different side walls of the tomb. The seismic methods showed there is no clear interface between undamaged and damaged stone material where the limestone is soft and the strength is slightly lower in the most humid zones.

1 INTRODUCTION

Today experts agree that a precise damage diagnosis is required for comprehensive characterization, interpretation, rating and prediction of stone damage and thus is vital for its conservation and mainly for sustainable monument preservation. Geophysical techniques applied in historical monuments (Vaish & Sharma 2000, Piro et al. 2003, Linford 2004) are non-invasive and allow us to obtain a mapping of different physical parameters of the geological materials. Another important factor to obtain meaningful responses is to perform a survey with different methods, which can provide information on different physical aspects of the investigated media (Cammarano et al. 1998). Self-potential (SP) and seismic methods (refraction and reflection), provide non-invasive methods of sensing the water contents of porous media. The seismic methods also allow assessing and quantifying the state of degradation, i.e., to determine whether the phenomenon of decay is merely superficial or has strong development in depth. The seismic methods can provide elements of interest to detect the thickness and position of the weathering layer, physical properties of the different materials, including mechanical characteristics, location of cavities, fractures and other discontinuous elements. Therefore, the seismic methods can be used for characterization of stones and assessing their state of decay when applied to monuments (Aires-Barros et al. 1998, Recheis et al. 2000).

This study presents the results of the application of a geophysical (Self-potential (SP) and seismic reflection and refraction) and geochemical (Fourier Transform Infrared spectroscopy and ion chromatography) and IR thermography survey carried out on a fifteenth century Portuguese stone tomb located inside Igreja da Graça (Santarém, Portugal). Our study seeks to appraise the mechanisms involved in the stone decay and to measure the extent and severity of stone decay processes in progress, which is vital to the conservation and sustainable preservation of tomb. In this work we present the results obtained in one surface.

2 MATERIALS AND METHODS

2.1 *Description of the tomb*

The tomb, with 2.90 m width and 1.50 m height, consisting of a large ark of limestone, based on eight lions is located t on the right arm of the church's cross (Fig. 1a). The stone material is a light, whitish-yellow, fine-grained, compact, very soft and homogeneous limestone. A detailed survey of stone decay phenomena was carried out on the tomb and several weathering forms were identified (ICOMOS-ISCS proposed terminology, 2008), including powdering, scaling and multiple exfoliation (Fig. 1b, c) as the most relevant. On the lid grey crusts mainly in the overlying sculptures were also identified.

2.2 *Methods*

The passive approach was adopted for infrared thermographic survey and was carried out on the sides and lid of the tomb and also on the walls and floor around the tomb. The IR system was a Fluke TI45 camera with Focal Plane Array detector operating in the band 8–14 µm. The system has a thermal resolution of 0.08 °C and a instantaneous field of view of 2.60 mrad. The self-potential (SP) survey in the tomb was performed on all four side of the tomb using the potential amplitude method. In the larger faces was used a rectangular grid with 13-by-5 equally spaced measurements points (20 cm) in the x and y directions, respectively. The base station (electrode fixed) was located in the seventh position of the first

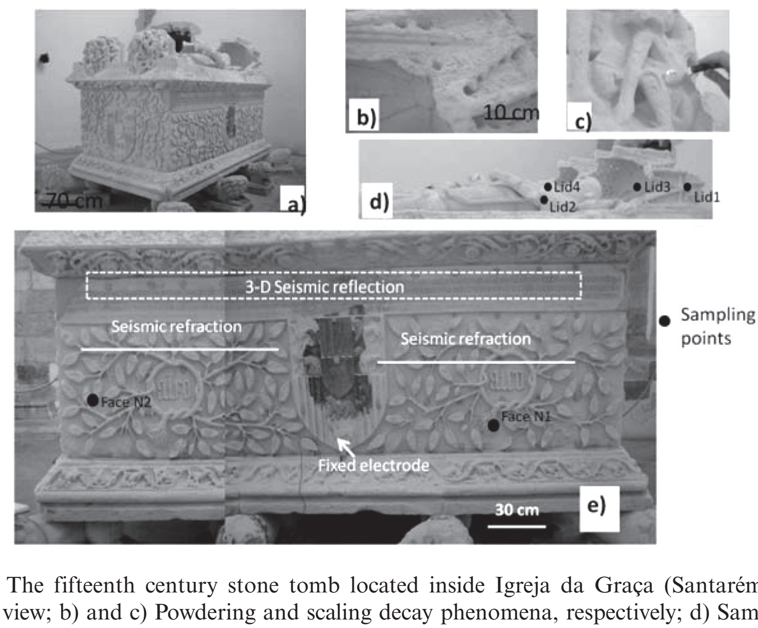

Figure 1. The fifteenth century stone tomb located inside Igreja da Graça (Santarém, Portugal): a) General view; b) and c) Powdering and scaling decay phenomena, respectively; d) Sampling points of stone decay products in the lid; e) Location of the seismic, SP surveys and sampling points of stone decay products in the E side of the tomb.

row (from the bottom) as can be seen in the Fig. 1e. Non-polarizable Cu/$CuSO_4$ electrodes were used. The seismic surveys were performed with ultrasound method that allowed measuring the S-waves velocity at different sites of the tomb. The refraction measurements were conducted using a portable device (STEINKAMP-model BP-7). Two profiles with 90 cm length were performed in the areas of lower and higher values of temperature and SP, for comparison (Fig. 1e). The transducers were positioned at distances multiple of 1 and 5 cm. In both profiles direct and reverse shot were performed. The 3D reflection survey was carried out only in the frieze (Fig. 1e) since it's the only site of the tomb without major irregularities, with MIRA equipment (based on the Ultrasonic Shear Wave Test Method), composed of a console with 40 transducers in an array of 10 rows each containing 4 Shear wave transducers. In order to evaluate if water and salts were some of the tomb's degradation factors, 6 surface samples of stone decay products were collected (Fig. 1d, e). Two different approaches were used: analyses of water-soluble fraction by Ion Chromatography and analyses of the decay products by Infrared Spectroscopy (FTIR).

3 RESULTS AND DISCUSSION

Figure 2a confirms the presence of water soluble salts in the tomb. Despite the presence of chlorides, the concentration of nitrates is clearly higher than the former; sulphates are almost non-existent. Moreover salts are rather uniformly distributed, i.e., there are no significant differences between the salt concentrations in the face and in the lid of the tomb. FTIR results confirm the presence of niter and calcite (primary mineral composing the limestone).

The Figure 2b show the thermogram obtained on the face of the tomb. As can be seen, the lowest temperature (about 22 °C) occurs at the bottom right and the highest in the top left. With exception of the frieze where all SP values are low, the low temperatures are coincident with SP negative values (–2 mV) while the high temperatures are coincident with SP positive values (2–3 mV) (Fig. 2c). The SP lowest values (between –4 and –8 mV) are observed on the crest area. These potentials are related, probably, with the redox potentials established between the paint materials and limestone. Self-potentials are generated by a number of natural sources, although the exact physical processes by which some are caused are still unclear. The common factor among the various processes thought to be responsible for self-potentials is groundwater. The potentials are generated by the flow of water, by water acting

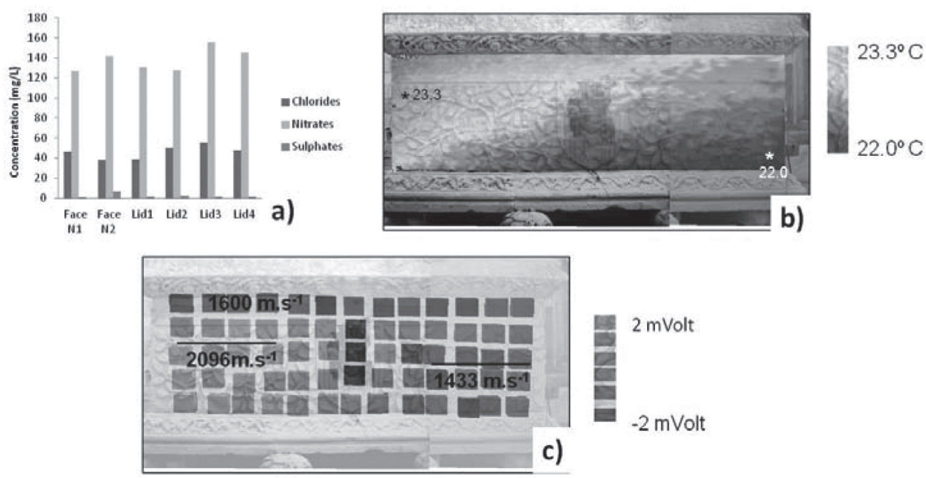

Figure 2. a) Concentration of ions (Cl^-, SO_4^{2-} and NO_3^-) in the water-soluble fraction of the samples; b) Thermogram obtained on the face of the tomb; c) Distribution of SP values and S-wave velocity on the face of the tomb.

as an electrolyte and as a solvent of different minerals, and so on (Reynolds 1997). Two of the main types of source mechanisms of spontaneous potentials are related, one with the flow of fluid through a capillary or porous medium that may generate an electric potential (called the electrofiltration or streaming potential) along the flow path and the other, with differences in the mobilities of electrolytes having different concentrations within groundwater (called the "liquid-junction" or "diffusion" potentials) (Reynolds 1997). The distribution of salt concentrations shows that the observed SP values are not the result of diffusion potentials. The thermogram (Fig. 2b) shows that there are temperature differences along the face of the tomb which indicates different degrees of moisture and, therefore, movement of water through the stone, originating electrofiltration potentials (Fig. 2c). The comparison of the SP values with temperature data show a good correspondence between SP negative values and the lowest temperatures and vice versa. The right part of the face is more humid than the left part; there seems to be a movement of positive ions to the more humid areas (SP negative values) while the negative ions move in the opposite direction. This movement of ions present in the water solution through the pores of the stone is the source of the spontaneous potentials observed. The moisture is probably related to atmospheric moisture; the differences between left and right parts are due to the fact that the left part of the tomb is more ventilated (less humid) than the right that is close to the walls of the church. The seismic survey were performed in order to 1) define the extent, in depth, of the high degree of degradation of the stone; 2) establish a possible correspondence between the more humid areas and more weathered stone. This survey allowed to determine the S-waves velocity in different sites of the face of the tomb (Fig. 2c). As can be seen from Fig. 2c, the velocity is lower on the frieze and on the right part, where the self-potentials are negative and the temperatures are lower (areas where the moisture content is higher). This means that limestone can be a little more weathered in these areas and that this decay is not primarily caused by the salts (similar concentrations are observed in different areas) and other factors, such as moisture, stone heterogeneities must be considered. No interface between sound and weathered stone was identified in the seismic survey (only direct wave was detected). So, it seems the observed degradation is taking place from the outside and is underway.

4 CONCLUSIONS

In this paper a study was presented regarding the application of non-destructive techniques for diagnosing stone decay of an emblematic Portuguese tomb. The multi-analysis approach provided useful and complementary information regarding stone intrinsic characteristics (internal and external), the extent/severity of stone decay which are essential to design an effective conservation strategy.

The results indicate that 1) the stone of the tomb has low resistance (low values of S-waves velocity); 2) the resistance of the stone is slightly lower in the right part of the face of the tomb where the moisture content is higher (lower temperatures and negatives SP values) and 3) the decay of the stone visible on the outside should have a thickness too small since it was not possible to locate any interface.

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Conservation of historic book bindings by means of facsimile reproduction: The Torres Notarial Register (1382–1400) in the Archive of the Royal Chancellery of Granada, Spain

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ABSTRACT: This article presents the results of the tests undertaken to establish the suitability of selected support materials and ink to be used in the substitution of the cover of the *Torres Notarial Register* (1382–1400) by means of a facsimile. The process followed strict intervention and methodological criteria in testing the technical efficacy of the materials to be used in making the new cover.

The tests were carried out in a climatic and ageing test chamber, paying particular attention to chromatic variations (tone, value and saturation), pH, dimensions, and risk of transfer onto a contact paper. The ageing conditions and periods were fixed according to ISO norms for the stability of paper, cardboard, paints and varnishes.

These studies have verified the selection of the most stable and innocuous materials for the facsimile reproduction of the cover, guaranteeing that its substitute retains a protective function while preserving the physical appearance of the original.

1 INTRODUCTION

The re-using of manuscript or codex parts for book binding has been common throughout history. Once studied, these fragments may acquire in their own right certain historic or aesthetic relevance. Such is the case with the currently unpublished *Torres Notarial Register (el Registro Notarial de Torres)* (1382–1400), which is preserved in the Archive of the *Royal Chancellery of Granada* in Southern Spain and whose parchment cover is a bifolio that belonged to a Visigothic codex from the 12th Century.

Paleographic and descriptive studies of this document have revealed a unique historic importance that transcends its function as a cover. Once the archivistic, preservation and organoleptic technical aspects had been considered, the results of this research were conclusive in the decision to preserve the cover as an independent documentary element of the registry of notaries (Torres 2012).

So as to ensure the correct conservation of this document, the substitution of the cover with a facsimile reproduction followed a rigorous methodology and strict intervention criteria in order to test the technical efficacy of the materials to be employed in making the new cover. This approach required an in-depth study of the materials to be used, so as to ensure their durability without threatening the stability of the original materials that they would come into direct contact with. As regards the technical characteristics of the paper and inks used nowadays, there was a lack of information as regards their suitability for use on historical documents. Hence it was necessary to implement age assays so as to evaluate variations in pH, colour, and the potential risks associated with the transference of ink onto a contact paper.

2 MATERIALS AND METHODS

Following an initial assessment of different papers used in the graphic arts and in conservation treatments, three types of high quality acid-free papers were selected, these being: Heritage Archival pHotokraft, 170 gr/m^2 weight and 0.20 mm thickness (P1); Somerset Book® Soft White, 175 gr/m^2 weight and 0.30 mm thickness (P2); Kawasaki Japanese paper, 35 gr/m^2 weight and 0.25 mm thickness compressed into five layers (P3). Printing was carried out on Xerox equipment using EA liquid toner (yellow, magenta red, cyan blue, and black) with developer and oil included, at a resolution of 2400 × 2400 ppi. For each type of paper, two 50 × 30 mm sets of samples were prepared. Both sets comprised one sample with no ink, one sample printed with yellow ink, one with magenta, one with cyan and one with black. The first set of samples was exposed to light, humidity and increasing temperature, while the second set was protected from the light but was exposed to controlled humidity and temperature. The variations produced in the samples for accelerated ageing were tested in a Solarbox 3000eRH climate test chamber equipped with Xenon lamp and indoor filter (S208/S408). The conditions selected for the climate test chamber were a constant temperature of 80 ºC, H_R of 65% and irradiance of 550 Wm^{-2}, in line with ISO 5630-3:1996 and ISO 11341:2004. The ageing intervals were set at 24 h, 48 h, 72 h and 144 h. To test the reliability of the results, three instrumental replicas for each condition were carried out. Thanks to the high volume of data obtained, the results and conclusions reached can be said to be valid. In order to test the possible transfer of the ink onto the original document, papers printed with each of the inks were introduced into the camera, in direct contact with a filter paper. The possible traces of colour at the different time intervals were observed by means of a Micro Capture Veho_vms004 (v-1.3) microscope, with magnifications between 20x and 400x. To test the acidity of the paper and its evolution, a flat-tip combined electrode (Hanna Instruments) was used to ascertain the superficial pH values of the different samples. The samples were humidified with a single drop of ultrapure water, and measurements were taken once two minutes had passed, in line with the TAPPI 529-2004 standard. For the colorimetric analysis, a Konica Minolta CM 2600d portable spectrophotometer was used, together with 'Spectramagic' v. 3. 61, 1996-2002: CM-S9w software. The measurement conditions applied were as follows (CIE 2004, UNE-EN ISO 2011, UNE 1994a, UNE 1994b): 10º observer pattern (CIE 1964); D_{65} illuminant pattern (CIE 1967); measurement/illumination area—SAV: 3 mm; measurement mode—3 automatic measurements a each measurement point; illumination—specular component excluded (SCE), 0% UV (illumination with no UV component), and 100% UV (illumination with UV component); and colour space/colorimetric data: CIE 1976 CIE94 L*a*b* (CIELAB), and CIE 1976 L*C*h* (CIELCH). For each sample, absolute colour measurements were made, according to CIE 1976 L*a*b*-L*C*h on the basis of the calculation of the XYZ tristimulus values (CIE 1931 X, Y, Z) and of the differences in colour between the various test samples (aged) and the reference sample (not aged): (ΔL^*, Δa^*, Δb^*, ΔC^*_{ab}, ΔH^*_{ab}, ΔE^*_{ab}).

3 EXPERIMENTAL DATA AND RESULTS

3.1 *pH measurements*

Measurement of the pH values was undertaken on samples with and without ink, before and after each ageing session. To corroborate the reliability of the results three replicas of each assay were run. The results obtained are shown in Table 1. No significant variations were observed in either the light-exposed samples or in the protected samples. The inks used in the printing were sufficiently alkaline and stable when exposed to a combination of heat, light, and high relative humidity.

The Japanese paper (P3), which in principle is recommended for use in conservation, has a slighly acid pH, both printed and when left unprinted. Of the three papers, it also presents greater pH oscillations (albeit minimum) and more differences between the light-exposed and the protected samples. In light of the values obained in the assay, we consider that, as

Table 1. pH values of the non-aged reference samples and the differences between printed and non-printed paper.

	0 hours			Differences		
COLOUR	P1	P2	P3	P1	P2	P3
No ink	6.68	8.07	5.93			
Yellow	7.21	7.82	5.89	0.53	−0.25	0.04
Magenta red	6.76	7.80	5.97	0.08	−0.27	−0.04
Cyan blue	6.96	7.82	5.88	0.28	−0.25	−0.05
Black	7.00	7.83	5.83	0.32	−0.24	−0.1

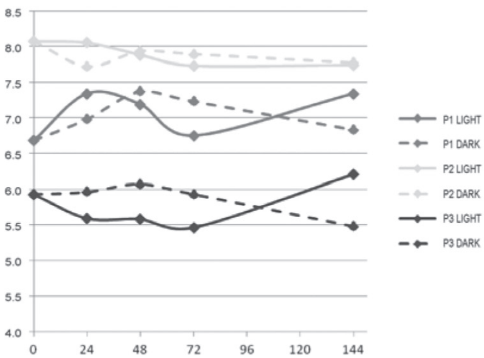

Figure 1. Variations in pH for unprinted papers P1, P2 and P3. Ageing points: 0 h, 24 h, 48 h, 72 h y 144 h. LIGHT: samples subjected to conditions of light, humidity and heat. DARK: samples subjected to humidity and heat but protected from light.

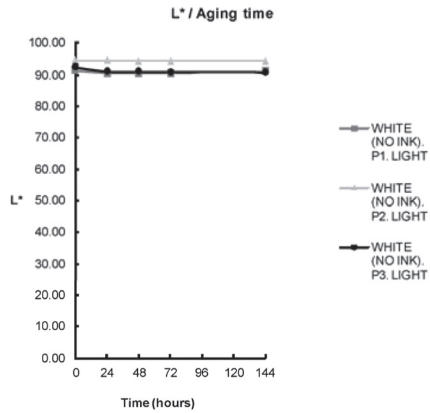

Figure 2. L* coordinate (CIELAB brightness) values, by ageing time in hours for unprinted papers P1, P2 and P3.

supports, both P1 and P2 fulfil the optimum characteristics, although in terms of stability during the ageing process, P2 would seem the more appropriate (see Fig. 1).

3.2 *Colorimetric study*

Considering he results obtained from the colorimetric analysis (ΔE^*_{ab}), it can be derived that of the three un-printed papers, it is P2 that gives the best chromatic results ($\Delta E^*_{ab} = 1.27$), whilst P3 registers the greatest variation in the value obtained ($\Delta E^*_{ab} = 7.78$). Of the three papers printed yellow, P2 offers the lowest ΔE^*_{ab} ($\Delta E^*_{ab} = 3.50$) and P3 the highest ($\Delta E^*_{ab} = 6.27$), hence the former is the paper that suffers the least deviation of total colour. Of the three papers printed magenta, P1 is the one that suffers the least differentiation of total colour ($\Delta E^*_{ab} = 2.55$), while P2 presents the most ($\Delta E^*_{ab} = 6.71$), although the Magenta P3 samples present total colour differential values very similar to those of Magenta P2. Of the three papers printed cyan, P1 registers the least chromatic alteration, with a value of $\Delta E^*_{ab} = 2.01$, while P3 presents the greatest alteration, with $\Delta E^*_{ab} = 3.00$. Of the three papers printed black, the one with the least chromatic alteration is P2 ($\Delta E^*_{ab} = 1.55$), while P1 presents the most marked changes in this regard ($\Delta E^*_{ab} = 4.24$).

With regard to the variations in total colour (ΔE^*_{ab}), under the conditions established for ageing and illumination, paper P2 ($\Delta E^*_{ab} = 1.27$) could be considered the most suitable, thanks to its greater chromatic stability, with P3 ($\Delta E^*_{ab} = 7.78$) being the least suitable as it was the paper that underwent the greatest changes.

The present study demonstrates, furthermore, that the colorimetric variations in the inks that were subjected to artificial ageing for the conditions of the assay, are acceptable for the intended use as they do not substantially alter the appearance of the reproduction achieved.

3.3 *Transfer of ink*

As regards the potential transfer of ink due to contact with other papers and the ageing process, no cases of traces of ink on the contact paper were observed, hence this should not be a determining factor in the choice of materials to be used.

4 CONCLUSIONS

We conclude that the most suitable paper for the proposed aims is P2 (Somerset Book® Soft White) and that the inks we studied do not present alterations due to age that may damage the support or the document it comes into contact with. Therefore, both the paper and inks can be considered appropriate for use in conservation treatments.

In-depth analysis of the notarial register has provided invaluable data with which to understand this document and its parchment cover, reinforcing the latter's historiographic importance as a unique document in its own right, above and beyond its function as a cover for the codex. The results derived from the present study were decisive in arriving at the ultimate decision to conserve it whilst considering all the technical issues involved in fulfilling the archivistic, conservational and organoleptic normative criteria.

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Hybrid sol-gel based protective coatings for historical window glasses

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ABSTRACT: Medieval glass is generally attacked by atmospheric pollutants conveyed by water in liquid or vapor form, which activates the corrosion process. Since the conservation strategies are currently addressed to maintain the windows in their original contexts, it is necessary to protect them from further degradation phenomena. We report here on the results of water-repellent hybrid sol-gel coatings obtained by using tetraethyl orthosilicate (TEOS) mixed with different amounts of Si-alkoxides functionalized with alkyl groups. Static contact angle measurements were performed to check the water-repellency of the surfaces. On the basis of the transparency, the contact angle values and the lowest amount of the organic component, three compositions were selected and applied on medieval-like glass samples that were colorimetrically characterized. The silica-based protective materials don't lead to reaction by-products, are water-repellent, compatible with the glassy substrate, colorless and transparent, hence satisfy the main requirements of the conservation of Cultural Heritage.

1 INTRODUCTION

The early 20th century brought a number of experimental treatments for degraded historical windows (Newton & Davison 1989, Frenzel 1995) and currently two main approaches exist for their protection: i) installation of protective glazing, i.e. secondary slabs mounted on the external surface of the panels; ii) application of chemicals on the glass surface, often partially modified by corrosion products. These substances must hence provide good adhesion to both the corroded and unaltered substrates to substantially reduce the diffusion of water and pollutants. Additionally, other requests from the conservation point of view must be fulfilled, as the chemical and physical compatibility with the substrate, the absence of reaction by-products, long-term thermal and light stability, employment at room temperature, transparency and lack of color, absence of chromatic changes, chemical resistance, ease of application and removal.

In this work the results of a study on the synthesis and testing of hybrid water repellent protective coatings for glass windows are presented. The products were obtained by sol-gel process to create a silica-based inorganic matrix, compatible with the glassy substrate, functionalized with organic chains, to obtain surface water-repellency and a certain degree of elasticity of the film, to avoid the formation of cracks during the drying process.

2 EXPERIMENTAL

The sols were obtained mixing tetraethyl orthosilicate (TEOS), the main precursor, with different proportions of Si-alkoxides functionalized by different alkyl groups, as octyltriethoxysilane (OTES, $CH_3(CH_2)_7Si(OC_2H_5)_3$), hexadecyltrimethoxysilane (HDTMS, $H_3C(CH_2)_{15}Si(OCH_3)_3$), 3-(trimethoxysilyl)propyl methacrylate (TMSPM, $H_2C{=}C(CH_3)CO_2(CH_2)_3Si(OCH_3)_3$), trimethyl ethoxysilane (TMES, $(CH_3)_3Si(OC_2H_5)$) and methyltriethoxysilane (MTES, $CH_3Si(OC_2H_5)_3$). Isopropanol was used as solvent, due to its steric hindrance, instead of the most commonly used methanol or ethanol in order to achieve a longer gel time T_{gel}; moreover it is less flammable and toxic. HCl 11 M was used as catalyst and a silicon molarity of 0.5 was always maintained (Table 1). The functionalized alkoxides and their proportions with respect to TEOS were chosen on the basis of recent studies on the protection of glass (Dal Bianco et al. 2008, Dal Bianco & Bertoncello 2008, Carmona et al. 2009, Gurav et al. 2011).

The functionalized alkoxides, TEOS, solvent and water were stirred in a round-bottom flask for 15 minutes before adding the catalyst. The sols were further stirred for 8 hours at room temperature, to allow the hydrolysis and condensation reactions. The hybrid sols were applied on laboratory glass slabs and on PLS (potash-lime-silica) medieval-like glasses (de Ferri et al. 2012) by speed controlled dip-coating technique at 9.6 cm/min, subsequently dried at room conditions (T ~ 25°C, RH ~ 50%) and then thermally treated at 50°C for 1 h.

UV-VIS spectra of the coated glass slabs were collected with a Perkin Elmer double ray Lambda 25 UV-VIS spectrophotometer in the spectral range 300–750 nm, using an untreated slab as reference.

Static contact angle measurements were carried out by adapting to glasses the recommendations given by the UNI 11207:2007 norm (Cultural heritage—natural and artificial stones—Determination of static contact angle on laboratory specimens) and using a home-made apparatus. The samples were placed on a xyz micro-positioning system: three 5 µl water drops were deposited through a flat-ended needle micro-pipette on the glass surface and illuminated from behind, with an incandescent white-light source and a diffuser screen. The images were acquired 15 s after the deposition of the drops by a PC controlled digital camera Canon D70, set in macro mode and placed at about 15 cm from the sample. A Matlab® custom-made graphical-user interface program was used to determine the contact angle of the drop in spherical approximation by:

$$\alpha = 2\mathrm{arctg}(2h/d) \tag{1}$$

where h is the drop height and d is the drop width deposited on the surface.

Three selected sol compositions were applied on three different model glasses mimicking the medieval chemical composition (De Ferri et al. 2012): SiO_2 = 52.10%, CaO = 17.65%, MgO = 2.65%, K_2O = 25%, P_2O_5 = 1.76%, Na_2O = 0.37%, Al_2O_3 = 0.26 and containing impurities of Fe giving slightly different optical appearance.

Table 1. Amounts of functionalized alkoxides (wt%) in the synthesized hybrid sols. TEOS adds up to 100%. The asterisks (*) indicate the sols producing opaque, iridescent or inhomogeneous films.

Coatings		
5% OTES	20% OTES + 5% HDTMS	
10% OTES	20% TMSPM	20% TMES
20% OTES	60% TMSPM	60% TMES
30% OTES	10% TMSPM + 10% OTES*	10% TMES + 10% OTES*
40% OTES	15% TMSPM + 5% OTES*	20% TMES + 20% OTES*
5% HDTMS	20% MTES	40% TMES + 20% OTES*
10% HDTMS*	60% MTES	5% TMES + 15% MTES
20% HDTMS*	10% MTES + 10% OTES*	15% TMES + 45% MTES
10% OTES + 10% HDTMS	40% MTES + 20% OTES*	

Colorimetric measurements were performed acquiring spectral images by means of a spectrophotometric scanner (Antonioli et al. 2004). According to colorimetric standards, a D65 illuminant and a white standard certified by a metrological laboratory were employed for the image acquisition, keeping constant the optical geometry (45°/0°). Samples were placed on a white substrate and the data were acquired at a scan rate of 1 mm/s, collecting 700 frames. Color values were obtained in the CIE$L^*a^*b^*$ space from the spectral reflectance factor for every pixel of the image.

Mean values of L* (lightness), a* (redness) and b* (yellowness) data were utilized to obtain the average color difference ΔE* (Briggs et al. 1998, Oleari 1998) between treated and untreated samples, defined as:

$$\Delta E^* = (\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2} \tag{2}$$

3 RESULTS AND DISCUSSION

All the sols appeared transparent and no precipitates were observed; part of them, anyway, formed opaque, iridescent, or inhomogeneous films and were consequently excluded as the transparency and the homogeneity are the most important characteristics required for coatings applied on transparent glasses. The excluded compositions are indicated by asterisks in Table 1.

A more detailed optical characterization was performed on the transparent coatings of the OTES and HDTMS groups by UV-VIS spectroscopy: all the OTES-bearing films absorb light for wavelengths shorter than ~340 nm, showing no significant absorption in the VIS range. This also occurs for the 5% HDTMS coating. Within the transparent coatings the best optical behavior is shown by the 20% OTES film. The most common way to evaluate a surface wettability is through the measurement of the static contact angle: for $\alpha < 90$ a surface is defined hydrophilic, while for $\alpha > 90$ it is considered hydrophobic. Table 2 shows the contact angle α values for all the tested coatings and the amounts, in wt%, of the organic component of the dried coatings: the best water-repellency performances are observed for those containing alkoxides functionalized with long alkyl chains as OTES and HDTMS containing -C8 and -C16 groups respectively.

On the basis of the static contact angle values α and of the amount of organic component in the dried films, that was chosen as low as possible to achieve the highest chemical and physical compatibility with the glass substrate, three sol compositions were selected for the application on three different model glasses mimicking the medieval chemical composition (de Ferri et al. 2012). They were colorimetrically characterized before and after the application of the coatings to evaluate their aesthetic impact, i.e. if significant color changes were induced. L*, a*, b* data and the color differences ΔE*, calculated between the coated and the uncoated samples, are reported in Table 3.

Table 2. Average static contact angles ($\alpha \pm 3°$) of the transparent coatings and organic component in wt%. The three compositions chosen for the application on the model glasses are indicated by *.

Coating	α (°)	Organic component	Coating	α (°)	Organic component
5% OTES	100	5.61	20% TMSPM	38	14.37
10% OTES	101	10.71	60% TMSPM	48	31.42
20% OTES*	105	19.64	20% MTES	81	2.73
30% OTES	103	27.2	60% MTES	79	6.56
40% OTES	103	33.68	20% TMES	94	9.46
5% HDTMS*	103	8.6	60% TMES	86	29.14
10% OTES + 10% HDTMS	97	35.14	5% TMES + 15% MTES	93	4.24
20% OTES + 5% HDTMS*	107	30.65	15% TMES + 45% MTES	91	10.71

Table 3. L*, a*, b* values for the uncoated and coated medieval-like glass samples (PLS glass) and their color differences ΔE*.

	L*	a*	b*	ΔE*
PLS Glass	90.1	0	−5.1	2.6
5% HDTMS	88.4	−1.2	−3.5	
PLS Glass	87.7	−2.3	−3.1	1.8
20% OTES	88.3	−2.7	−1.5	
PLS Glass	88.5	−2.1	−3.8	2.2
5% HDTMS + 20% OTES	86.6	−2.2	−2.8	

4 CONCLUSIONS

The silica based hybrid organic-inorganic films, obtained by sol-gel process, and containing alkoxides functionalized with long alkyl chains (OTES, HDTMS) seem suitable for the protection of antique window glass: they are transparent, colorless, water repellent, compatible with the glass substrate and do not give any reaction by-product, hence fulfilling most of the requirements of the conservation of Cultural Heritage.

Accelerated aging treatments are in progress to assess the light and chemical stability of these hybrid coatings.

No significant changes occur due to the coating presence for all the selected hybrid materials, being ΔE* << 4, a value normally accepted as limit for the visual impact of surface treatments (Sasse & Snethlage 1996, Malavelaki et al. 2008).

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Mineralogical and textural considerations in the assessment of aesthetic changes in dolostones by effect of treatments with $Ca(OH)_2$ nanoparticles

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ABSTRACT: The present paper shows the results of the application of calcium hydroxide ($Ca(OH)_2$) nanoparticles on dolostone substrates. A commercial product with nanoparticles was obtained by colloidal route. The main objective is to associate the possible aesthetic changes of a dolomitic stone substrate with the mineralogical and textural characteristics caused by the applied product. The nanoparticles were applied in three different concentrations onto classical dolostone samples used as construction material. During the whole process the relative humidity was controlled. Final results correspond to an exposure period of 45 days, indicating that the aesthetic changes produced on the stone have a direct connection with the porosity and the compatibility between dolomitic stone and $Ca(OH)_2$ nanoparticles. The presence of carbonate efflorescences has been identified in samples subjected to treatments with higher concentrations applied on heterogeneous porous substrates.

1 INTRODUCTION

In recent years, nanotechnology has been used in the field of cultural heritage conservation. The main uses are mainly focused as consolidating material (Dei et al. 2006), water repellents, self cleaning or as material for controlling the biodeterioration. Nowadays, there are a variety of commercial products based on nanoparticles, obtained by different experimental procedures (i.e. different processes of synthesis), which are offered as products with different properties. Among them, nanomaterials for application in the field of preservation of stone materials are provided. One of them, is calcium hydroxide ($Ca(OH)_2$), which has the property of absorbing easily the ambient CO_2 and releasing water in the same chemical reaction. In this way, calcium carbonate ($CaCO_3$) is obtained. It is used as a consolidating product in carbonate rocks (Gomez-Villalba 2011c), (López-Arce et al. 2010) rich in calcium and magnesium (limestones, dolostones, marbles). Besides, it is used as binding material in mortars, wall paintings, paper or wood (Baglioni et al. 2006). However, in the restoration field is common to hear about how a product is not suitable for the desired purposes and even cause further deterioration. In other words, sometimes the cure is worse than the disease. The use of inadequate treatments, which modify the aesthetics properties of materials causing new pathologies is increasingly reported (Sierra-Fernández 2012), being very important to take into account the application method and concentration of the product and the mineralogical and porosity of the substrate.

2 METHODOLOGY

Dolostone samples correspond to typical materials used as construction materials that have been exploited in quarries located in Redueña in the northern province of Madrid (Spain). Samples were studied before and after treatment using $Ca(OH)_2$ nanoparticles in alcoholic solutions obtained by colloidal synthesis. Specimens were subjected to treatment by brushing (Zornoza-Indart et al. 2012) calosil® product dispersed in isopropanol with 3 different concentrations, 5%, 15% and 25%. The specimens were exposed to 75% relative humidity (RH) for 1 month and then at around 35% RH for 15 days. The specimens were characterized by different microscopic techniques including polarized optical light microscopy (PLOM), zoom binocular macroscopy and scanning electron microscopy (SEM) using the secondary electron detector. Thin sections of samples with different lithological and textural characteristics were prepared for the optical study. The SEM characterization was conducted under the microscope Jeol JSM 6400 equipped with EDS detector (Inca-Link). Digital micrograph™ Gatan Team software was used for the interpretation of the SEM images including the optical roughness profiles. This software allows to calibrate the images so that rows and columns correspond to physical distances. With the correction, the intensity values represent the physical height of the sample. The secondary electron images come primary from the sample topography, so that peaks are bright and valleys are dark.

3 RESULTS

The Redueña dolostone observed by PLOM shows a massive structure with predominant anhedral crystals (25 to 93 μm) of dolomite ($MgCa(CO_3)_2$) and occasional anhedral calcite crystals (>8.5 μm) generated by cementation processes in pores. Porosity is fundamentally intercrystalline (20%), with regular morphology and size (12 to 70 μm). Pores develop irregular morphologies generating sub rounded and elongated forms, which can coalescence, whose size can reach up to 1 mm in diameter being locally calcite-filled (Gomez-Villalba et al. 2011b).

Samples of dolostones were checked before and after treatments. The results indicate more or less aesthetic variations, depending on the scale of observation. It is worth noting the development of a series of carbonate efflorescence which are deposited on the surface and side faces of the specimens, more accentuated in the specimens treated with the product at higher concentration (25%), however no changes were observed in samples whose treatment was performed with a solution of lower concentration.

3.1 *Low magnification*

The inspection in low magnification (~10 mm^2-Figure 1a) indicates local variations in the distribution of white carbonate efflorescences along the stone (25% and 15% calosil). In addition, there are certain differences in the reddish hue of the original stone, which show an increase after treatment; however these only affect reddish areas close 0.5 mm, corresponding to iron-rich minerals scattered along stone. In addition, there are changes in the geometry of pores, with the appearance of molds, which may or may not be filled with this whitish layer. The distribution of the white layer is controlled by the own texture of the rock. In this way, the power of penetration is affected by the geometry of the rock. Local variations in the lamination or small discontinuities, inherent to the source rock, coincide with differences in the grain size of dolomite or calcite enriched areas. In addition, marked differences in the pore sizes can even develop areas of weakness, by fracturing and/or washing of oxides, carbonate efflorescences, etc, which favor the penetration of the product, even being affected by the method of application with brush (Zornoza-Indart et al. 2012).

3.2 *Scanning Electron Microscopy (SEM)*

The SEM image (Figure 1b) resembles a topographic surface, where bright areas correspond to peaks and dark to valleys. Certain differences in the surface of dolostone as a result of the treatment are observed. At first sight it can be seen how the outline of the pores is modified. Although the specimens treated with more concentrated solutions show greater changes in both the geometry of the pores as in size, also the samples subjected to treatments with lower concentrations have been modified, albeit to a lesser degree. As a result of the interaction between the alcoholic solution of $Ca(OH)_2$ nanoparticles with the dolomitic surface, it has

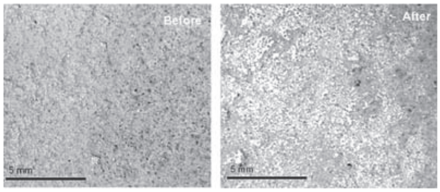

Figure 1a. Low magnification images of dolostone after and before treatment (calosil® 25%).

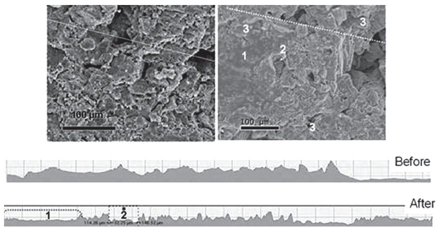

Figure 1b. Typical secondary electrons SEM images of surfaces before (left) and after (right) the treatment (calosil® 25%).

been identified a pattern of behavior for all applications, which is summarized in three steps: i) Surface smoothing effect due to treatment with nano $Ca(OH)_2$; ii) Moldic porosity produced by partial dissolution of dolomite and subsequent precipitation of nano-$CaCO_3$ and iii) Crystalline edge rounding by the partial dissolution processes in dolomite.

It has been established through the study of the behavior of nanoparticles obtained by colloidal synthesis (Gomez-Villalba et al. 2011a, 2012b), important differences in the nucleation and growth which are controlled by RH and time of exposure. Among the $CaCO_3$ polymorphs, the most common are aragonite and calcite, which can co-exist (Gomez-Villalba et al. 2012c) It has been observed how acicular aragonite crystals are larger, although they remain associated with small rhombohedral crystals of calcite. However, these polymorphs vary in crystallinity depending on RH, leading to develop smaller and less stable crystals like vaterite or amorphous $CaCO_3$ (Gomez-Villalba et al. 2011b, López-Arce et al. 2011). Taking into account this behavior, it is assumed that $CaCO_3$ present in the pores of the dolomite obeys to different forms of crystallization. In this way, the great carbonate efflorescence developed on the surface of the stone after treatment at higher concentration would correspond with acicular aragonite forms. However, $CaCO_3$ cementing pores in dolomite may vary among different polymorphs, developing needles, spheres, short prisms, rhombohedral shapes or amorphous surfaces. The tendency to develop the unstable and common variety of $CaCO_3$ (aragonite) presupposes the generation of tensions that might cause further deterioration on the surface (Gomez-Villalba et al. 2012a). It should be noted that the incorporation of nanoparticles of $Ca(OH)_2$ and the subsequent transformation to $CaCO_3$ by carbonation entails a change in the dolomite crystals of dolostone. Any modification in the nucleation and growth of crystals may produce aesthetic modifications. It can be expected that changes in brightness can be caused mainly by the presence of acicular aragonite crystals observed as carbonate efflorescence. Another aspect to consider is that the areas where partial dolomite dissolution has taken place may eventually cause changes in brightness and possibly modify the color. Although at larger scale is not detected a change in the red tones, a major alteration by degradation processes in iron oxides can cause forward a significant change in color.

4 CONCLUSIONS

The results of treatment with $Ca(OH)_2$ nanoparticles from colloidal synthesis applied on dolomite stones with different concentrations have demonstrated the development of surface carbonate efflorescences, observed in samples treated with the product in high concentration (15 and 25%) and heterogeneous porosity. Changes in the color and brightness are reason enough to discourage the application of this treatment in high concentrations on this type of porous dolostones. It is essential to conduct a previous study of mineralogical and chemical compatibility between consolidating product/stone to avoid developing unaesthetic neo-mineralizations in the stone. Therefore a mineralogical and textural control can early diagnose possible pathologies developed as a result of no suitable treatments.

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

The *Arabic Manuscripts Collection* of the School of Arabic Studies-CSIC, Granada: Characterisation of decorative covers using new resources for their documentation

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ABSTRACT: This paper presents a review of the most commonly-used practices for capturing images of decorative drawings from the covers of historical bindings. In particular, the work focuses on studies that are being carried out on 12th–19th Century manuscripts from the Arabic Manuscripts Collection of the Arabic Studies School-Spanish National Research Council (EEA-CSIC) in Granada. The key objective is to establish a methodology in order to optimise these practices, by implementing the latest technological resources and systematising the process of identifying and cataloguing the decorative motifs, as a fundamental part of their conservation.

This registration process, together with other intrinsic parameters of conservation, forms part of a broader research process focusing on the material characterization and codicological analysis of the bindings included in this collection.

1 INTRODUCTION

While the decoration of book covers historically is subject to the technical, artistic and societal influences prevalent in any given era, it is also closely connected to the book's function and to its owner's social status. The systematic registration of these decorations offers a complementary basis from which to discuss the results of the codicological studies being undertaken. However, there are challenges involved in capturing the images correctly, particularly when the manuscript is in a poor state of conservation. It is within this context that the present paper describes the results of studies undertaken on a series of decorative motifs from 14 bindings (12th–19th Century) from the Arabic Manuscript Collection of the EEA-CSIC in Granada. Applying different registration and documentation techniques, the cover decorations were systematically reproduced and recorded. A methodology was established for the purpose, based on adapting the latest technological resources to suit each particular type of decoration and its state of conservation. The different techniques applied were then subjected to a comparative test describing the advantages and disadvantages of each of the different procedures for capturing the image (González 2010).

One of the objectives of the study on the manuscripts in this Collection was to develop a design pattern for each of the decorative elements found, in order to better understand how this bibliographic heritage was originally put together.

When searching for decorative models in bibliographic sources, we found linear designs, based on simple outlines and schematic drawings of ornamental motifs (Deroche 2000). This type of representation shows the lines, curves and shapes of the various different elements, but does not provide any indication of the indentations made by the engraving, which presents a problem in terms of the formal analysis. In other words, examining the decorative motif that has been captured does not provide all the information necessary in order to establish the different levels of depth of the tracings, as it is not easy to distinguish the outline of the relief from that of the embossing marks. Bearing in mind the scarcity of documentary references and databases on ornamental motifs used in historical bindings, it is vital to be able to ascertain as many references as possible.

In the case of the manuscripts from the Collection of the Library of the School of Arabic Studies in Granada, the decoration presents symmetrical compositions, with opposing outward and inward curves, linear decorations, and regular series of closed 'compartments' with small elements and a clear central motif. This particular set of elements fulfils one of the requirements that, according to Riegl, any decorative composition on an Islamic binding should possess (Checa 2003). The base pattern of these motifs is enriched with fillet tracings in simple, double or triple straight lines or in different shapes such as rosettes, stars, floral figures, circles and other geometric elements, all with a refined and complex finish.

2 METHODS FOR CAPTURING THE MOTIFS

When we started the process of capturing the motifs, using computer programmes to treat and enhance the images taken, we began to have doubts as to the ideal procedure to follow, give that a linear drawing in this scenario would provide little information. We also knew that that data on the indentations/relief would be important for a number of reasons, namely: in order to complete the details of the motif; because if we were to undertake a search for one particular decoration or element, we might find the same pattern but inscribed (embossed or engraved) differently; and because of the need to acquire that particular reference so as to be able to make a reproduction of the iron stamp used or of the motif.

The registration process for the decorative motifs of the Collection included the covers, the flaps, the spines, the corners of each cover, the central elements, trimmings, and individual decorative motifs. Firstly, we made a direct copy by tracing onto a layer of polyester or vegetable paper, and then we made a rubbing using varying grades of soft graphite on tracing paper. We then used a scanner and digital photography to complete the process of registering each element. Whilst scanning, we maintained a strict discipline for appropriate handling of each piece, even though there was no need to register its interior. During the photography process, for specific details we used a spotlight so as to highlight the particular areas with relief work, outlines or incisions, and for general images we used neutral fill light.

We should point out that the registrations obtained with the first two techniques provide unique examples that inevitably retain the impression of the decorative element that has been reproduced, and hence the tracings also retain the true dimensions of the original.

3 RESULTS AND DISCUSSION

Rubbing with soft pencil onto tracing paper gives a clean, precise result that provides important information on the engraved drawing. Tracing paper is thin, translucent, and flexible, making it ideal for our objective of identifying the details of the decoration. For best results in terms of reproduction, a soft 2B pencil is the recommended option.

On the other hand, direct tracing can reproduce the outline of the motif with precision, but it does require a good level of knowledge and control of the drawing as it needs to be done freehand and ultimately depends on the skill and experience of the tracer. This method gives good results in the reproduction of motifs if the cover is in a reasonable state of conservation.

Registration by means of rubbing or tracing can be considered sufficient if we simply need a formal approximation of the decorations found on historical bindings. These approaches also provide an impression on a1:1 scale. However, they cannot give us information about any lines below the level of the pencil strokes, and nor do they offer sufficient data for recuperating the design in the case of covers that have suffered mechanical damage.

Scanning, meanwhile, delivered acceptable results: high resolution digitalisation of the motifs enabled us to reproduce the decoration to an excellent level of quality. Images can be taken at full size or to a given scale, and the object appears evenly-lit. However, as there is insufficient depth of field, in those decorations with deep incisions we observed areas that were out of focus, where we could not see the deeper details correctly (Fig. 1).

We found that the optimal method for the formal characterisation of the decorations was to take one or several photographs of each motif, in addition to micro and macro-photographs, using the correct lighting so as to ensure a precise registration of all the details required by our study. That said, having previously taken reference shots to establish the dimensions and colour of each piece, there were cases in which the image taken in the aforementioned condi-

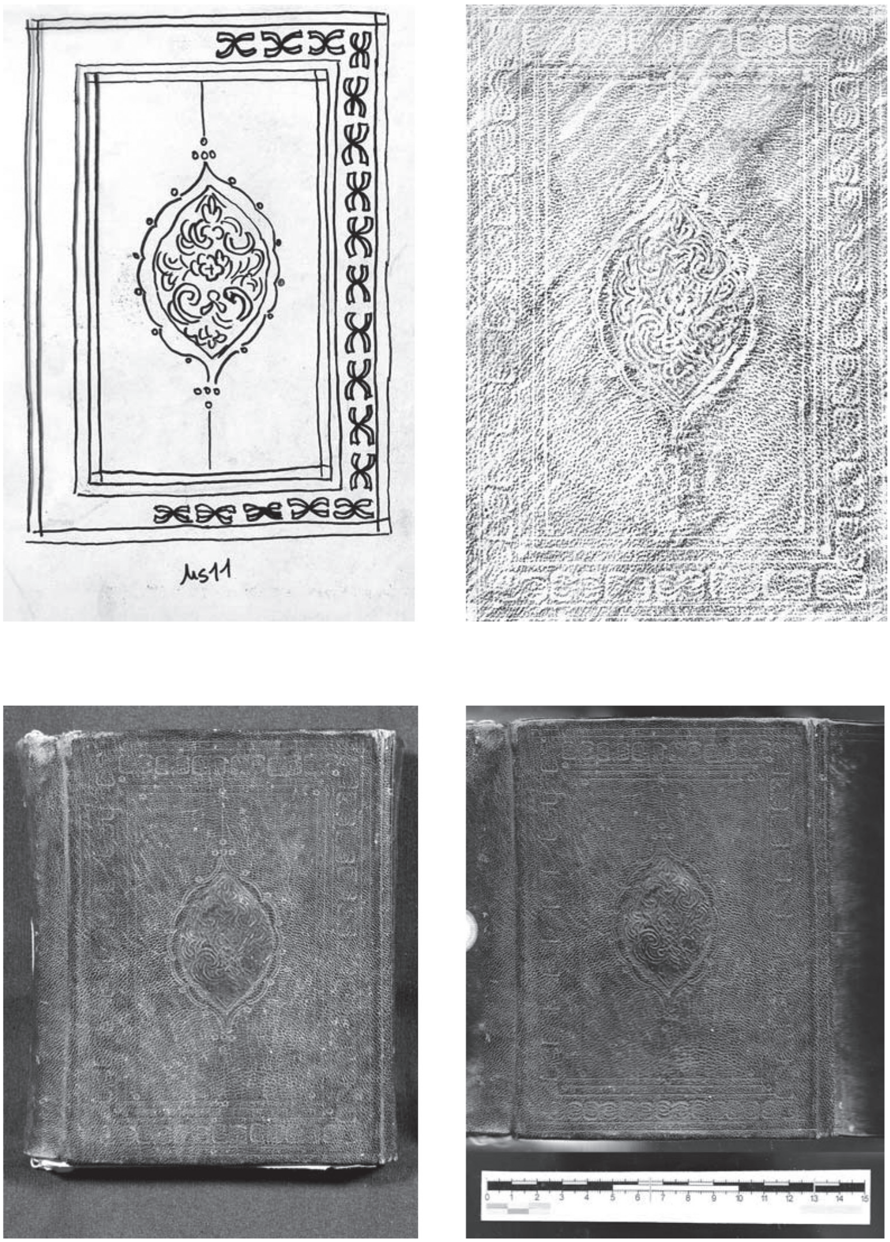

Figure 1. Ms 11: top left, tracing; top right, rubbing; below left, photography; below right, scanning.

tions was of no use if we wanted to see significant details in order to understand how the decorations had been made. This occurred when the cover was in a poor state of conservation.

In some cases we took photographs using raking light, to achieve details that were otherwise imperceptible using light from other angles.

4 CONCLUSION

Capturing the elements that make up the external decoration of historical bindings should be considered to be a fundamental task and a pre-requisite for subsequent studies. The collection of visual data should therefore form part of a systematic approach that facilitates ongoing study of a manuscript whilst avoiding its continual handling. The use of one single technique for capturing the decorations only allows researchers to go so far in achieving a full representation. Without the use of at least two of the techniques outlined in the present paper, it is not possible to arrive at comprehensive understanding of the design, in the sense of the entire set of actions that have gone into its making. In the case of tracing or rubbing, these provide real dimensional information but the data derived from these techniques are dependent on the state of conservation of the object in question, or the interpretation of the researcher who is taking the data. With tracing, it is possible to discern the sequence of execution in the outline of the drawing used as the basis for the decoration because this technique highlights the superimposed outlines. This makes it possible to establish, in negative form, the design of the original iron stamp used in making the decoration, which gives us an insight into the processes and techniques employed. However, the lack of colour and the limited scope for discerning the design if the piece is not well conserved are the key drawbacks to using this technique on its own. Without doubt, photography and/or scanning, depending on the case, are the most effective resources in terms of the information they provide. Digital treatment of the images, using specific software, gives access to a level of detail that is otherwise imperceptible in normal vision. Therefore when seeking to fully understand a design, its vectorial reproduction is unnecessary. However, the fact that it is a two-dimensional representation means that it does not provide depth information, even in those cases where the original colours captured are then modified, and so the use of digital systems alone is inadequate for obtaining the volume of data demanded by this work.

In conclusion, then, in order to achieve our objectives we need to apply two methods—digital and manual. This approach allows us to work with all the possible references with which to ascertain the embossed motif pattern.

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Low-cost airborne ultrasounds scan for Cultural Heritage

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ABSTRACT: Non-destructive methods are of great interest for the analysis of Cultural Heritage. This work presents a low cost ultrasound sensor without direct contact with the test specimen studying variation of the phase shifts between the emitter and the ultrasound detector. This acoustical method meets the requirements to perform in situ non-invasive studies of bricks position supporting mural paintings and simple plasters, and could be extended to other antique artifacts such as mosaics, etc. Its simplicity and the low data acquisition time could be put together to obtain real time measurements, which in addition to a position tracking system would enable a fast and versatile non-destructive system. Using this prototype system, an early moisture detection system has been installed in a dome that supports a fresco. We used this prototype for the detection of brick joints under a XVth century Renaissance fresco of the Metropolitan Cathedral of the city of Valencia (Spain), with full success in detecting these joints. Both laboratory and in situ results are in agreement. Although this is a preliminary study and more tests and theoretical simulations must be performed, the result is encouraging and opens interesting prospects for future research in this field.

1 INTRODUCTION

In 2004, the metropolitan basilica cathedral of St. Mary in Valencia started the restoration of the main chapel and its renaissance fresco paintings (http://www.frescosdelacatedral.com). During the restoration process, the presence of efflorescence causing deteriorating problems due to high humidity was observed (Marías 2007). In an attempt to solve the infiltration of rainwater through the ceiling above the apse, it was remodeled and a sheet of asphalt roofing was placed. The importance of waterproofing the outside of these kinds of monuments is discussed in the literature (Bernardi et al. 2000).

The restoration team decided to implement a monitoring system composed of relative humidity sensors (García-Diego & Zarzo 2010, Zarzo et al. 2011). To install the sensors, it was necessary to drill holes in the vault, specifically in the joint between bricks, because this is the most sensitive to the variation of moisture due to its porosity. Springing the question: how to locate the joints without affecting the wall painting?

Among the wide variety of methods for non destructive testing, elasto-acoustic waves provide a good alternative which have been exploited mainly for biomedical and industrial applications (Storani et al. 2007, McIntyre et al. 2001, Cinquin et al. 2005, Dos Santos & Prevorovsky 2011).

Some of the techniques developed in biomedical and industrial areas have been exported for its use in heritage conservation. Furthermore, an analysis of acoustic reflections using audible frequencies below 1 kHz in a Kundt tube as an assessment of wall painting detachments has been recently proposed to overcome the drawbacks of the traditional empirical method (Del Vescovo & Fregolent 2005a, Del Vescovo & Fregolent 2005b).

Other method for studying paint detachment is the vibro-acoustic technique based on the application of the Laser Doppler Vibrometry under acoustic excitation (Collini et al. 2011). Both aforementioned methods only give information about superficial vibrations.

This paper deals with the results on the location of the joints between the bricks of the wall behind the frescoes obtained by using a noninvasive ultrasound prototype.

This prototype has the peculiarity of using air as a coupling medium, thereby avoiding problems with cleaning of gel and reducing the possibility of damages in the test object. However, new problems arise, mainly due to the large difference in acoustic impedance between air and solids. In recent decades, many ways to overcome these problems have been studied (McIntyre et al. 2001, Cinquin et al. 2006, Maev et al. 2008, Siddiolo et al. 2005, 2007, Robertson et al. 2005).

2 METHODS

The equipment of the automated scan is described in detail elsewhere (García-Diego et al. 2012).

In-situ measurements of the frescoes were made manually in two stages.

First we found a section of wall where bricks were visible and a template on a transparent plastic sheet was drawn. This plastic was used as a guide of the size of bricks and joints since the arrangement of the bricks beneath the frescoes is the same in all points.

Second, in areas where the joint was intended to locate, a manual scan was performed to mark the points where the phase changes were evident. These points were compared with the template to ensure certainty. Ten points were marked by this procedure (Fig. 1).

Holes of 16 mm in diameter were drilled to a depth of 15 cm (Fig. 2) and the resulting powder was stored for microscopic analysis to see if its color was red (brick) or white (joint).

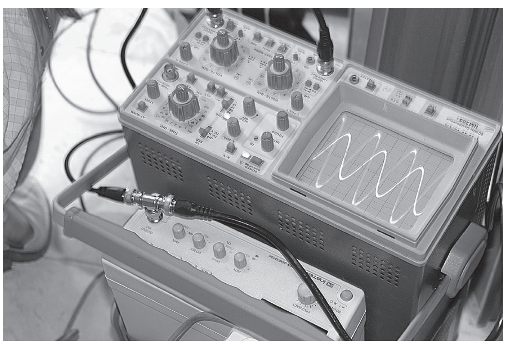

Figure 1. Manual scanning for detecting the sensors insertion points in frescoes.

Figure 2. Temperature and humidity sensor detail inserted by the ultrasound technique.

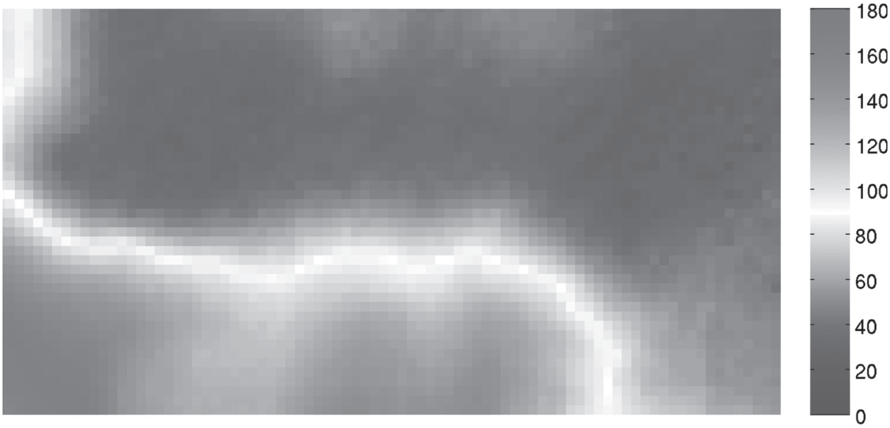

Figure 3. Acoustic photography of one brick, representing the phase values.

3 RESULTS

An analysis of the phase shift was performed. The results of the scan are shown in Figure 3. The gray scale depicts phase variations from 0 to 180 degrees as a function of the transducers position over the test specimen.

Small changes in the scale (phase) in one area may be due primarily to the bricks used in the laboratory experiment are handmade. Therefore, the surface may have small irregularities that justify these changes in tonality. This is because the phase value of a position depends on the distance traveled by the wave between the emission and reception. The height variation produces different values of phase shift, although being the same pattern.

Despite the limitations mentioned, is readily discernible in Figure 3 that the phase value remains fairly constant within areas of the same material. However, at the material change zones (brick-masonry interfaces) abrupt changes of phase appear. These abrupt changes allow clearly appreciate the limits of the joints.

4 CONCLUSIONS

Considering that this is a preliminary study and that several variables (transmit-receive angles, height between specimen and sensors, etc.) should be studied in more detail, the results are enough hopeful to be published.

The prototype presented meets the requirements for the analysis of not superficial materials, with the advantage of being noninvasive. This is especially interesting for the analysis of artworks.

Our experimental results show that the phase changes correlate well with the changes in impedance of the material. This allows a good location of the joints between bricks.

The development of a theoretical model is necessary for a better understanding of the underlying physical phenomenon, which will allow us to set limits as to the limits of the prototype.

ACKNOWLEDGEMENTS

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Molecular approach for the characterization of ancient/degraded *Cyperus* sp. specimens

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ABSTRACT: The aim of this work has been to apply and improve the efficiency of molecular tools for the identification of *Cyperus* sp. from different sources. Total DNA was extracted from fresh, degraded and ancient specimens. DNA molecules were the template for *in vitro* amplification of specific target regions referred to rcbL plastid gene (ribulose-1,5 -biphosphate carboxylase/oxygenase large subunit). Dedicated DNA extraction and amplification protocols have been applied specifically for fresh/degraded and ancient samples. Particularly, specific set of primer, annealing temperatures and reaction mixtures have been performed. The PCR products, single DNA fragments, were resolved on agarose gel electrophoresis and sequenced. The sequences were compared by dedicated software and this allowed us to obtain genetic information.

1 INTRODUCTION

Molecular tools were applied in order to obtain genetic information from *Cyperus*: fresh, degraded, ancient samples. It is known that this plant was considered of naturalistic interest, universally known for its employment since III millennium B.C. in the production of writing material and had been employed in a widespread of applications. This plant was also cultivated in Sicily and especially in the South-East (documented for the first time in 17th century) of the island, in Anapo and Ciane valleys. Related to its importance, many samples are stored in the *Herbarium Mediterraneum Panormitanum*, housed in the Botanical Garden of Palermo (Fig.1a, b) and the extensive use of this plant during the century makes it of remarkable interest under an archaeological, ethnographic and naturalistic point of view.

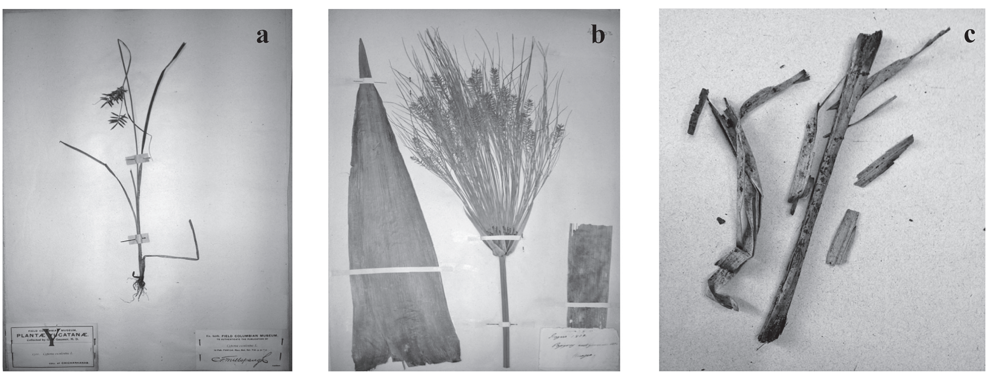

Figure 1. *Herbarium Mediterraneum Panormitanum* specimens. (a–b) ancient samples: a) *Cyperus esculentus* L.; b) *Cyperus papyrus*, Anapo valley (1829); (c) degraded sample.

2 MATERIALS AND METHODS

2.1 *Sampling*

Cyperus specimens were collected from: the *exsiccata* of Herbarium Mediterraneum Panormitanum) and labeled as ancient samples (aDNA); from fresh plant in the Palermo Botanic Garden (fDNA); from degraded, partially burned (Fig. 1c), samples (dDNA). aDNA was extracted from the *Cyperus esculentus* L. and *Cyperus papyrus* L., fDNA from *Cyperus alternifolius* L., dDNA unknown sp.

2.2 *DNA extraction*

Total genomic DNA molecules were extracted from 200 mg of fresh (fDNA) or degraded (dDNA) specimens by the NucleoSpin Plant II kit (Macherey-Nagel). From 10 mg aliquots of ancient samples (aDNA) a dedicated protocol was set up in collaboration with BioNat-Italia in order to extracts DNA molecules useful for PCR amplification reactions.

2.3 *PCR reactions*

Cyperus rcbL plastid gene sequences (Demesure et al. 1995, Dumolin-Lapègue et al. 1997, Muasya et al. 2002, Soltis et al. 2000, gene bank accession numbers M91627, AM999811) were the reference for design and synthesize (MWG Eurofin Operon) new set of primers specific for fDNA and dDNA, or aDNA.

500 bp amplification fragments were obtained using fDNA or dDNA molecules as template in PCR reactions, with the following primer pairs: Cyp 1-f (5′ AGT ACA TCC CAA TAG AGG ACG ACC A 3′) and Cyp 1-r (5′ TGT CAC CAC AAA CAG AGA CTA AAG C 3′); Cyp 2-f (5′ CCA GCG TGA ATA TGG TCT CCA CC 3′) and Cyp 2-r (5′ TCC ACC TCA CGG TAT CCA ATC TGA 3′); Cyp 3-f (5′ TAC CTT CAC GAG CAA GAT CAC G 3′) and Cyp 3-r (5′ TGA CTA CTT AAC TGG GGG ATT CAC 3′). PCR reactions mixture containing: 200 μg of genomic DNA; 20 μl PCR Master Mix 2X [50 units/ml Taq DNA polymerase, (pH 8.5), $MgCl_2$ 3 mM, dNTP 400 μM]; 2 μl of each primer 10 mM, sterile H_2O up to 50 μl. Reactions were performed following the amplification protocol: denaturation 94°C-5′; 25 cycles: 94°C-1′, 60°C -1′, 72°C-1′; final step 72°C-7′.

90 bp amplification fragments were obtained using aDNA molecules with the following primer pairs: CLO-f (5′ CTC CTG AGT ACG AAA CCA AAG A 3″) and CLO-r (5′ CGC TAC TGC AGC TCC TGT C 3′); CALL-f (5′ AGC TTA TCC TTT AGA CCT TTT CG 3′) and CALL-r (5′ TCG TAA GGC TTT GAA ACC AA 3′). PCR reactions were performed following the amplification protocol: denaturation 94°C-2′; 40 cycles: 94°C-30″, 50°C-45″, 72°C-45″; final step 72°C-5′.

In vitro amplifications were performed by 2720 Thermal cycler Applied Biosystem and Mastercycler Eppendorf, assembling the reaction mixtures under a laminar flow to avoid external contaminations (Palla et al. 2002, 2010). The PCR products, were resolved by electrophoresis on 2% agarose gel in 1X TAE (40 mM Tris-acetate/1 mM EDTA, pH 8,3); amplicons were stained by SYBR® Safe™ DNA Gel Stain (Invitrogen) and observed under UV light The marker used for estimate amplification bands size, was 100 bp ladder (Biolab).

3 RESULTS

Total DNA molecules were extracted from different specimens, applying *ad hoc* DNA extraction protocols in relationship with the origin of the specimens. These molecules were used in PCR reactions distinguishing fresh/degraded and ancient samples. Particularly, for fresh/

degraded DNA was used the NucleoSpin Plant II kit (Macherey-Nagel). Considering the potential oxidation and hydrolysis processes, over the centuries, occurred to the ancient DNA that can modify the chemical structure of these molecules (Dumolin-Lapègue et al. 1999, Schlumbaum & Tensen 2008), the extraction of genomic DNA was performed by a specific protocol set up in collaboration with BioNat-Italia.

Basing on the same speculation, PCR reactions were performed with different primer sets that produced 500 bp DNA fragments using fDNA or dDNA (Fig. 2) and 90 bp fragments, using aDNA (Fig. 3) as templates.

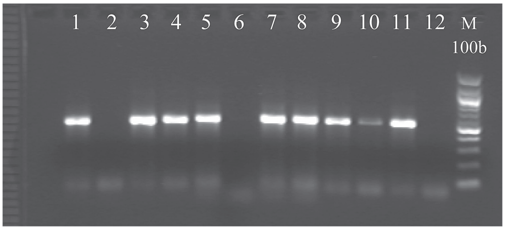

Figure 2. Gel electrophoresis of PCR reactions products (500 bp): lines 1–5, degraded samples and lines 7–11, fresh samples; lines 6 and 12 negative control reactions. M = 100 bp ladder.

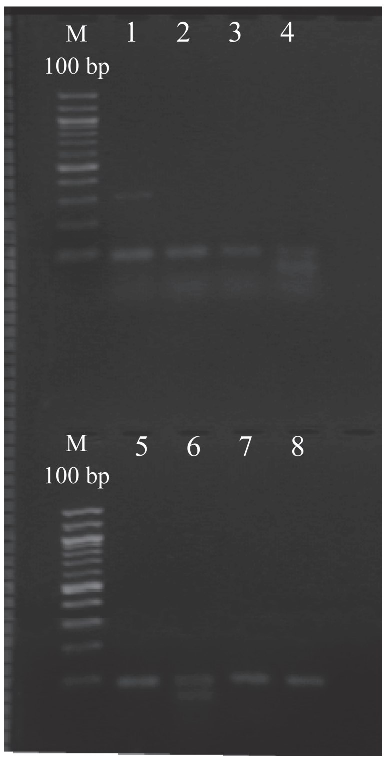

Figure 3. Gel electrophoresis of PCR reactions products (90 bp): lines 1–4, Cyperus esculentus; lines 5–8 *Cyperus papyrus*. M = 100 bp ladder.

4 CONCLUSION

The application of molecular methods allowed us to develop extraction and PCR amplification protocols specific for different *Cyperus* specimens. Particularly for ancient specimens (*exsiccata* from *Herbarium Mediterraneum Panormitanum*) these procedures can be useful for the development of a DNA Barcoding database, as done by Consortium for the Barcode of Life CBOL (http://www.barcodeoflife.org/) for avifauna and fish species, and particularly for plants (Simpson et al. 2007).

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Roman glasses from Augusta Emerita: Study of degradation pathologies using LIBS

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ABSTRACT: Thirteen Roman glass samples, including seven entire glass beads, from the ancient town of Augusta Emerita (SW Spain) have been characterized by LIBS to explore its feasibility and their possibilities in the full study of non-destructible historic glasses. Along with LIBS other conventional techniques, such as SEM-EDS, XRF and visible spectrophotometry, have been also used in the present work. LIBS stratigraphic analysis, which consist of the application of successive laser pulses on the same spot, has been especially addressed at characterizing particular features of historic glasses, such as bulk chemical composition, surface degradation pathologies (dealkalinization layers and deposits), chromophores, and opacifying elements. The obtained results indicate that LIBS can be considered as a useful and alternative technique in the study of non-destructible glass samples, above all in those archaeological and historic glasses which have been conserved under burial conditions.

1 INTRODUCTION

Glass has been regularly employed and produced in the Mediterranean region from more than four thousand years ago. Most of historical glasses have been conserved under burial conditions and, consequently, have experienced degradation processes strongly dependent on their chemical composition and particular environmental parameters.

Common techniques used for characterizing historical glasses are usually destructive. In such a way they cannot be applied for sensible samples as those from museum collections. Laser-Induced Breakdown Spectroscopy (LIBS) is a valuable analytical tool for the study of historical glasses (Müller & Stege 2003), which allow the identification of major, minor and trace glass elements. The LIBS technique has been applied for the characterization of chromophores, chemical species responsible of glass colour; for the analysis of corrosion crusts formed on model glasses artificially weathered, and for the quantitative determination of the lead oxide content (Carmona et al. 2005, Carmona et al. 2007).

In the present work a total of thirteen Roman glass samples, including seven entire glass beads, coming from the town of Augusta Emerita (Spain) have been studied. These Roman glasses are dated from the first to the sixth century AD.

The main goal of this work was to explore the feasibility and possibilities of LIBS, in combination with conventional techniques, in the full study of those glasses from Augusta Emerita. In pursuit of this goal, LIBS was especially targeted at characterizing those particular features of historical glasses which result more inaccessible to conventional techniques for non-destructible samples, such as surface degradation pathologies, chromophores, and opacifying elements. The results obtained could be thus useful for future studies of historical glasses, especially for those conserved under burial conditions.

2 EXPERIMENTAL

2.1 *Description of samples*

All the glass samples studied come from the grounds of the National Museum of Roman Art (MNAR, Mérida, Spain). They were unearthed from seven different archaeological sites located within or in the proximity of the ancient Roman town of Augusta Emerita (SW Spain). The set of glasses is dated from the first to the sixth century AD and it was formed by seven entire glass beads (M-4, M-5, M-6, M-9, M-11, M-12, and M-13), one fragment of a mosaic glass (M-3) and five glass fragments. Three beads (M-4, M-5, M-6) and the mosaic glass were decorated.

2.2 *Analytical techniques*

Apart from LIBS, the characterization techniques used to study the set of glass samples selected were X-ray fluorescence spectrometry (XRF), scanning electron microscopy coupled with energy dispersive X-ray spectrometry (SEM-EDS), and visible spectrophotometry (VIS).

The LIBS system consists of a Nd:YAG laser (Quantel Brilliant B, pulse width 5 ns, repetition rate 10 Hz) operating at the fourth harmonic (266 nm). The laser beam was directed to the surface of the samples by the use of mirrors at an incidence angle of 45°. Focusing with a f = 10 cm lens allowed the achievement of fluences up to 6.6 J cm^{-2}. The shot to shot laser energy (measured with a Gentec ED-200 joulemeter) fluctuation was less than 10%. LIBS spectra were recorded at 70 nm intervals in the 275–600 nm spectral range with a 0.30 m spectrograph (TMc300 Bentham, 1200 grooves/mm, 500 nm blaze) coupled to a time gated ICCD camera (2151 Andor Technologies). Spectra were recorded at a 0.025 nm resolution at the nominal wavelength of 266 nm with a gate delay and width of 0 and 1 μs, respectively.

Chemical analyses by XRF were carried out by a PANalytical Axios wavelength dispersed X-ray spectrometer equipped with a tube of rhodium of 4 kW and 60 kV. Analytical determinations were undertaken through the standard-less analytical software IQ + (PANalytical) from synthetic oxides and natural minerals. XRF analyses were accomplished on powder samples prepared by grinding body glass fragments in an agate mortar. After that, pressed boric acid pellets were made, using a mixture of n-butylmethacrylate and acetone (10:90 wt%) as binding medium. SEM observations were carried out through a S-3400-N Hitachi electron microscope (CCHS), using acceleration voltages of 15 kV and both secondary (SE) and backscattered (BSE) electron modes. The samples were observed on their surfaces and on polished cross-sections and were coated with a carbon thin-film as a conductive medium, using a Sputter Coater Polaron SC7620. EDS micro-analyses were accomplished by a Bruker AXS XFlash Quantax 4010 spectrometer with energy resolution of 133 eV attached to the electron microscope. Finally, VIS spectrophotometry was carried out with an Ocean Optics HR 4000 CG equipment. Spectra were recorded at the 250–1100 nm range on glass samples of approximately 1 mm in thickness obtained by polishing both sides of the samples to optical quality.

3 RESULTS AND DISCUSSION

3.1 *Degradation pathologies*

Except the glass bead M-6, which was supposedly restored, the rest of the samples presented degradation pathologies associated to burial conditions. The most common degradation pathologies identified in the glass samples were dealkalinization layers and dark deposits.

Dealkalinization layers were originated from chemical attack of the ground water to the glass surface. Stratigraphic analyses carried out by using LIBS showed the progressive dealkalinization of glasses, from the most external surface to the unaltered bulk glass. The first ten pulses show the increase of the sodium and calcium intensity signals which are related with the dealkalinization layer, while the analysis from the tenth to the twentieth pulses were undertaken on the bulk glass, in which the signals' intensity were constant (Fig. 1a). The stratigraphic analysis of Figure 1b shows that intensity of the spectrum assigned to the bulk glass is three times higher than that of the spectrum attributed to the dealkalinization layer. This result could be connected with the relative density of the two zones analyzed. The bulk glass is characterized by a more compact structural network than that of the dealkalinization layer.

Dark deposits were detected in samples M-2, M-8, M-10, and M-11. In sample M-11, dark deposits appeared either on the glass surface (Fig. 2a, zone 1) or inside in the dealkalinization layer (Fig. 2a, zone 2). LIBS stratigraphic analyses show that during the first eight pulses on zone 1 and during the first three pulses on zone 2, high contents of manganese were recorded. In addition, the content of manganese strongly and abruptly decays up to 88%.

3.2 *Chromophores and opacifying elements*

The best method for detecting chromophores is VIS spectrophotometry, while opacifying elements can be determined by elemental analytical methods. They are techniques which require sample preparation; therefore it cannot be applied for non-destructible glass samples.

VIS spectra were recorded from samples M-1, M-2, M-7, M-8, and M-10 and the principal chromophores were Fe^{2+}/Fe^{3+}, Mn^{3+} and Cu^{2+}-ions (Table 1). These chromophores were confirmed by LIBS. The blue glass fragment M-7 exhibited an intense VIS band due to Fe^{2+}-ions which probably overlapped the contribution of Cu^{2+}-ions detected by LIBS. The chromophores of the glass beads and the mosaic glass were characterized by LIBS. The chromophores detected in sample M-4 were copper and cobalt ions, which are responsible of the dark blue colour displayed by the glass. The LIBS spectra derived from glass beads M-3, M-5,

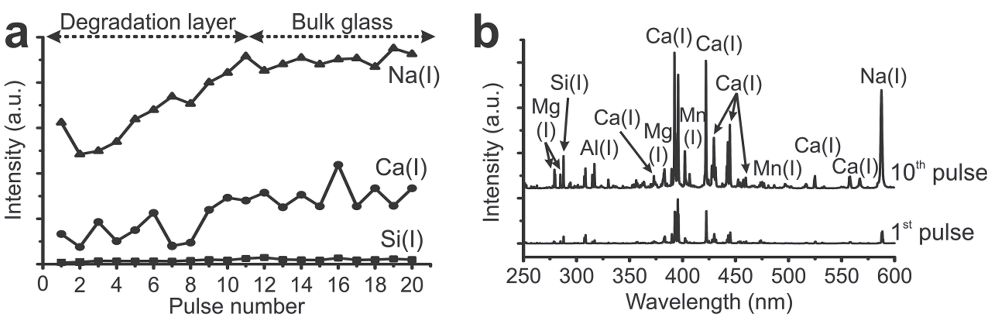

Figure 1. a) LIBS stratigraphic analyses of sodium, calcium and silicon from dealkalinization layer of sample M-7. b) LIBS spectra from external (1st pulse) and internal zones (10th pulse) of sample M-8.

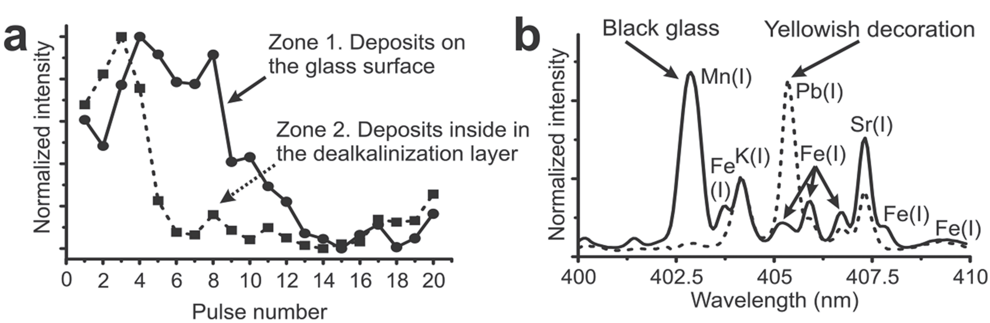

Figure 2. a) LIBS stratigraphic analyses of manganese at 402.36 nm in sample M-11. b) LIBS spectra from the black base glass and the yellowish decoration of sample M-12.

Table 1. Identification of chromophores and opacifying elements.

Sample	VIS	LIBS
Glass bulk assignment		
M-1	Cu^{2+}	Cu
M-2	Fe^{2+}, Fe^{3+}, Mn^{3+}	Fe, Mn
M-3	–	Fe
M-4	–	Cu, Co
M-5	–	Fe
M-6	–	Fe
M-7	Fe^{2+}, Fe^{3+}	Fe, Cu
M-8	Fe^{2+}, Fe^{3+}	Fe
M-9	–	Fe
M-10	Fe^{2+}	Fe, Mn
M-11	–	Fe
M-12	–	Mn
M-13	–	Cu

Sample	VIS	LIBS
Decoration assignment		
M-3 white	–	Sb
M-3 dark	–	Mn
M-4	–	Sb
M-5	–	Sb
M-12	–	Sb, Pb

– Not determined.

M-6, M-9, and M-11 showed peaks attributed to iron ions. In addition, the LIBS spectrum of the black glass bead M-12 determined manganese as the main chromophore (Fig. 2b), while that corresponding to the blue glass bead M-13 displayed the peaks of copper (Table 1).

Four samples presented decoration on their surfaces. Antimony was detected in all of them either by LIBS or by EDS. On the one hand, antimony may crystallize as white calcium antimonite ($CaSb_2O_6$, $Ca_2Sb_2O_7$) and, on the other hand, it may crystallize as yellow lead antimonite ($Pb_2Sb_2O_7$). In samples M-3, M-4, and M-5, the colour of decoration is white, which suggests that antimony is present in some form of calcium antimonite. On the contrary, the yellowish decoration of the glass bead M-12 could be attributed to the presence of lead antimonite since either antimony and lead were detected by both EDS and LIBS (Table 1).

4 CONCLUSIONS

LIBS has been used to explore, in combination with other conventional techniques, its feasibility and possibilities in the integrated study of thirteen Roman glass samples, including seven glass beads, from the ancient town of Augusta Emerita (SW Spain).

LIBS has proved to be able to adequately characterize degradation pathologies. Stratigraphic analyses have enabled the identification of progressive dealkalinization layers from the external surface to the bulk glass, as well as the determination of manganese as the main component of dark deposits. LIBS is also an analytical tool sensitive enough to determine chromophores in the glass. All the chromophores identified by VIS spectrophotometry (Cu^{2+}, Mn^{3+}, and Fe^{2+}/Fe^{3+}) were confirmed by LIBS. In addition, the corresponding chromophores of non-destructible samples were only determined by LIBS. The opacifying elements were identified in surface decorations. It is suggested that white decorations were due to small crystals of calcium antimonite and the yellow decoration was probably due to small crystals of lead antimonite.

An overall evaluation of the results obtained point out that LIBS, in combination with other conventional techniques, may provide valuable information on historical glasses regarding degradation pathologies, chromophores and opacifying elements, especially when it deals with studying non-destructible samples.

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Evaluation of the reinforcing action of consolidating treatments applied on cement mortars using the micro-sandblasting technique

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ABSTRACT: This work is a feasibility study on the application of the micro-sandblasting technique for evaluating the strengthening action of consolidating treatments applied on natural and artificial stones. The micro-sandblasting system is composed by a micro-sandblasting device and a micro-photogrammetry apparatus. The former creates a shallow crater on the surface operating at constant conditions (pressure of the jet, distance nozzle-surface), while the latter allows quantifying the volume of the crater through a 3D digital reconstruction. The micro-sandblasting method was applied to evaluate the strengthening effect of nano-compounds applied on cement mortars. The consistency of this method compared with three other tests (namely paper abrasimeter test, peeling test, and DRMS test) was considered together with the advantages and disadvantages in order to asses the feasibility of this method in the field of conservation of Cultural Heritage.

1 INTRODUCTION

In the field of the research applied to the conservation of historical and monumental buildings made of natural and/or artificial stones, one of the most difficult tasks is the on site assessment of the state of conservation of stone materials and the evaluation of the performances of conservation treatments. Concerning the use of consolidating or strengthening products, standard methods (Uniaxial Compressive Strength, microseismic, windsor probe, pull-out, tests) are often unfitted for the field of Cultural Heritage (invasivity and/or destructivity). In the last years great attention has been dedicated to find out innovative devices for this application. The Drilling Resistance Measurement System (DRMS) is an example of the results of these researches (Fratini et al. 2006). As other devices, the DRMS system exhibits instrumental (range of the min-max value determined by the load cell) and methodological (wear of the drill bit) restrictions. In order to overcome these restrictions, a new methodology based on the controlled micro-sandblasting technique has been tested. A recent study performed in our laboratory displayed the repeatability of the micro-sandblasting data and the possibility to discriminate among natural stone materials and mortars having different physical characteristics and mechanical behaviour. In order to study the feasibility of such method for the evaluation of the performance of consolidating treatments, we have carried out laboratory tests on cement mortar specimens treated with nano-compounds (lime and silica) as reinforcing agents. These products determine a very little increase of the "superficial mechanical" properties. Thus they are ideal to test the sensibility of the new method. The micro sandblasting action creates a shallow crater in the material as a function of the pressure, type of abrasive sand and time of blasting. The control of this action has been made measuring the amount of the removed material with an analytical balance (only in laboratory test) and the volume of the crater using the micro-photogrammetric system. The sandblasting methodology has been compared with other methods utilized in our laboratory to evaluate the performances of consolidating treatments, namely paper abrasimeter test, peeling test and DRMS test.

2 MATERIALS AND METHODS

The hydraulic mortar has been realized mixing 1 part of Portland cement 32.5 (ENV 197-1), 2 parts of hydraulic lime (NHL 5), 9 parts of sand and 1.5 parts of water. The various components have been mixed until complete homogenization. Then the paste has been cured for 2 months in conditions of high humidity (80%). A total of 10 specimens of $5 \times 5 \times 3$ cm for each treatment and for the references were utilized. The products applied by brush were: nano-silica, traded as Syton 30x (Kremer) in aqueous solution (0.300 g/l of solid); nano-lime, traded as Calosil IP 25 (Freiberg), in isopropanol (0.025 g/l of solid). On each mortar specimen the peeling test was performed, followed by the micro-sandblasting technique and finally by the DRMS method. The paper abrasimeter test was utilized on another set of mortar specimens.

3 RESULTS AND DISCUSSION

3.1 *The micro-sandblasting test*

The micro-sandblasting system is composed by a Dental Farm apparatus (model A1067 Pressure Blaster) for the micro-sandblasting operation and a micro-photogrammetric device (Menci Software) for the determination of the crater volume (Fig. 1). The test was carried out inside a blast cabinet equipped with a vacuum system. A flat metal (hard steel) interface is put between the nozzle (0.8 mm diameter) and the sample before starting the test. Once the pressure of the jet flow is stabilized at the value of 4 bar, this interface is suddenly removed and switched on the stopwatch. When the established time is reached, the hard steel is put again between the nozzle and the sample. Afterwards the device is switched off. An abrasive powder made of Al_2O_3 with spherical geometry (80 μm diameter) and exposition time of 15 s was selected after preliminary tests. The sample is weighted before and after the test with a Gibertini balance (±0.001 g). For each sample a total of three tests were utilized (namely three dips for each sample). The micro-photogrammetric records to evaluate the volume of the craters were realized at the end of the three tests. The volume was computed with the ZMAP software of the micro-photogrammetric system utilizing the dedicated approximation algorithms. In Table 1 the results of the micro-sandblasting

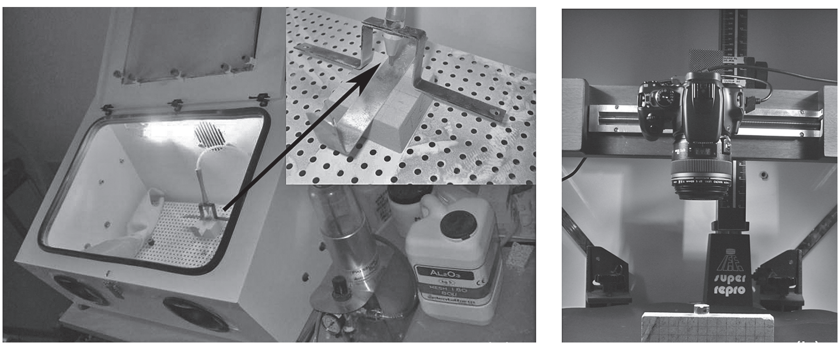

Figure 1. Micro-sandblasting system: micro-sandblaster with the particular of the nozzle (left) and micro-photogrammetry (right).

Table 1. Amount of material removed by the micro-sandblasting.

Treatment	Amount in weight (g)	Amount in volume (cm^3)
Syton 30x	0.172 ± 0.021	0.064 ± 0.005
Calosil IP 25	0.286 ± 0.042	0.092 ± 0.008
Reference	0.286 ± 0.047	0.107 ± 0.008

test expressed as amount in weight and in volume of the material removed are reported. The data show that the best strengthening effect is produced with the Syton 30x treatment while the Calosil IP 25 behaves very similar to the untreated reference sample. Further information can be achieved through the visual inspection of the crater on the micro-photos (Fig. 2). In fact smaller diameter crater is observed on sample treated with Syton 30x compared to Calosil IP 25 and not treated. This is in agreement with a better strengthening action of Syton 30x.

3.2 *Peeling test*

The peeling test was realized using a bi-adhesive tape (TESA, bind capacity 1 kg/10 cm). The strips (6 cm length) were weighted on a Gibertini balance (±0.001 g) and the weight difference (after and before the peeling action) corresponds to the amount of superficial material removed. For each specimen, on the same peeling area, three tests using new strips are performed in order to evaluate the cohesion of the surface in the bulk. In Figure 3a the results of the peeling test expressed as the amount of the material removed for each single test are reported. In the case of Calosil IP 25 the high and not homogeneous amount of material removed during the first test is due to the removal of the superficial deposition of the treatment not adherent to the surface of the sample (Fig. 3a). Only in the third test the values of the amount of material removed are lower than the reference. This behaviour can be explained only with a low strengthening power of the Calosil IP 25 treatment, in fact also the reference material displays a decreasing trend of the amount of material removed starting from the first (superficial) up to the third (internal) test due to a higher cohesion of the material in the bulk. These results also confirm that the best strengthening performance is displayed by the Syton 30x.

3.3 *Paper abrasimeter test*

The tests were carried out with a home made device (load applied 1 Kg; 120 mesh abrasive paper; constant speed). The specimen was weighted before and after each single meter of abrasion with a Gibertini balance (±0.001 g) for a total of three meters of abrasive paper.

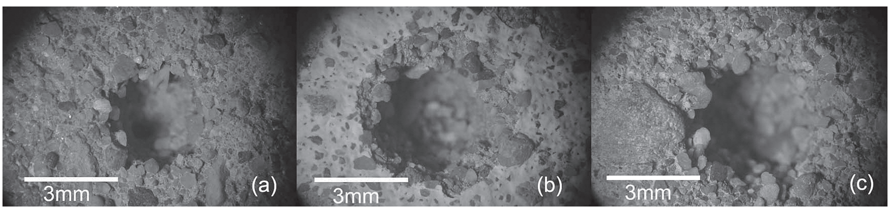

Figure 2. Micro-photo (1.0x) of the dips made with the micro-sandblasting: sample treated with Syton 30x (a), Calosil IP 25 (b) and reference (c).

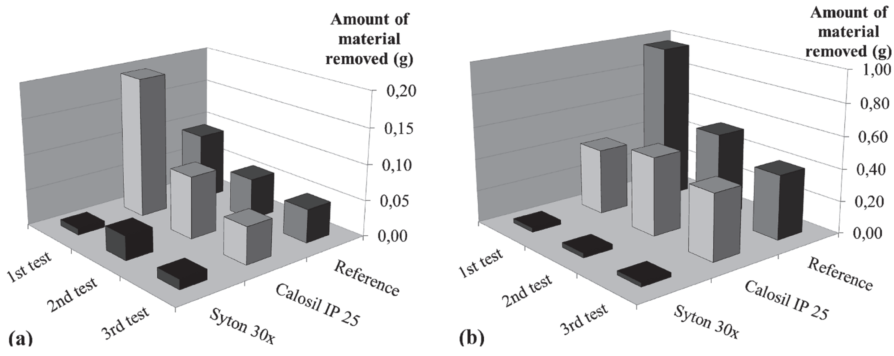

Figure 3. Results of peeling (a) and paper abrasimeter tests (b).

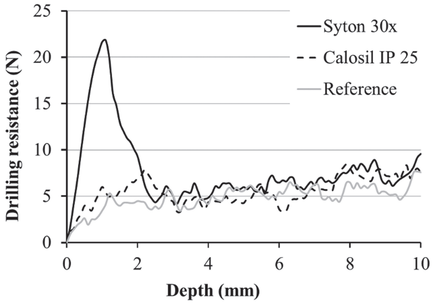

Figure 4. Drilling resistance average curves.

The data of the values of weight removed for single abrasion test (each meter) are displayed in Figure 3b. In the case of the reference, the amount of abraded material decreases according to the presence of a less cohesive superficial layer. In the case of the Calosil IP 25 treatment, an initial weight loss lower than that registered for the second test can be observed. This behaviour is in agreement with the presence of a superficial layer not well adherent to the underline sample. In the case of the Syton 30x treatment with the amount of weight lost for each meter of abrasion is about the same and the value of weight loss is much low (about 0.030 g).

3.4 *DRMS test*

The drilling resistance tests were realized with the DRMS by Sint Technology. The tests were performed with the following operative conditions: rotational speed 300 rpm, penetration rate 40 mm/min, depth of the hole 10 mm, drill bit with polycrystalline diamond tip of 5 mm diameter. The results of the drilling tests (represented as cohesion profiles) display that reference and Calosil IP 25 have similar behaviour (Fig. 4). The samples treated with Syton 30x show a peak in the first part of the curve with higher value of the drilling resistance. This harder layer has a thickness of about 2 mm.

4 CONCLUSIONS

This work shows the feasibility to use the micro-sandblasting tests to evaluate the performances of the strengthening treatment. In fact the micro-sandblasting tests are completely in agreement with other methodologies (paper abrasimeter, peeling test, DRMS test) utilized to evaluate the strengthening power of consolidant products in the field of Cultural Heritage. Moreover the micro-sandblasting tests display the following advantages with respect to the paper abrasimeter and peeling test: the test can be realized in laboratory and on site (paper abrasimeter is only an in lab test); the results can be expressed in volume and not only in weight. In a treated or in a weathered material the bulk density can be quite low with respect to a sound material and it would be difficult to evaluate the cohesion or the strengthening action only by weight difference; the results are mainly dependent on the operative conditions while in the peeling test the removal of the strip is strongly dependent on the operator. With respect to the DRMS, the following advantages can be observed: abrasive power is constant; possibility to measure very soft or very hard stones (modifying the operative conditions such as: exposition time, pressure level of the abrasive jet and the type of abrasive powder). The disadvantages are: lacking of the cohesion profile; possibility of large data scattering in presence of stone materials with high degree of heterogeneity (as granite) due to the very thin diameter of the nozzle.

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Cachão da Rapa prehistoric rock art paintings revisited: Digital image analysis approach for the assessment of Santos Júnior's tracings

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ABSTRACT: The tracings of Cachão da Rapa rock art site elaborated by Santos Júnior in the early 1930s were assessed by means of digital image analysis techniques. This new approach allowed the discovery of new figures present in the panel but not visible by the naked eye.

1 INTRODUCTION

Cachão da Rapa (Trás-Os-Montes, Portugal) was the first rock art site described in the Iberian Peninsula (Carvalho da Costa 1706), and one of the pioneers in Europe. It is considered to be among the most original paintings of the Iberian schematic rock art. Since the publication of its first tracings by Jerónimo Contador de Argote (1734) (Fig. 1a), the site was referred although not studied until 1933, when the Portuguese scholar Santos Júnior newly published a hand-made drawing of the pictorial remains (Fig. 1b). This monograph constitutes nowadays the most complete study of the site.

Both Contador de Argote and Santos Júnior described a dichromatic rock art panel, designed in red and dark blue colours and composed of several geometric and abstract motifs painted on a fine grained granite panel over four meters high (Fig. 1c). The use of blue colour and the type of some of the painted motifs are unique in the Iberian rock art tradition, increasing the importance of this rupestrian manifestation. Nevertheless, although the importance of these paintings is well recognized by both the Iberian and international archaeological communities, no further research nor documentation was undertaken after Santos Júnior's rediscovery (Santos Júnior 1933).

The recording of rock art motifs by means of traditional techniques as hand-made drawings or traditional tracings has been found problematic because these methods usually present geometrical incoherences and are often highly subjective, offering thus a poor tool for both research and conservation issues (Rogerio-Candelera 2009). Hence, in order to elaborate an updated tracing and also to assess the available tracings of the Cachão da Rapa panel, a new approach was performed. This new strategy implied the use of digital image analysis techniques, as they have demonstrated to be strong enough for elaborating accurate tracing of rock art motifs (even if they are highly affected by biodeterioration processes) without threatening the conservation of the panels due to their nule invasivity (Rogerio-Candelera & Élez Villar 2010, Rogerio-Candelera et al. 2011).

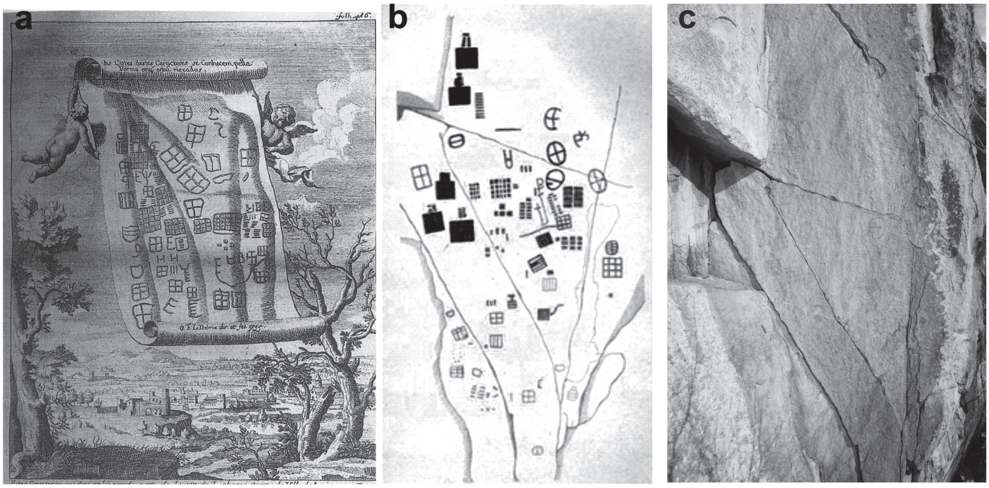

Figure 1. (a) Cachão da Rapa panel, as published by Jerónimo Contador de Argote in 1734. (b) Handmade drawing of the panel, made by Santos Júnior in 1933. (c) Present day state of Cachão da Rapa rock paintings.

2 MATERIALS AND METHODS

2.1 *Cachão da Rapa rock paintings*

Cachão da Rapa is located in Tras-Os-Montes province, northern Portugal, in the right bank of the Douro river. The site is composed of one rock panel painted on a vertical wall of fine grained granite of about four meters height. The available tracings describe 63 painted motifs of Schematic style, some of them delineated in red, others in a dark colour described as "blue" and another ones bichromatic (red and "blue"). These paintings have not counterpart among the Iberian painted rock art. Only Galician rock carvings have been signaled as typologically related (López Cuevillas 1951).

2.2 *Digital image analysis*

The panel was photographically recorded under sunlight conditions using a Canon EOS 5D Mark II digital camera. The RGB colour mode images produced were then uncorrelated by means of Principal Component Analysis (PCA) following the protocols developed in Rogerio-Candelera et al. (2011). Three and six bands colour cubes were elaborated using the bands corresponding to Principal Components (PC) in order to distinguish the different elements included in the image (Rogerio-Candelera et al. 2009). Once the motifs were recorded, 2D mosaics were built, recalculating the position of the different elements by means of the application of the nearest neighbour algorithm. All these operations were performed using the software package HyperCube (Army Geospatial Centre, USA).

3 RESULTS AND DISCUSSION

Preliminary data obtained by digital image analysis by emphasizing digital decorrelation of pixel values allowed to reach good results for the delimitation of the red colours. The most suitable band was that corresponding to the 3rd PC of the different images. For the register of the dark ("blue") painted motifs, it was necessary to compose false colour images from three or six bands image cubes. In some cases, the spectral behaviour of both the unpainted wall, and the dark painted motifs was essentially the same, thus contributing to the masking of these elements and difficulting its recording.

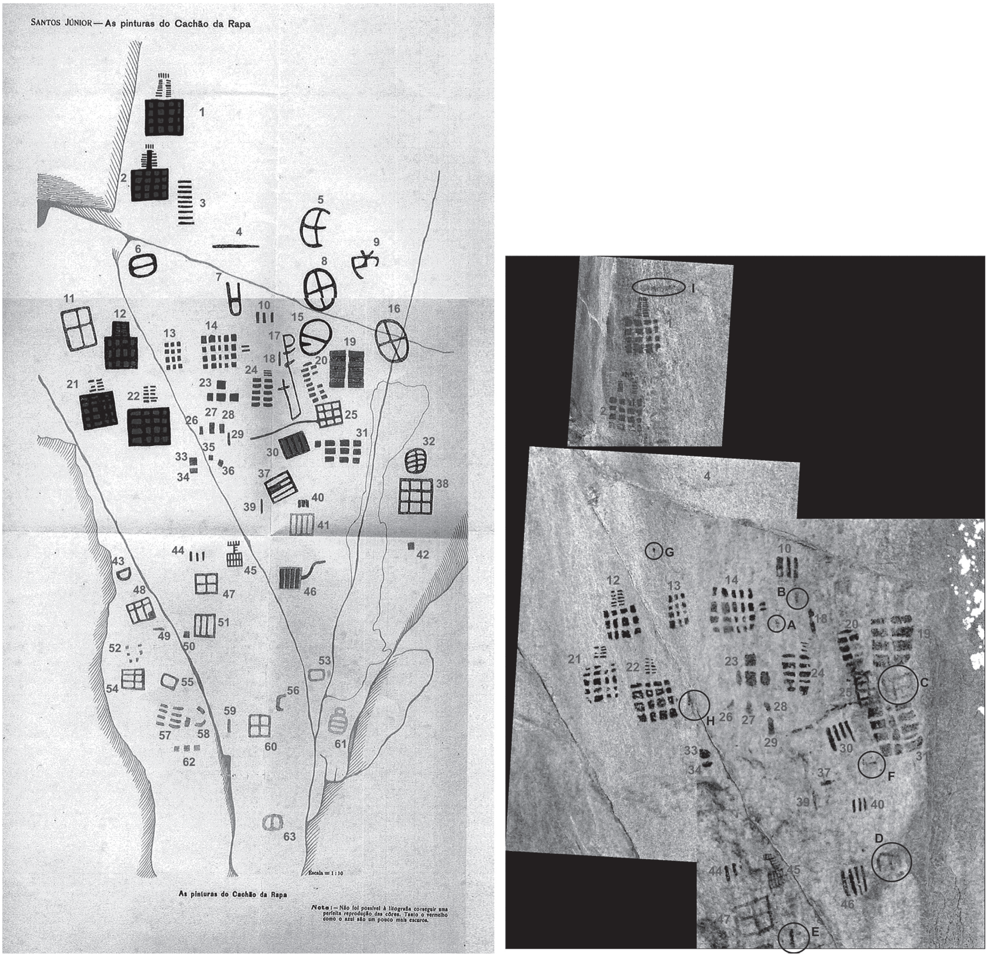

Figure 2. (a) Painted motifs recognised by Santos Junior (our numbering). (b) Partial mosaic of the panel elaborated with the bands corresponding to the 3rd PC showing some of the motifs delineated in red.

The comparison of the original drawing performed by Santos Junior in the 1930s and the mosaics elaborated by means of digital image analysis techniques enabled the verification that the geometrical relationships of the traditional tracing were essentially correct, although some motifs were distorted or idealised in the drawing. Nevertheless, not all the originally painted motifs were detected by Santos Junior. Santos detected 63 pictorial motifs (Fig. 2a), most of them designed in red or bichromatic (red/blue). Our approach allowed detecting the presence of new complex motifs (Fig. 2b, motifs C and D), or simple dots or linear elements not represented in Santos Junior's tracing (Fig. 2b, motifs A, B, E–I). The finding of an spectral window for every kind of painting is a crucial task that only was achieved for the reddish colours. The information obtained is, thus, biased to the detection of red-painted motifs. Nevertheless, although without the quality necessary to automatically perform vertorial tracings, some black or blue painted motifs have been detected (Fig. 2b, motif I). As we can see, one of the most outstanding hits of the use of digital image analysis techniques lies on the possibility of obtaining information not present in the ancient tracings currently used by the archaeological community. Another important consequence of the detection of all the elements originally included in the panel is the possibility of using these new tracings as a tool for establishing conservation strategies.

4 CONCLUSIONS

This work presents a new approach to the recording of the rock paintings, based on the use of digital image analysis techniques, to assess the accuracy of the tracings currently utilised by the researchers (basically, Santos Júnior's work), and also exemplifies the possibilities offered by these techniques in order to perform low cost, low time-consuming and non invasive tracings, avoiding the subjectivity inherent to traditional recording methods.

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Benefits of applying spectrometric techniques and chemometric methods to identify interaction between historic painting materials

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ABSTRACT: One of the main goals in Heritage Science is to characterize painting components and their interactions under diverse conditions to promote their conservation. This work is based on an overview of our analytical studies which deal with problems that concern the field of art paintings. The approaches were based on the combined use of different spectrometric techniques with multivariate statistical tools, particularly, principal component analysis (PCA). Chemometric evaluation of spectral data is well accepted as a powerful tool for different purposes, including sample identification and recognition in the field of Cultural Heritage.

1 INTRODUCTION

The study of artworks requires the application of analytical techniques and statistical methods to extract the maximum information from samples with high complexity and small size. Artistic paintings are often very complex matrix based on heterogeneous micro layered materials made by mixtures of inorganic and organic compounds applied on diverse supports, i.e. stone, canvas, wood and paper. The components may vary depending on the school of painting, historical epochs, and the painting technique employed by the artists. Therefore, their identification has always been one of the most important goals of analytical chemistry in conservation studies, since it provides crucial information not only for art historians, but for restoration and conservation purposes.

In this regard, chemometric techniques such as principal component analysis (PCA), classification methods, and cluster analysis, allow the discrimination of pigments and binders in mixtures (Bacci et al. 2000, Navas et al. 2010), and help with identifying sources of materials, ageing or alteration processes due to environmental conditions from analytical data (Navas et al. 2008, 2010, Manzano et al. 2009, 2010, Romero-Pastor et al. 2011, 2012a, b). In particular, spectrometric techniques such as Fourier Transformed Infrared Radiation (FTIR), Raman Microscopy (RM) and Mass Spectrometry (MS) offer a powerful tool in order to solve problems related to the characterization of Cultural Heritage items. They have been used as a source of characteristic and crucial molecular information. Also, a main advantage of abovementioned spectrometric techniques is that spectral data are suitable inputs for multivariate analysis techniques. Among the different chemometric tools, PCA is a powerful data-mining technique that reduces data dimensionality obtaining more interpretable representation of the system under investigation (Jackson 1991). In addition, valuable information about the main variables involved in the process studied is also obtained. Some contributions in this area have been proposed by our interdisciplinary research team, formed by chemists, geologists, physicists, statisticians, biologists and restorers.

This work includes a summary of the researches developed by the authors over the years 2007 to 2012. In this regard, the application of PCA on spectrometric data, e.g. from Transmittance (T)-FTIR, Diffuse Reflectance FTIR Spectroscopy (DRIFTS), Attenuated Total Reflection (ATR)-FTIR. RM and MS in order to study artificial UV-ageing processes of tempera paintings and interactions among painting materials (proteinaceous binders and mineral pigments). For all cases, the principal components were obtained using both the covariance data matrixes (scaling by mean-centered data) and the correlation data matrixes (scaling to unit variance). The results were clearly better when PCA was performed on the correlation data matrixes, so the results shown and discussed in this review correspond to autoscaled data. At each sample or check time studied, the five/ten replica samples were characterized by five/ten spectra, respectively, in order to gain a representative statistical analysis.

2 FTIR SPECTROSCOPY AND PCA APPROACHES

2.1 *T-FTIR*

An UV-accelerated ageing process on replica samples of azurite glue tempera, pure azurite and pure rabbit glue was designed, all elaborated according to Medieval recipes (Manzano et al. 2010). The FTIR spectra were registered from 400 cm^{-1} to 3999 cm^{-1} and formed by 3734 data points. Several IR regions were selected to perform the PCA in accordance with the sample composition. The IR region between 1500 cm^{-1} and 1750 cm^{-1}, representative of adsorption bands due to carbonyl stretching, and the IR region between 2900 cm^{-1} and 3600 cm^{-1}, that included the amide bands A (around 3300 cm^{-1}) and B (around 3100 cm^{-1}) were tested in the PCA of the pure glue samples. The study of pure glue revealed degradation before 200h of UV exposition. The PCA results showed that chemical changes were related with amide A and B bands of glue. In particular, the presence of azurite seemed to improve the photostabilization of the glue against UV damage, irrespective of their concentrations in the mixture.

2.2 *DRIFTS*

This approach explored the application of DRIFTS to the examination of historic blue pigments and blue tempera paintings commonly found on works of art (Navas et al. 2008). The discussion was mainly focused on the practical benefits of using this technique joined to PCA. Thanks to the study of several replica samples that contain either pure blue pigments (azurite, lapis lazuli and smalt), or pure binder (rabbit glue) and mixtures of each of the pigments with the binder (tempera samples), different aspects of these benefits were highlighted. Results showed an excellent ability of PCA on DRIFT spectra for discriminating replica samples according to differing composition. Several IR regions were tested with this aim similar to the previous work; the fingerprint IR region exhibited the best ability for successfully clustering the samples. The presence of the binder was also discriminated. Only using this approach it was possible to completely separate all the studied replica samples in opposite to the same study on T-FTIR data. This demonstrated the potential benefits of this approach in discriminating historical pigments and binders for conservation and restoration purposes in the field of Cultural Heritage.

2.3 *ATR-FTIR*

To investigate the physico-chemical behavior of one or more painting components (in the same sample) using different spectroscopic techniques, commonly internal standards were used, since the applied analytical and statistical methods can be susceptible to both systematic and random errors. These internal standards are chemically and mineralogically inert, and are added to the sample without causing spectral interferences within the matrix of interest. Such materials could be a natural component of the sample under study or purposely added.

This study was framed in one of our innovative lines of research based on the assessment of interferences among painting materials exposed to different alteration agents, and analyzed with diverse analytical techniques and PCA (Romero-Pastor et al. 2012a). In particular, this study focused on the validation of two analytical techniques to optimize the characterization of painting materials. Thus, to evaluate data quality by measuring substances with well-known and accurate spectral data, we analyzed samples subjected to similar thermal processes by ATR-FTIR and RM. To this end we studied the thermal alteration of traditional proteinaceous media used in tempera such as albumin and collagen together with quartz (SiO_2) and hydroxyapatite (HAp) respectively, which had been used commonly as historical pigments and extenders. These mineral phases, which are chemically inert at these temperatures, behaved as internal standards during the thermal processes taking place. Two sets of samples were studied. Then the ideal ratio was used to prepare the next samples containing collagen and HAp. It was found that 70% was the ideal standard proportion to be added since both sets of samples showed similar behavior under the thermal ageing test.

3 RAMAN SPECTROSCOPY AND PCA APPROACHES

3.1 *Raw Raman spectra*

The identification of proteinaceous binding media using Raman Spectroscopy was based on the detection of characteristic bands in the spectra. The main bands assigned to the presence of proteinaceous materials were the amide bands I and III located at ca. 1650 cm^{-1} and 1200 cm^{-1} respectively. The amide band II, between 2800 cm^{-1} and 3100 cm^{-1}, has been considered as analytically less important. Nevertheless, this region has recently proved its importance in the identification of different kind of proteins (Nevin et al. 2008). This study sought to identify fine changes in this characteristic protein band of natural egg yolk, which could occur as a result of the interaction with three blue pigments, namely azurite, smalt and lapis lazuli. Painting samples were prepared according to Old Master recipes. PCA was applied for this purpose, since small changes were expected. PCA was performed on Raman spectroscopic data from 2800 cm^{-1} to 3080 cm^{-1} for all these samples (Romero-Pastor et al. 2011). It could be assumed that the contribution of the whole Raman region studied suffered a general increase when the smalt or azurite was present in the composition, with greater effect for azurite model samples. Since the scores corresponding to the lapis lazuli model samples showed similar scores to those from the pure egg model samples, we concluded that this pigment did not interact with the protein within this spectral region. On the contrary, smalt and particularly azurite could interact with this characteristic protein spectral region since significant spectral variations were detected by PCA.

3.2 *Derivative Raman spectra*

Other innovative application of PCA on Raman data in the study of artworks has been reported by our research team (Navas et al. 2010). This approach explored a valuable tool based on the derivative Raman spectra for the investigation of tempera historical paint model samples. Thanks to the study of various paint model samples that contained pure blue pigments (azurite, lapis lazuli and smalt), pure red pigments (cinnabar, minium and raw Sienna), pure white pigments (lead white, calcite and gypsum), and pure egg yolk as binder, as well as mixtures of each of the pigments with the binder, different aspects of the benefits of this novel analytical approach were highlighted. Results showed an excellent ability of PCA on derivative Raman spectra for discriminating model samples according to differing composition, as well as to track alteration of sensitive pigments to laser interaction. This demonstrated the potential benefits of this approach in identifying historical pigments and binders for conservation and restoration purposes in the field of Cultural Heritage. PCA performed on derivative Raman spectral data marked advantages when compared the results obtained with the same approach but using direct Raman spectral data. This was the first attempt to use this approach in Cultural Heritage Science, and the results were very promising to identify pigments and temperas used in historical paintings.

4 MASS SPECTROMETRY AND PCA APPROACHES

Other study presented an ageing process of proteinaceous binder materials, i.e. rabbit glue, used in painting under UV light by MALDI-TOF-MS and PCA (Romero-Pastor et al. 2012b). This approach suggested some possible answers regarding the interaction and the role of the mineral pigments cinnabar and azurite in the UV ageing process of collagen, when present in glue tempera paintings. Results also showed that chemical changes occurred in different ways when these pigments were present. In particular, the novel application of PCA on mass data allowed discrimination of significant differences in mass fragmentation patterns of glue in presence of every pigment. This fact indicated diverse interactions between pigment and collagen that could influence the ageing process. In addition, the formation of a protein copper complex could justify the photostabilization of the glue tempera as suggested Manzano and co-workers (2010) when azurite was present. The high identification ability of MALDI-TOF-MS as well as the usefulness the PCA to detect slight different were linked in this study. Consequently, this analytical methodology represented a powerful tool for the investigation and characterization of painting materials.

5 CONCLUSIONS

This research supplied valuable information in the study of artificial UV-ageing processes of proteinaceous tempera paintings. In addition, multivariate analysis of DRIFTS spectra data showed a great ability to discriminate tempera replica samples according to their composition. Moreover, PCA results demonstrated the capability of PCA on ATR-FTIR to detect changes in the painting components comprising our samples while the internal standard remained stable. The PCA results on Raman spectra also demonstrated its suitability to detect interactions associated with the specific pigments and to discriminate samples based on their composition. Therefore, this research demonstrated the potential benefits of these approaches in studying historical pigments and binders for conservation and restoration purposes in the field of Cultural Heritage.

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Study of degree of alteration of enamels using Micro-ATR-FTIR and SEM-EDS

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ABSTRACT: Ancient enamels on gilded copper from a collection of archaeological horse harness pendants were studied in order to test the benefits of the combined use of non-destructive analytical techniques such as Micro-ATR-FTIR and SEM-EDS. The novelty of this approach is threefold: i) it allowed the discrimination of the different harness pendants according to the chemical composition, nanostructure, glass weathering and/or coloring mechanisms, ii) it is a cheap, easily available and non-destructive methodology that enables to iii) draw archaeological conclusions about manufacture and chronology.

1 INTRODUCTION

Studies of the structure and the weathering of glass or enamels require the use of a wide range of advanced analytical techniques in order to explore their chemical composition and alteration mechanisms. However, these techniques are often expensive, not easily available or quite unsuitable for the study of whole archaeological objects due to their destructive impact. These pieces which are often of great artistic value can therefore only be analyzed using non-destructive analytical methodologies. Indeed, the complex composition and nanostructure of ancient glass pieces, their unstable thermodynamical properties and the fact that they have no crystallographic restrictions or stoichiometric ratios means that a detailed knowledge of properties such as color and durability can only be acquired with advanced techniques (Pollard & Henron 1996). Fortunately, there are a number of non-destructive analytical techniques (i.e. Micro-Attenuated Total Reflectance Fourier Transform Infrared Spectroscopy, Micro-ATR-FTIR; Raman Microscopy, RM; Scanning Electron Microscopies-Energy dispersive X-ray Spectroscopy, SEM-EDS; etc.), which can provide detailed information about alteration processes or the different methods used in the manufacture of ancient glass (Colomban 2003, Climent-Font et al. 2008, Feller et al. 2010, De Ferri et al. 2012).

In particular, the degree of polymerization of the glass network and its related structural stability were assessed using IR/Raman spectroscopy and were found to vary depending on the content of Pb-O or the smelting temperature (Colomban 2003, Ricci et al. 2007, Feller et al. 2010). In addition, as regards colorimetric properties of glass, different colors were obtained using different coloring methods, i.e. by transition metal ions (e.g. Fe, Co, Ni, Cr, Mn) or through the incorporation of colloidal particles or microcrystals. The metal ions produce different colors depending on their oxidation state, while the colloidal particles require a specific heat treatment process such as in the case of copper-ruby red glass (Fernández-Navarro 1985).

This work describes a non-destructive approach to the study of the state of conservation of colored glasses. Bronze horse harness pendants with red, purple, blue and white enamel decorations were analyzed by Micro-ATR-FTIR and SEM-EDS with the goal to tell apart the role of specific compounds on the structure of the glass network and its relationship with the degree of degradation of glasses. Furthermore, the ultimate aim is to draw archeological conclusions to help clarifying their manufacture and their origin.

2 MATERIALS AND METHOD

2.1 *Samples*

Seven 14–15th century horse harness pendants decorated with gilded copper (i.e. *Champlevé*) were selected from the archaeological jewelry collection of the *Instituto Valencia de Don Juan* (Madrid, Spain). These pieces are decorated with rich-colored enamels (i.e. red, purple, blue and white) depicting coats of arms, human figures, animals and symbols.

2.2 *Analytical techniques*

A polarized optical microscope (OM) in reflected light (Olympus SZX16) equipped with a digital camera for microphotography (Olympus DP21) was used in order to examine the morphology and color of the enamels. In addition, we performed a detailed chemical and morphological analysis using an FTIR microspectroscopy system, an ATR-FTIR spectrometer Bruker Tensor EQUINOX in conjunction with a FTIR Bruker Hyperion-2000 microscopy attachment equipped with a 20x viewing objective with a pixel resolution of 2.7 µm, equipped with CCD-camera and germanium crystal. IR spectra were collected within the wavenumber range 4000–600 cm^{-1} and measured with 4 cm^{-1} resolution and 32 scans coaddition. The spectrometer was linked to a PC equipped with Bruker OPUS 5.5 software, which collected the IR spectra in ATR mode. Spectra. The pendants were mounted in the sample holder and no additional sample preparation was done. We also carried out an in-depth chemical and morphological analysis using a Hitachi VP-SEM S-3400 N coupled with an EDS microanalysis Bruker Quantax X-Flash SDD. The operating SEM-EDS conditions were from 60 to 70 pA filament current and 125 eV/ch resolution for single analyses. The beam energy used was 125 keV. Single-point elemental analyses were registered and the average for the chemical quantification.

3 RESULTS AND DISCUSSION

3.1 *Red enamels*

The general state of conservation of red enamels varies from one pendant to the next and even within the same pendant, with damage such as pits, cracks and dark opaque areas often adjoining healthy, undamaged surfaces. The analysis of IR region between 1250 and 600 cm^{-1} and EDS-SEM results revealed in some areas of the studied red enamels a changeable content of cuprous oxide and lead oxide. On the basis of the well-known depolymerization effect of the silicate network due to high PbO content (Feller et al. 2010), the higher Pb content found in the enamels on pendants 1, 3 and 6 could possibly increase the sensitivity to alteration processes. These pendants were alkali-lead (K-Pb) glass, while pendants 2 and 4 were mainly soda-lime and alkaline earth (Na-Ca) glass. Consequently, glass weathering could occur and hence, ion exchanges could justify the low alkali and alkali-earth contents in some areas. These facts would suggest low production costs and consequently, poor quality glass, also corroborating the hypothesis about a manufacturing process in which the atmosphere is not controlled, as resulting from the identification of Cu-O by ATR-FTIR (Fernández-Navarro 1985, Brun et al. 1991). In addition, IR spectra showed different glass networks, i.e. Q^0 (isolated tetrahedra at 804 cm^{-1}) and Q^1 species (tetrahedra linked by a common oxygen atom, Si_2O_7 at 943 cm^{-1}) for some areas of pendants 2 and 4. Moreover, spectra of pendant 3 showed the shift of the Si-O stretching mode attributable to Q^2 and Q^0 species and hence, this enamel showed some areas in a good state of conservation while others were altered as a result of depolymerization processes (Colomban 2003).

3.2 *Purple enamels*

A visual examination using OM mainly showed loss of material, cracks and pits in some areas of pendants 1 and 5, which were therefore analyzed in detail in order to identify the alteration mechanisms. On the other hand, a good state of conservation was observed for the pendant 6. The IR spectra revealed a slight shift of Si-O stretching modes associated to Q^1 species for the different areas we studied of pendant 1 and 5. This suggested varying behavior in the different areas studied of the same enamel due to different composition and/or microstructure, which meant that a different degree of surface alteration could occur. In fact, the different degree of alteration of areas of purple enamel from pendants 1 and 5 was mainly associated with depolymerization processes. However, the chemical composition using EDS-SEM did not show significant differences between the samples, except for a high chlorine content for pendant 5. This suggests that these purple enamels had a microstructure and alteration mechanisms that were not influenced by the chemical composition, as we proposed for the red enamels, and consequently, the high chlorine content could be responsible for the opaque aspects as a result of the presence of pits, fissures, cracks and grooves in pendant 5. In addition, the fact that the purple enamel from pendant 6 was in a good state of conservation was attributed to its polymerized structure according to the IR profile.

3.3 *Blue enamels*

The visual examination of surface blue enamels from pendants 2, 3, 4, 6 and 7 showed decay manifested in the presence of dark and opaque enamels as well as loss of material. The ATR-FTIR spectra revealed diverse patterning for the different pendants and even for different areas of the same enamel. In general, a decrease and shift of IR bands around the silicate network region was observed (Fig. 1), suggesting that some areas suffered alteration due to depolymerization processes. In addition, ion exchanges of Ca and Na were also noticed for these pendants. EDS analysis showed a normal proportion of Na and a strikingly low amount of Pb in blue enamel 7, which may be ascribed to different weathering behavior and a possible different origin of this object. As regards coloring agents, the presence of Co as a pigment explained the blue color of the enamels from pendants 2, 4, 6 and 7. However, the absence of cobalt in the corresponding enamel from pendant 3 could suggest another ionic coloring mechanism, eventually due to. Fe(II) or Cu(II) ions. As a matter of fact, Fe(II) ion was the most frequent blue coloring agent in ancient glass-making (Fernández-Navarro 1985, Arletti et al. 2008).

3.4 *White enamels*

The OM study showed many pits and dark impurities located inside the white enamels from pendants 2, 6 and 7, and cracks in pendant 4. In addition, the visual examination of IR spectra showed a significant difference between the analyses performed on each altered and each undamaged surface. In particular, in the case of pendants 6 and 7 IR spectra between 1250 and 600 cm^{-1} showed a shift of the Si-O stretching mode, although this band showed a stable position and a decrease for pendants 2 and 4. The information for pendants 4 and 7 was therefore mainly related to the shift of Si-O stretching to Q^2 species and low Pb-O content, corroborating the good state of conservation for these areas.

On the other hand, the scattered distribution of the content of Si and Pb could suggest that the white enamels had different composition or different durability properties. In particular, the

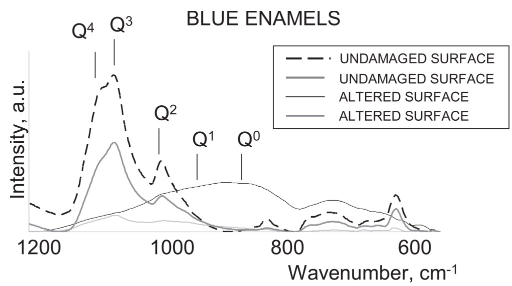

Figure 1. ATR-FTIR spectra of blue enamels.

EDS results showed lead-glass for pendants 2, 4 and 6, but poor-lead enamel for pendant 7. In addition, significantly higher content of tin opacifier was identified in pendant 4 and traces of uranium in pendant 2 and 6. In addition, the fact that uranium was only present in pendants 2 and 6 suggested that these two white enamels may have been manufactured using similar recipes. According to the literature, uranium has been used extensively in oxide form in glass-making since the 18th century owing to its brightness properties (Strahan 2001). In addition, the EDS results from pendant 7 also suggested a different origin thanks to the low proportion of Pb and the fact that contaminants such as sulfates and chlorite were only present in this pendant.

4 CONCLUSIONS

The proposed non-destructive analytical methodology enabled to perform an in-depth study of 7 harness pendants in terms of chemical composition, glass weathering and coloring mechanisms. In particular, the enamels were made of alkali and/or alkaline earth lead-glass with a wide range of chemical compounds in the form of pigments or opacifiers. Two types of coloring mechanisms were identified, colloidal particles, as in the case of copper-ruby, and ionic mechanisms based on Fe(II) and Co(II) (blue pigments), Mn(III) (purple pigment), and on tin oxide as an opacifier (white enamels). In addition, the poor state of conservation of some of the enamels was justified through the identification of depolymerization processes and ion exchanges, well-known harmful effects of glass weathering. Finally, it is worth mentioning that such results provided evidence and information about their possible age and origin of these pendants.

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Non-chemical methods to control pests in museums: An overview

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ABSTRACT: In search for safer alternatives to replace biocides like methyl bromide and hydrogen cyanide, Integrated Pests Management (IPM) has since the1980s become an important aspect in preventive conservation in museums. Today the most widespread non-chemical methods to control pests used by museums are anoxic treatments (nitrogen or carbon dioxide), or treatments with heat or cold. Many museums have nitrogen chambers or make use of air tight bubbles and reduce oxygen levels with oxygen scavengers, nitrogen bottles or nitrogen generators. Other methods used by museums include microwaves, high frequency radiation or gamma radiation. Still quite new in the application in museums and storage facilities is the use of parasitoid wasps against pests like webbing clothes moths, biscuit or tobacco beetles. This paper provides a brief review and comparison of the non-chemical treatment methods by analysing their benefits and disadvantages, cost and time for treatment.

1 INTRODUCTION

The concept of Integrated Pest Management (IPM) has been successfully applied in museums since the 1980s (Querner et al. 2012) to reduce the population of pests, for example, webbing clothes moths *Tineola bisselliella* (Hummel 1823), drugstore beetles *Stegobium paniceum* (Linnaeus 1761), common furniture beetles *Anobium punctatum* (De Geer 1774) or different carpet beetles (*Attagenus* sp. and *Anthrenus* sp.) and thus preserve museum collections.

IPM is an important part of preventive conservation focusing on the prevention of pest infestations and the reduction of pesticide application. This is achieved by sealing the entry points of buildings against the pests, adapting the (micro-) climate, maintaining high hygienic standards, quarantining new and incoming objects, and monitoring for pest infestations with traps. Today, after the prohibition of methyl bromide and limited use of hydrogen cyanide, the use of biocides are limited although not completely abandoned. Treatment methods are changing towards non-chemical methods like heating, freezing or anoxic treatments, mainly with nitrogen or CO_2. Chemicals are used in emergencies when no other method can be applied, for example, when only a few days remain before the opening of an exhibition with infested objects.

This paper provides an overview of the different non-chemical treatment methods used by museums presently. They should all be considered and applied as part of a modern IPM strategy. The methods are evaluated against the following criteria: work required before and after treatment, time, treatment costs and possible damaging effect on museum objects. Relevant references are provided for each method. The aim of this paper is to assist museums in deciding on the treatment most applicable for their particular pest problem and collection as part of developing an IPM strategy appropriate for their institution. The main argument of this paper is that museums should make an informed and careful decision about the methods used to control pests in their collections.

2 NON-CHEMICAL TREATMENT METHODS

In Table 1 all non-chemical treatment methods we are aware of is used in museums today are described and compared. Relevant literature is cited but only a small selection can be mentioned here.

Table 1. Methods of non-chemical insect pest treatments in museums.

Method	Time for treament	Time for handling	Equipment and relevant citations	Notes
Freezing	7 d	8 h–4 d	Household freezer, freeze container or built-in freeze chamber; low costs for household freezer*** Bergh et al. (2006), Mecklenburg (2007), Strang & Kigawa (2009), Berzolla et al. (2011b), Kjerulff (2010)	Risk of mechanical damage when handling cold brittle objects. Risk of damage to surface treated wood and composites with surface treated metal, fusty paper, and objects with tensions, like saddles, drums and mirrors.
Heating	24 h***	0,5 d	Built in heating chamber, truck with heating chamber, heat bubble or solar tent. Child (1994), Strang (2001), Roux & Leary (2001), Ackery et al. (2002, 2005), Brokerhof (2002), Ball et al. (2011)	Risk of damages after heating for some keratin, teeth materials, lacquer (Urishiol), low-melt adhesives, animal glue, Paraloid B 72, mother of pearl, fish skin. In solar tent: no control of RH and high risk of damages due to drying of object materials.
Microwaves	5–15 min	1–2 h	Microwave Radiator Steinbach (2006)	Mostly for wood with no surface treatment such as structural timber. Bubbles and heat stains on surface can occur.
Heat blankets	3–8 h	0,5 d	Heat blankets. Low cost	Same as for microwaves
Nitrogen chamber	3–5 w	1–2 d	Chamber, nitrogen (bottles or generator), equipment to moisturize nitrogen and measure oxygen level. Valentin (1993) Rust & Kennedy (1993), (1998) Selwitz & Maekawa (1998) Gilberg (1989, 1991), Maekawa & Elert (2003), Rowe (2003), Berzolla et al. (2011a)	Can be used for most materials.*** Caution must be exhibited for Prussian blue as it can be reduced, altering the colour.
Nitrogen under pressure	1 w***	1–2 d	Special chamber www.consolidas.de	Still very new method, more tests for different insect species as well as object materials needed.
Nitrogen bubble	3–5 w	1–2 d	Bubble and see Nitrogen chamber	Same as for nitrogen chamber
Smaller bags with scavenger	3–5 w	0,5 d	Bags, heatsealer, oxygen scavengers	Easy to use for museums***

(*continued*)

Table 1. Methods of non-chemical insect pest treatments in museums. (*continued*)

Method	Time for treament	Time for handling	Equipment and relevant citations	Notes
CO_2 bubble	3–5 w	1–2 d	Bubble, CO_2 bottles	Risk of corrosion on metals.
Gamma radiation	1 h***	1 d	Gamma Radiator	Used for insects and fungi, especially applicable for books; Special registration for generator needed, 1–2 per country.
High frequency radiation	1 d	–	High frequency Radiator	
Parasitoids	12 w	non***	Parasitoid insects Schöller (2010), Schöller et al. (1997) Querner & Biebl (2011)	Each parasitoid is specific for one pest species only. Local and controlled application is possible.

min = minutes, h = hours, d = days, w = weeks.
***highlight specific advantage of certain methods.

3 DISCUSSION

Insect pests can be killed with low oxygen concentration (and dehydration), physical damage due to freezing or heating (destruction of individual cells or enzymes), gamma or high frequency radiation or by parasitoids. No single treatment method is perfect and suitable for all object materials. As illustrated in table 1 each method has its advantages and disadvantages. The table illustrates that there is a variety of methods to choose from when planning an IPM strategy that avoids the use of chemicals. In order to accommodate the requirements for safe treatments for most object materials and variations of available resources such as time and finances it is favorable for a museum to have access to several methods.

Treatments with high or low temperatures are among the fastest, cheapest and relatively easy to use methods of pest control. For these reasons they are commonly used by natural history museums, ethnological and cultural history museums both, as a preventive measure for incoming material and to treat infested objects (see Pinniger 2003, Beiner & Ogilvie 2005, Strang & Kigawa 2009, and Kjerulff 2010, for general application of these methods). Yet, they have limitations. For example, it has been observed that freezing at −38°C for 72 hours will not eliminate all stages of the common furniture beetle *Anobium punctatum* (work at The Conservation Centre Vejle, Denmark, Kjerulff 2010). The thermal methods might be used alongside each other though, as some of the surface treatments which can be damaged by freezing like shellac, have not been observed to be damaged by heating.

Presently, the anoxia treatment is on one hand, expensive and time consuming with three to eight weeks turnover, but, on the other, it is the least damaging for a broad range of object materials. So far it is only known to cause loss of color in Prussian blue due to the reducing atmosphere (Rowe 2003) but more investigation is needed.

Anoxia treatment times depend on oxygen content, temperature, RH and the type of pests to be eradicated. New research suggests that it might be possible to perform successful anoxia treatments at higher oxygen levels and within shorter periods, which should lead to reduction in treatment time and costs (Berzolla et al. 2011a). While this makes anoxia the method of the widest application possibilities, it is important to consider, develop and investigate alternative methods of pest control. Among these, are the biological methods using parasitoids or heat treatment with handheld portable microwaves, that holds potential benefits which have been demonstrated recently (Querner & Biebl 2011, Querner et al. 2012).

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*Science and Technology for the Conservation of Cultural Heritage –
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Novel proteases from marine organisms with potential interest in restoration procedure

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ABSTRACT: In the last decades, molecular biology allowed the development of innovative protocols in the field of conservation/restoration of cultural assets. In this work new hydrolyses, isolated from marine invertebrate organisms, are applied to remove protein layers form works of art surface. Proteolytic zymography assay evidenced that these enzymes are active in a broad temperature range, between 4° and 37°C. The enzymatic cleaning by these proteases, tested on wooden furniture of the second half of the eighteenth century showed positive results, without needing to heat the enzyme solution or the surface on which they were applied. The present report proposes novel proteases more appropriate than other, which usually are active at temperature ≥37°C, for a controlled removal of protein layers from wooden painted artifacts.

1 INTRODUCTION

Enzymatic cleaning dates back to 1970 and was initially utilized on paper and later on canvas and polychrome works of art, but they were isolated experiences. Wendelbo (1970) reported the enzymatic hydrolysis (Trypsin in phosphate buffer—pH 8.0, for 10 minutes at 40°C) of animal glues, on glued book pages. Segal & Cooper (1977) described the removal of starch and protein adhesives from parchment by Amylase (phosphate buffer pH 7.0, at 38°C up to 60 minutes) and microbial protease (phosphate buffer pH 7.5, at 40°C). Bio-remediation on painted canvas was first described by Makes to remove glue paste (1982) or protein/oily binder (1988). Bonomi (1994), described the application of a protease solution heated at 40°C, to remove the protein patina from a polychrome ceramic sculpture. Bellucci & Cremonesi (1999) described the enzymatic cleaning (by Lipase) of an acrylic resin coating. The combined action of the metabolic activity of viable bacterial cells (*Pseudomonas stutzeri*, strain A29) and purified enzyme (Protease), was described by Ranalli et al. (2003, 2005), for the bio-cleaning of frescoes (Camposanto Monumentale di Pisa). The application was performed keeping the bacteria solution onto the fresco surface for 10–12 hours, at 28–30°C, followed by using the Protease (Type XIX), to remove the glue residues. Recently, bio-remediation of mural paintings by *P. stutzeri*, has been described by Bosch Roig et al. (2011).

The rational use of an enzyme or of an enzyme mixture requires information on their hydrolytic activity and on the specificity of action, on the nature of the material to eliminate (proteins, starches, oils, fats), on temperature, pH and salt concentration.

In this study, hydrolases isolated from marine organisms allow us to remove protein layers (mainly animal glue) at "room temperature" (19–24°C), without heating the enzyme solution or the artwork surface on which they have been applied.

2 MATERIALS AND METHODS

2.1 *Sampling on protein layers and samples preparation*

Micro-fragments were carefully collected from the surfaces of wooden furniture of the 18th century (MUDIPA), homogenized by Ultra-Turrax in dH_20 (W/V) for 5 minutes in ice, then centrifuged (Eppendorf microfuge) at 13000 rpm for 20 minutes and the supernatant recovered for successive analysis.

2.2 *Characterization of the protein layers samples*

The characterization of each sample was carried out by size exclusion High-Performance Liquid Chromatography (Waters: BioSuite 250-10 Tm, SEC-7.5 × 300 mm, stable pH 2.5–8.0); the pressure was equal to 350 psi (24 atmospheres). 200 µl aliquots of each sample were inserted in a silica column by a rheodine manual injector, and the reading was carried out simultaneously at 280 nm and 220 nm (mAU) for 30 minutes in T.B.S. solution (150 mM NaCl, 10 mM TRIS-HCl pH 7.4).

Quantitative analysis was performed according to the Bradford method using the bovine serum albumin (BSA, concentration 0.1–10 mg/ml) as standard (Salamone et al., 2012).

2.3 *Marine organisms proteases*

Proteases were isolated from tissues or organs of two marine invertebrate species, *Palinurus* and *Anemonia*, and their molecular weight was determined by Sodium dodecyl sulphate–polyacrylamide gels, SDS-PAGE (Laemmli 1970), using 5% (w/v) stacking and 15% (w/v) separating gels. After running (190 V for 45 minutes) the gel was stained in Coomassie solution (2 gr *C*oomassie *B*rillant *B*lue, 500 ml methanol, 100 ml acetic acid, 400 ml distilled water), and destained by DS (10% acetic acid, 40% methanol, 50% dH_2O) The molecular weight was estimated by Bioloabs marker.

2.4 *Protease activity*

The protease (gelatinolytic, caseinolytic) activity was tested by:

- SDS-PAGE containing 0.1% Gelatin as substrate. After running, the gel was incubated in 50 mM TRIS-HCl pH 7.4/1.5% Triton X-100/0.02% Na azide/2 mM $CaCl_2$ solution. Staining was performed by Coomassie Brillant Blue R250 to detect the proteolytic activity (Salamone et al., 2012).
- Kembhavi method (1993), using 1% Casein as substrate. 0.5 ml aliquot of protease mix was dissolved in 0.5 ml of 100 mM TRIS-HCl (pH 8.0) and incubated at 20°C for 15 min. The reaction was stopped by addition of 0.5 ml of 20% Trichloro-Acetic Acid (TCA). After centrifugation at 13,000 rpm for 15 minutes, the precipitate was removed and the absorbance values (280 nm) of the solution determined.

The activity of each single protease was defined as the amount of enzyme hydrolyzing 1 mg per milliliter of Thyroxine, in 1 minute at room temperature (20°C).

2.5 *Bio-cleaning essays*

Proteases at the final concentration of 1 mg/ml have been applied onto 4 cm^2 test surface, by 5% Tylose (Methyl Hydroxyethyl Cellulose) gel as carrier, in order to ensure a selective and controllable cleaning.

The cleaning solution (100 µg/ml protease + 5% gel) respectively *Palinurus* Protease + Tylose gel (Fig. 1) or *Anemonia* Protease + Tylose gel (Fig. 2) were applied for 5 and 10 minutes at the environmental temperatures (22 ± 3°C); a control test was performed for each experiment using 5% Tylose gel without enzyme. After application times the gel was immediately removed by a dry swab first, then with some swabs moistened with dH_2O.

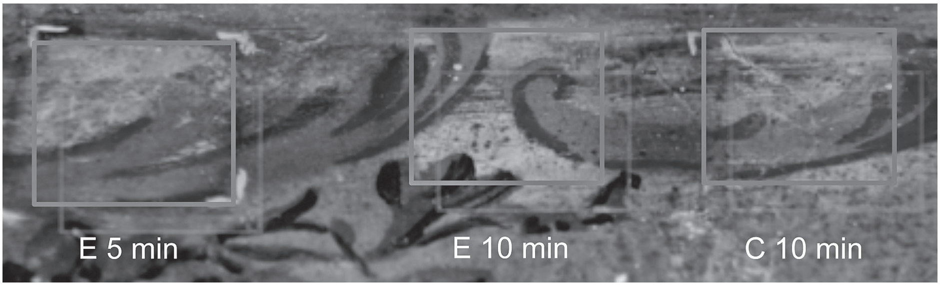

Figure 1. Bio-cleaning test by *Palinurus* protease, stratified by 5% Tylose gel, for 5 and 10 minutes (E). Negative control (C) corresponds to the gel alone applied, for 10 minutes.

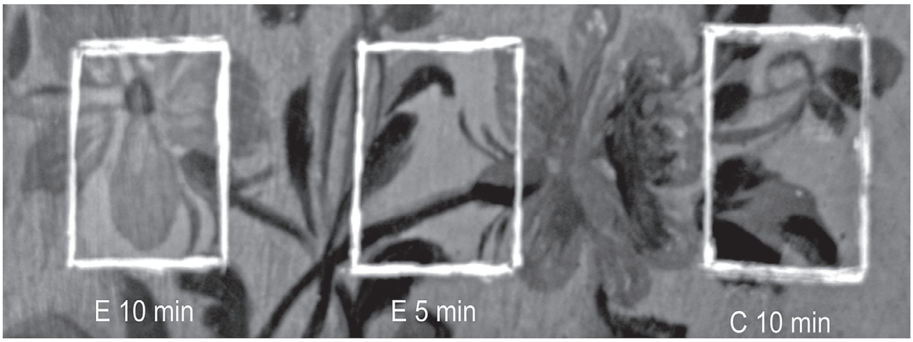

Figure 2. Bio-cleaning test by *Anemonia* protease, stratified by 5% Tylose gel, for 5 and 10 minutes (E). Negative control (C) corresponds to the gel alone, applied for 10 minutes.

3 RESULTS

The SEC-HPLC surveys, conducted on micro-fragments (few milligram) collected from the wood artifacts surfaces, revealed the presence of protein molecules at the concentration of 24–110 micrograms/ml with a molecular weight ranging 20–35 kDa and 60–90 kDa.

The enzymatic activity of the proteases isolated from marine organisms, *Palimurus* and *Anemonia*, was previously tested in laboratory by zymography, through the ability of these enzymes to digest gelatin or casein substrates, respectively at 4°C and 20°C.

The application of these proteases on the wooden artifacts surfaces allowed the hydrolysis of protein layers selectively, in a short time (5–10 minutes), especially in a temperature range which coincided with that for restoration or storage environments (22 ± 3°C).

4 CONCLUSIONS

In the last decades molecular biology has provided both diagnostic protocols and innovative molecules successfully applied in the field of conservation and restoration of cultural assets (Palla et al. 2002, 2006, 2010, Ranalli et al. 2005, Gonzalez 2003).

The cleaning assays reported in this study, were carried out to test the use of protease extracted from marine organisms *Palinurus* sp. (Fig. 1) and *Anemonia* sp. (Fig. 2), to hydrolyze and easily remove animal glue layers, from the surface of wooden furniture (18th century).

They fulfill the criteria of the modern restoration: compatibility with the original constitutive materials; minimal intervention; selectivity and controllability of the cleaning (reduced invasive action); applicability at environmental temperature.

Considering the results we hypothesize that these enzymes will implement the efficiency of bio-cleaning protocols, according to the conservative procedures.

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Nanostructured materials for stone consolidation in the Temple Valley of Agrigento: *In situ* evaluation of their effectiveness

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ABSTRACT: The present study is focused on the testing of new nanostructured products for the consolidation and protection of archaeological stone blocks located in the Roman-Hellenistic quarter of the Temple Valley of Agrigento (Sicily). In particular, an *in situ* measurement methodology was applied for testing different nanostructured products. The consolidation effectiveness was validated by non destructive tests in order to monitor the absorption capacity and the color change of the samples after the treatment. The research has been developed in the context of the Master on "Nanotechnology and Nanomaterials for Cultural Heritage", held at the University Centre of Agrigento during the Academic Year 2010–2011.

1 INTRODUCTION

This study has faced the problems of biocalcarenite's conservation, testing in field some nanostructured products for the consolidation and protection of stone surfaces, and monitoring the results through the use of some non destructive investigations. This has been made possible thanks to the collaboration of the Laboratory of Physics and Technology, the UniNetLab-System Laboratory of the University of Palermo and the PH3DRA Laboratory, Department of Physics and Astronomy, University of Catania & INFN Catania. Thanks to the "Ente Parco Archeologico e Paesaggistico Valle dei Templi", it has been possible to carry on some tests directly on some stone blocks located in the Roman-Hellenistic quarter discovered in *Contrada San Nicola*, close to the Temple Valley of Agrigento (Sicily). The quarter, developed from the 2nd-1st centuries B.C. and lasted until the 4th century A.D was composed of approximately twenty houses on the sloping terraces, arranged within a regular urban plan in three blocks (Fig. 1). The study focused on the colorimetric and water absorption variations, before and after the treatments.

2 MATERIALS AND METHODS

The first phase of the investigations consisted in the study of the mineralogical-petrographic characteristics and physical properties of the stone material and the subsequent assessment of its conservative problems. Then, the goal has been to test a few nanostructured products

Figure 1. View of the Roman-Hellenistic quarter discovered in *Contrada San Nicola*, Temple Valley (Ag).

for the consolidation and protection of the stone surfaces. The “traditional” products, in fact, generally have certain limitations related to a low penetration depth, excessive cortical stiffening and evident color change of the treated surfaces. In order to avoid these problems we wanted to test some new products, monitoring their performance using different non-destructive techniques.

2.1 *Selection of products and their application*

The products were carefully selected on the basis of the typology of deterioration detected on the archaeological stone materials. In particular, six nanostructured products, namely Idrostop New (CIR), Compact (VILO), Consolida Nano e Consolida ProNano (CIR), Stone e Marmo (MP), and NanoEstel (CTS), and two traditional products (Acquacons, CIR, and Estel 1100, CTS) were evaluated in accordance with the procedures and the timing of application for the specific case of biocalcarenite.

The products were applied on the stone surfaces, clean and dry, in condition of not direct sunlight, in the absence of rain and with a temperature between 18 and 20°C, following the recommendation of the producers. The solutions were applied with a natural fibers brush at low pressure and in more coats (*wet on wet*) up to the saturation of the support, taking care to eliminate the product in excess by dabbing the surface with a dry cloth, in order to avoid possible stagnations on the surface. In this phase, all the information concerning the characteristics of the product, the application procedure and any problem that occurred during the application, were collected and summarized in a file for each product. The selection of the areas of application was based on the homogeneity of the stone and the representativeness of the ongoing conservation problems, with respect to those commonly encountered throughout the site.

2.2 *Non destructive tests*

Colorimetric measurements were conducted using a portable spectrophotometer MINOLTA CM700d with the support of the SpectraMagic software. The data on each selected point, as an average of five repeated measurements, were compared with those acquired on untreated material in order to highlight any color changes due to the treatments. The *Karsten pipe* is a simple absorption test for masonry surfaces that measures the quantity of water absorbed by a small area over time. It consists in the application of a special glass pipe, filled with water, onto the stone surface, following its absorption over time. For the test we predetermined a period of time of 30 minutes. The *Scotch Tape Test* is a simple method to verify the adhesion of a coating to the substrate. This technique allows measuring the level of superficial cohesion of the surfaces before and after the treatments, and consists in the application and subsequent removal of an adhesive tape on the stone surface, verifying the change in weight on the analytical balance. The superficial cohesion factor represents the amount of superficial mass remained adherent to the strip of scotch. So the higher value means less cohesion of the surface layer and a tendency to lose material by simple contact.

Color specifications were performed by PhD student D. Fontana and Prof. A. Gueli, absorption tests with Karsten pipe and Scotch tape test were performed by Arch. F. Fernandez.

3 RESULTS AND DISCUSSION

3.1 *Stone characterization and study of its conservation problems*

The stone used in the masonry was identifies as a biocalcarenite, composed of calcareous shells and micritic limestones fragments cemented by calcium carbonate. It is a sedimentary rock of detrital nature with a considerable porosity and capacity to trap water (Brai et al. 2003). The most important phenomenon of degradation, which compromises the stone conservation, is a widespread disruption that occurs with the detachment of granules under minimum mechanical strain. The high porous structure of the stone connected to the circulation of fluids favored an accelerated decay (Fernandez 2006) that in advanced stage leads to the spontaneous fall of material in the form of powder or granules (*pulverization*). In such cases, it is necessary to treat the parts disrupted and crumbling with consolidants, in order to increase the cohesion between the material granules, improving the mechanical strength and the stone resistance to the processes of alteration and degradation. Moreover, since all the decays phenomena are due to the presence of fluid circulating in the porous structure, it is also necessary reducing the water absorption with a water repellent product.

3.2 *In situ testing*

The effects of the treatments were evaluated through non-destructive analytical investigations, such as Colorimetric measurements, water absorption test by Karsten pipe and the scotch tape test, by comparing the results obtained on treated areas with those observed before the treatment.

As a result of the comparative tests, it may be affirmed that, the products used causes chromatic variations due to changes of L* coordinate (lightness). Figure 2 shows the variations in a*b* chromatic plane: ConsNano (CN), AcquaCons (AC) causes a superficial yellowing testified by increasing of b* values ($\Delta b^* > 0$), whereas Nano Estel and Idrostop causes limited chromatic variations. On such bases, the most suitable products appear to be Estel 1100 and Consolida Pro Nano.

Water absorption test by Karsten pipe pointed out that in the treated surfaces the water repellency property was increased in comparison with the untreated stone, with the only exception of the surface treated with the Compact-Vilo. It should be noted that this property was especially increased in the case of the surface treated with the consolidant/water repellent Consolida Pro Nano. This product is a nano-dispersion of silanized colloidal silica in aqueous solution.

Comparative scotch tape tests disclosed that the areas treated with Consolida Pro Nano show a lower cohesion factor in comparison with the untreated part, demonstrating that the treatment has contributed to compact the surface and to make it less vulnerable.

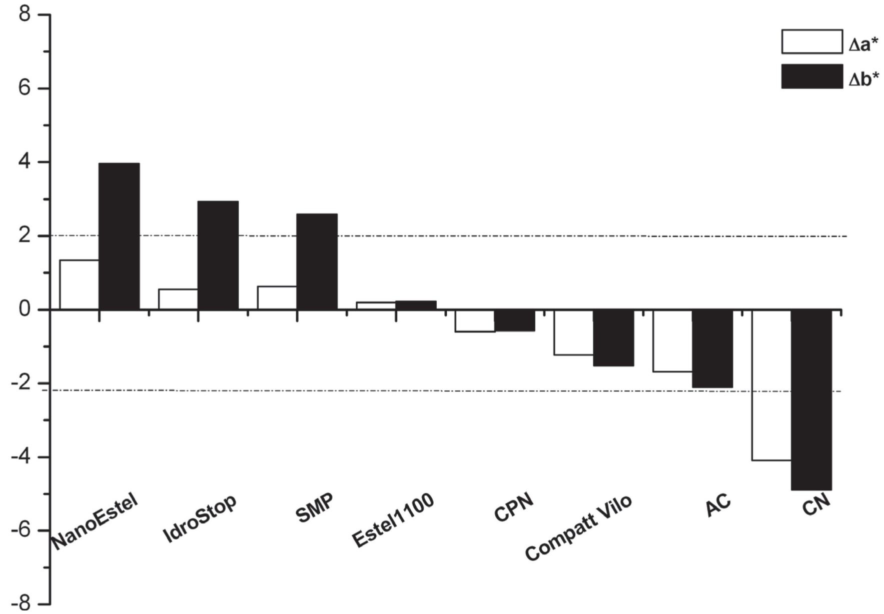

Figure 2. Variations in a*b* chromatic plane.

4 CONCLUSIONS

From the elaboration of all the data obtained by the comparative tests, we deduced that some of the tested nanostructured products, thanks to their properties of penetrability, viscosity, high interfacial area, are more effective than traditional ones, both in improving cohesion between the granules of the stone and in constituting a barrier to water.

Among the products tested as suitable for the preservation of the studied biocalcarenite the best results came from the Consolida Pro Nano, due to the fact it confers a general improvement in the characteristics of the stone, increasing cohesion and water-repellent properties in the treated surfaces, and causing no evident color changes of them. Some other products are to be excluded because they gave rise to the formation of a whitish coating on the stone surface, changing its original color and, in some other cases, they did not improve the mechanical properties of the treated surfaces. It is also necessary to specify that it would be desirable to test the products in laboratory on stone samples, in order to detect any changes caused by the treatments at microstructural level. The samples treated in the laboratory may also be subjected to artificial ageing to test the effectiveness and the duration of the treatments over time. Till today is still in progress the *in situ* monitoring of the treated areas, in order to evaluate how much the climatic conditions of the site impact on the effectiveness of treatment over time.

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Thermodynamic modeling of sulfate-resistant cements with addition of barium compounds

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ABSTRACT: Sulfate attack by ground waters, soils, etc. is one of the threats to the built heritage in concrete. This study validated through thermodynamic modeling with GEMS geochemical code a new sulfate-resistant formulation based on the addition of $BaCO_3$ and BaO to ordinary Portland cement (OPC), which could be used to replace weathered concrete. The thermodynamic calculations pointed out that Ba ions were able to form an insoluble salt, barite ($BaSO_4$) with the dissolved sulfate which inhibited the formation of ettringite, the latter occurred when the concentrations of $BaCO_3$ and BaO were ≥6 and ≥4 wt.%, respectively. The results of a simulated sulfate attack revealed that ettringite precipitated upon ingression of ≥46 ml of a Na_2SO_4 solution (44 wt.%) in OPC blends with 20 wt.% of $BaCO_3$; whereas with 20 wt.% of BaO, the sulfate that precipitated besides barite was monosulfoaluminate when sulfate solution was ≥40 ml (tested up to 52 ml).

1 INTRODUCTION

Much of the twentieth century's heritage (buildings, structures, sculptures and so on) is made of concrete, material susceptible among other weathering phenomenon (Reed et al., 2008) to sulfate attack (Schmidt et al., 2009). The sulfates origin is diverse: internal or external (sulfate-rich water or soil; polluted atmosphere, aggregates and so on). During Portland cement hydration, clinker tricalcium aluminate ($3CaO \cdot Al_2O_3$), gypsum ($CaSO_4 \cdot 2H_2O$) and water react to yield ettringite ($3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O$) (eq. 1), one of the main hydrates of cement after C-S-H gel and portlandite ($Ca(OH)_2$). The formation of ettringite during the first hours causes no damage in the cementitious materials as they are still in its plastic state (Collepardi 2003). Depletion of the dissolved sulfate leads to the reaction of ettringite with tricalcium aluminate, that yields calcium monosulfoaluminate hydrate ($3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O$) (eq. 2).

$$3CaO \cdot Al_2O_3 + 3\ CaSO_4 \cdot 2H_2O + 26H_2O \rightarrow 3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O \tag{1}$$

$$3CaO \cdot Al_2O_3 \cdot 3CaSO_4 \cdot 32H_2O + 2(3CaO \cdot Al_2O_3) + 4H_2O \rightarrow 3(3CaO \cdot Al_2O_3 \cdot CaSO_4 \cdot 12H_2O) \tag{2}$$

Changes in environmental conditions may destabilize these sulfates and reprecipitation may cause decaying of mortar or concrete. In the presence of external sulfates, the traditional sulfate phases, gypsum, ettringite or thaumasite ($CaO \cdot SiO_2 \cdot CaSO_4 \cdot CaCO_3 \cdot 15H_2O$) may crystallize and induce concrete deterioration. Thus, sulfate resistant cements may be needed when weathered concrete should be replaced in restoration works.

Several strategies have been developed to counteract sulfate attack such as sulfate-resistant cements with low C_3A content (<5%, ASTM C150), which avoid the destructive ettringite formation but not the gypsum or thaumasite crystallization. This work proposes the addition of barium compounds ($BaCO_3$ (witherite) and BaO) to cement to immobilize sulfate ions by precipitating barium sulfate, an insoluble salt, further to previous studies of ettringite stability in presence of barium ions (Carmona-Quiroga et al. 2011, Ciliberto et al., 2008).

The main objective of this study was thus to evaluate through thermodynamic modeling, the role of these barium additions on cement hydration and resistance to sulfate attack.

2 METHODOLOGY

The influence of barium compounds on cement hydration at 25ºC was determined using the GEMS geochemical code (Kulik et al. 2012). This thermodynamic modeling software which includes built-in thermodynamic databases (general and cement-specific [Lothenbach et al., 2008]), computes equilibrium phase assemblage and speciation of the defined systems by Gibbs free energy minimization (GEM). The bulk chemical composition of the system examined in the present study was the one of an ordinary Portland cement (OPC) (Table 1) blended with up to 20 wt.% of $BaCO_3$ (witherite) or BaO (total solid amount of 100 g), with a w/c ratio of 0.5 and 1 g of CO_2 free air (assuming 100% hydration). The effect of 10 and 20 wt.% barium compound additions on sulfate attack in cement was also modeled by adding to those systems an increasing amount (up to 52 ml/100 g of cement) of a very high concentration Na_2SO_4 solution (44 wt.%) (In ASTM C1012 the accelerating test is conducted with just 5% of Na_2SO_4).

3 RESULTS AND DISCUSSION

3.1 *Influence of $BaCO_3$ and BaO on cement hydration*

Figure 1 shows the influence of barium compounds on the cement hydrates assemblage. As can be seen, additions of $BaCO_3$ ≥6 wt.% and BaO ≥4 wt.%, destabilized ettringite and promoted the formation of barite ($BaSO_4$). If $BaCO_3$ was added, calcium monocarboaluminate hydrate ($3CaO \cdot Al_2O_3 \cdot CaCO_3 \cdot 11H_2O$) was stabilized, while all sulfate present was bound in barite. The use of BaO resulted in the conversion of calcium monocarbonate hydrate to hemicarbonate ($3CaO \cdot Al_2O_3 \cdot 0.5Ca(OH)_2 \cdot 0.5CaCO_3 \cdot 11.5H_2O$) and hemicarbonate to hydrogarnet ($3CaO \cdot xAl_2O_3 \cdot 1 - xFe_2O_3 \cdot 6H_2O$), which favoured the precipitation of more portlandite. Portlandite besides C-S-H gel and hydrotalcite, ($Mg_6Al_2CO_3(OH)_{16} \cdot 4(H_2O)$) a minor product in the hydration of Portland cement were the only common hydrates for the different concentrations of both barium additions.

3.2 *Role of $BaCO_3$ and BaO against sulfate attack*

To simulate external sulfate attack, an increasing amount (up to 52 ml) of a highly concentrated sodium sulfate solution (44 wt.%) was calculated to interact with four different model systems: OPC blended with 10 and 20 wt.% of each $BaCO_3$ and BaO (Fig. 2).

The results of thermodynamic modeling allowed predicting the protection limits of the different blends. 10 wt.% of $BaCO_3$ prevented ettringite precipitation up to 12 ml of Na_2SO_4 solution (0.45 mol/kg of S in dissolution) (Fig. 2a), whereas 20 wt.% of $BaCO_3$ avoided ettringite formation up to 44 ml of the aggressive solution (0.91 mol/kg of S in dissolution)

Table 1. Chemical composition of OPC before blending.

OPC	CaO	SiO_2	Al_2O_3	Fe_2O_3	MgO	SO_3	CO_2	Na_2O	K_2O
wt.%	65	20	4.5	2.8	2	2.5	2	0.4	0.8

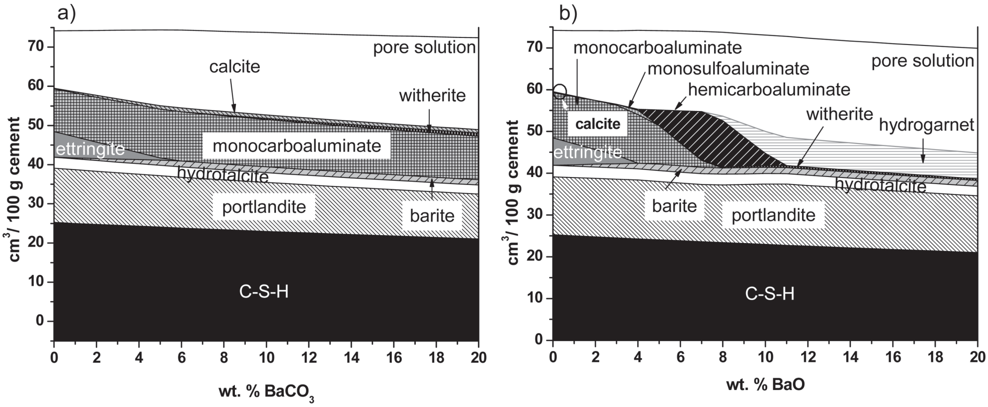

Figure 1. Volume of hydration products of OPC blended with up to 20 wt.% of $BaCO_3$ (a) and BaO (b).

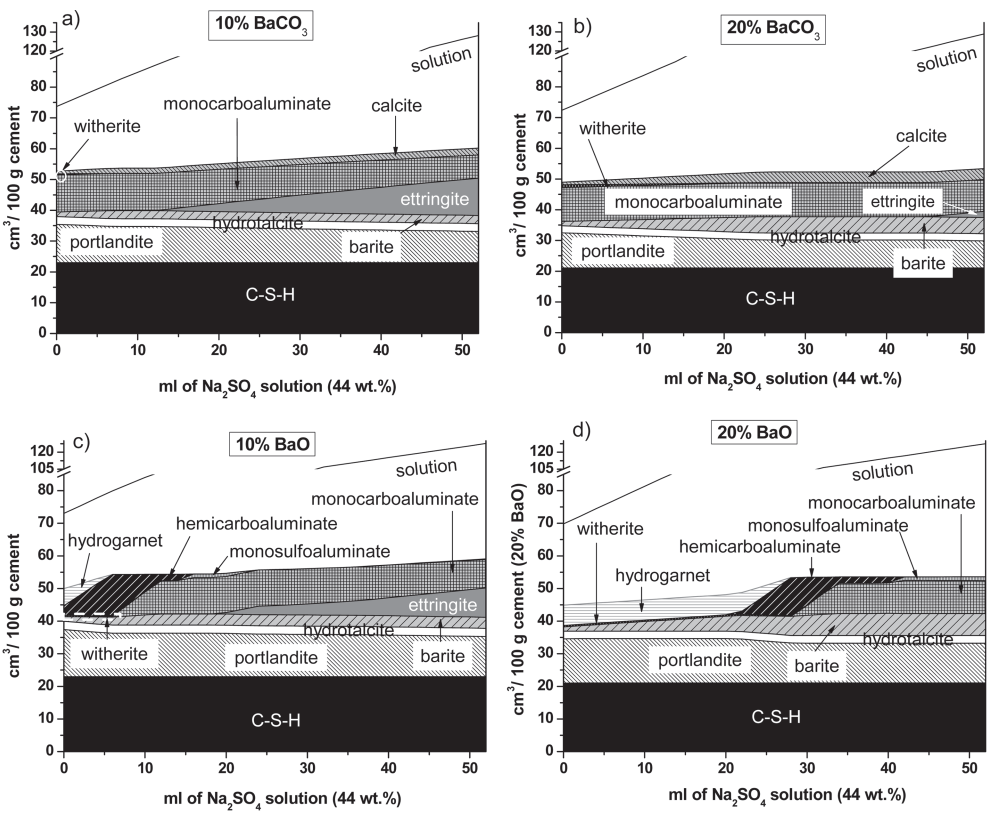

Figure 2. Volume of hydration products of different OPC blends, (a) with 10 wt.% of $BaCO_3$; (b) with 20 wt.% of $BaCO_3$; (c) with 10 wt.% of BaO and (d) with 20 wt.% of BaO, in contact with an increasing amount of a Na_2SO_4 solution (44 wt.%).

(Fig. 2b). Nonetheless, taking into account the aggressiveness of the solution both blends could be considered as sulfate-resistants.

Unlike $BaCO_3$, BaO did not prevent the formation of a small amount (maximum content around 1 cm^3) of monosulfolauminate prior to ettringite precipitation but guaranteed even a better protection against sulfate attack by delaying the formation of the ettringite. In fact, no ettringite was able to precipitate with 20 wt.% of BaO for the simulated attack (Fig. 2d) and with 10 wt.% of BaO started to precipitate with a higher amount of the aggressive solution, 20 ml, (Fig. 2c) in smaller quantities.

4 CONCLUSIONS

According to thermodynamic calculations with GEMS geochemical code, $BaCO_3$ and BaO additions ≥6 wt.% and ≥4 wt.%, respectively, stabilize cement sulfates by precipitating barite ($BaSO_4$), a very insoluble and thus stable sulfate, instead of ettringite. This explains the favourable results of OPC blends with 10 and 20 wt.% of these barium compounds, especially with 20% of BaO, against sulfate attack after modeling the ingression of highly concentrated (44 wt.%) Na_2SO_4 solution (up to 52 ml) in those systems.

These results endorse the addition of $BaCO_3$ and BaO to OPC to produce new sulfate resistant cements which can be used to replace weathered concrete of our recent heritage, although as a rule, predictions should be always experimentally confirmed.

ACKNOWLEDGEMENTS

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Semi-interpenetrating p(HEMA)/PVP hydrogels for the cleaning of water-sensitive painted artifacts: Assessment on release and retention properties

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ABSTRACT: Nowadays, aqueous cleaning systems are preferred for the cleaning of painted artifacts because they are environmental friendly and offer several advantages in terms of selectivity and gentle removal of undesired materials. However, materials interaction with water can lead to mechanical stress between the substrate and the paint layers. The confinement of water-based cleaning systems in a hydrogel with high retention capability can limit this disadvantage. Hence, the aim of this work was to develop novel chemical hydrogels, specifically designed for the cleaning of water-sensitive painted artifacts. These are based on highly hydrophilic semi-interpenetrating p(HEMA)/PVP networks with suitable mechanical strength to avoid gel residues after cleaning treatment. To assess on the potential of these novel hydrogels their release and retention properties were compared with the widely used agar-agar hydrogel.

1 INTRODUCTION

The usage of neat or blended organic solvents for painting cleaning presents several drawbacks due to the poor selectivity and environmental impact. The uncontrolled penetration of solvents into the painted layers may cause swelling or leaching of binders and varnishes (Phenix & Sutherland 2001). To overcome these issues, water-based cleaning systems, such as microemulsions, have recently received much attention (Giorgi et al. 2010), because the amount of organic solvents is very low and it is confined in a stable way. This ensures a bigger control of the cleaning process and a very low environmental impact. Obviously, this approach can be followed on artifacts that are not water-sensitive, i.e. wall paintings and stones. In fact, the hydrophilic layers of easel paintings in contact with water are prone to swell, which often leads to painting detachment (Pizzorusso et al. 2012).

In the last decades, conservators devised several methods to limit solvents action through the use of thickeners (e.g. cellulose ethers; polyacrylic acids, etc.).

More recently, a new class of gels, known as "rigid gels", has been applied for restoration purposes. Namely, polysaccharide-based gels (e.g. agar-agar and gellan gum) have been used as a container for the controlled release of water solutions (Campani et al. 2007). These gels can be described as 'physical gels', because the gelled state depends on the intermolecular and intramolecular interactions of polymer chains, which are weak (Van der Waals forces and hydrogen bonds) in terms of bond energy. In water-swollen physical gels the competition between water-polymer and polymer-polymer hydrogen bonds may reflect in the decrease of hydrogel mechanical stability. Thus, a small mechanical stress is enough for hydrogel rupture. Hence, from a practical point of view, these characteristics make the hydrogel hard to be handled, when the water content is high, and usually these gels leave residues on the painted surface because the interactions with the support are competitive with the gel cohesion forces.

Studies have been carried out in order to reduce the risk of gel residues and to enhance the hydrogel retention characteristics, as well as their exchange capability with the surface to be treated. As a result, some innovative confining systems have been developed, as described in literature (Baglioni et al. 2009, Pizzorusso et al. 2012).

The current study was focused on designing a new class of chemical hydrogels (i.e. able to load aqueous systems) that fulfill the right equilibrium between retention and release properties in order to ensure an efficient and controlled cleaning. Gelled state depends on the building of a polymer network that is characterized by the presence of covalent bonds, which are stronger than the weak intermolecular forces involved in physical gels. Chemical gels exhibit improved mechanical properties that avoid any left residues and can swell in a liquid medium without gel solubilization.

2 SEMI-IPN P(HEMA)/PVP HYDROGELS

The ideal hydrogel properties for application in cleaning of paintings are achieved if two important features are combined: mechanical strength and hydrophilicity. These two characteristics allow, on one hand, simple manipulation of gel and absence of gel residues after cleaning treatment and, on the other hand, an efficient exchange process between the cleaning system and the artifacts surface. In this contribution, the combination of these two properties is obtained through the synthesis of semi-interpenetrating polymer networks (semi-IPN).

Semi-IPNs are polymer blends in which linear or branched polymers are embedded into one or more polymer networks during polymerization. To obtain the semi-IPN hydrogels, the linear polymer polyvinylpyrrolidone—PVP—was embedded into the forming network of poly(2-hydroxyethyl methacrylate)—p(HEMA). P(HEMA) and PVP are extensively used and studied polymers. P(HEMA) forms very resistant hydrogels, however, their hydrophilicity is not sufficient for loading water-based cleaning systems. PVP, on the other hand, is an high hydrophilic polymer. The semi-IPN hydrogels can be designed by varying their component ratios (water, PVP, HEMA and cross-linker quantities) in order to tune their characteristics in terms of mechanical behavior (softness, elasticity, and resistance to tensile strength) and affinity to water (Domingues et al. in press).

Hydrogel synthesis was carried out by free radical polymerization of 2-hydroxyethyl methacrylate (HEMA) monomer and a cross-linker, N,N'-methylene-bisacrylamide (MBA), in a water solution with linear PVP (~1300 KDa). A series of different hydrogels was designed by varying the proportions of monomer/cross-linker ratio with PVP and water percentages. Physico-chemical characterization was carried out by thermal analysis that allowed calculating the free/bound water ratios and by a Field Emission Gun-Scanning Electron Microscopy (FEG-SEM) Sigma, from Carl Zeiss (Germany), for the study of micro-structure and porosity.

3 HYDROGEL CHARACTERIZATION

All the semi-IPN hydrogels formulations were found to have interesting macroscopic characteristics and satisfactory mechanical properties. Specifically, these hydrogels exhibit a wide range of features: from semi-rigid and completely transparent to pliable and translucent. In fact, they are to some extent softer than ordinary chemical gels, which is an important feature to obtain better adhesion to rougher surfaces. Moreover, the achieved mechanical strength permits to synthesize hydrogels that are film-shaped, with a thickness of ca. 2 mm.

These gels are able to load big amounts of water solutions or aqueous detergent systems; the equilibrium water content (EWC) value provides an estimation of the amount of cleaning systems that can be kept in contact with the artworks surfaces. EWC is calculated as follows:

$$EWC = 100(W_w - W_d)/W_w \quad (1)$$

where W_w and W_d are respectively the weights of fully water swollen and dry hydrogels.

The EWC values for the studied formulations vary from ca. 70% to 90% without any loss of transparency. High EWCs are strictly dependent on hydrogel porosity and hydrophilicity of the network. The obtained results highlight that the addition of linear chains of PVP into the reaction mixture permits to increase water affinity, porosity and, consequently, the EWC of the hydrogels.

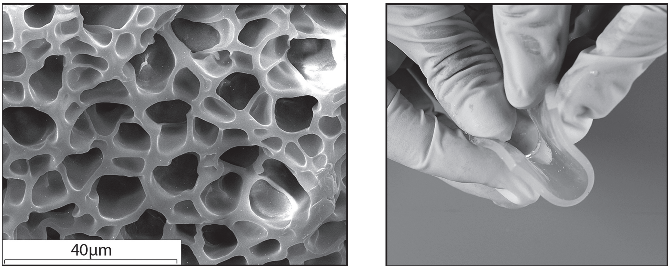

Figure 1. On the left, FEG-SEM image of semi-IPN xerogel. On the right, the pliability feature of the hydrogel is highlighted.

Water inside swollen hydrogels can be classified into three different states, depending on the interactions with the polar part of the polymer chains: unfreezable, bound-freezable and free water (Li et al. 2008). Free Water Index (FWI) parameter can be determined by thermal analysis (differential scanning calorimetry—DSC). The FWI can be obtained by the given formula:

$$FWI = \Delta H_{exp}/WC\Delta H_{theo} \quad (2)$$

where the ΔH_{exp} [J/g] represents the melting enthalpy variation for free water, WC is the water weight fraction in the hydrogel and ΔH_{theo} is the theoretical value of the specific enthalpy of fusion for bulk water. The FWI values obtained highlight that the free water amount inside the swollen hydrogels is much higher than bound water. Therefore, aqueous system loaded into the hydrogels will behave mostly as free water. The free water content varies from ca. 70% to 80% in respect of the total water quantity in swollen hydrogels.

In order to obtain some information about the structure and porosity of the lyophilized hydrogel (xerogel), FEG-SEM images were acquired. FEG-SEM image of one of the formulations is shown in figure 1. In general, sponge-like network morphology is observed and pore dimensions are approximately in the range of 5 to 40 µm. The difference of porosities between different hydrogel formulations is due to three main factors: the first is the water content in the initial polymerization mixture, which is the main responsible for the final gel porosity and the pore dimension; the second is due to the PVP loss during first washing steps after polymerization; and the third, the cross-linker amount, which contributes, at constant PVP/HEMA/H_2O ratios, to a more compact network structure. Although a compact network is present these hydrogels are highly flexible (see fig. 1 right). It should be noted that SEM images refer to xerogels, so hydrogels are expected to have much larger pores in the swollen state.

4 ASSESSMENT ON RELEASE AND RETENTION PROPERTIES

In order to evaluate the effectiveness and versatility of the investigated hydrogel systems, some assessment tests were carried out. The hydrogels dehydration kinetics (recorded at 55% RH and 20ºC) was evaluated to verify if during the time required for the cleaning process the amount of detergent solution is enough. This assessment confirmed that for the first hour the amount of water inside hydrogels is still above 95% of the initial water content. Additionally, water release tests were performed to quantify the water amount flowing into a high hydrophilic support during cleaning process. For this purpose, water-loaded hydrogels were gently dried on the surface, then put on 4 sheets of Whatman® filter paper and covered with a lid to avoid water evaporation. The filter paper sheets were weighted before and after 30 minutes of application. All hydrogels performed a homogenous release of water restricted to the paper contact area. After 30 minutes of contact, released water ranges from 16 ± 1 mg/cm^2 to 33 ± 3 mg/cm^2, depending on the hydrophilicity of the formulation, while the same test performed using an agar-agar hydrogel released 166 ± 8 mg/cm^2. It was important to compare semi-IPN hydrogel action with the widely used agar-agar hydrogel system. Agar-

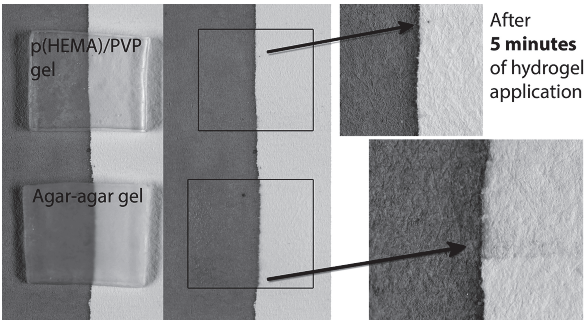

Figure 2. Comparison of water confinement capability of semi-IPN p(HEMA)/PVP (on top) and agar-agar (on bottom) hydrogels.

agar hydrogels were chosen because, like semi-IPN p(HEMA)/PVP hydrogels, they are used in conservation treatments in film shaped form and with water based solvent systems. In order to highlight the effective confinement of the cleaning process, some release tests on paper painted with a water-soluble colorant were performed. Few minutes of application are enough to evidence the difference between the two systems. In fact, while the area treated with agar-agar gel (fig. 2) shows color leaching, semi-IPN p(HEMA)/PVP hydrogels do not present any alterations also after 5 minutes of contact. Furthermore, abundant color absorption is shown by agar-agar gel, while few color traces were observed on the semi-IPN hydrogel surface.

5 CONCLUSIONS

The assessment carried out on semi-IPN hydrogels has shown that these polymeric networks have most of the desired properties to achieve a high-controlled cleaning action, i.e. the appropriate equilibrium between release and retention properties. These features allow obtaining a real confinement of the cleaning system on the hydrogel-artifacts interface, and thus permit to use water based systems also on water–sensitive substrates, e.g. canvas paintings.

The direct comparison with the agar-agar hydrogel has highlighted that using semi-IPN hydrogels it is possible to obtain an enhanced control of the fluids penetration and to limit the interaction volume between cleaning system and treated surface.

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Application of new organic-inorganic materials as consolidants for deteriorated plasters

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ABSTRACT: This paper reports a study of two organic-inorganic hybrid materials used as consolidants. Both formulations were synthesized from an inorganic precursor, i.e. tetraethoxysilane, added in different percentages (up to 60% per hundred resin) to a polysiloxane epoxy formulation (TEGO RC 1411) and to a cycloaliphatic epoxy resin (3,4-epoxyciclohexylmethyl-3,4-epoxyciclohexane carboxylate), cured in the presence of ytterbium as acid catalyst. The film properties and the formation of silica clusters were investigated. The products were applied on a plaster and their compatibility and effectiveness were verified. Lately sustainability and green chemistry are important issues in the field of conservation; for these reason no solvents, amines and nanoparticles were used in this study.

1 INTRODUCTION

The external plasters based on lime mortars often suffer some degradation phenomena such as detachment, lacunae and loss of cohesion. For this reason, different approaches and technologies, either innovative or linked with the local constructive traditions, should be used depending on the type of intervention needed. These considerations are the basis of an extensive research program currently in progress regarding the conservation of ancient plasters at the Sacro Monte of Varallo Sesia, a UNESCO World Heritage site in Piedmont (Italy). We are now focusing our attention on the external plaster surfaces and we are studying new consolidant products (Formia et al. 2011). It is well-known that a consolidant should penetrate in depth, restoring the material strength and continuity without modifying the surface's properties. In any case, the treatment is risky because the consolidation action is often irreversible, regardless of the product used. Recent studies have used hybrid materials where the limitation of organic and inorganic products is avoided. Tetraethoxysilane TEOS and its oligomers are often used as consolidants, even if their cohesive effects are poor and related to the type of catalyst, water amount, solvent and temperature and substrate (Wheeler 2005). Epoxy resins are used because they are characterized by excellent adhesion properties but the yellowing and the high viscosity in some cases does not allow the application of this product. The problem of photo-oxidative ageing has recently been solved using cycloaliphatic epoxy monomer, while the use of solvents is currently the common way to reduce the viscosity of the formulation. Notwithstanding, reverse migration, reduction of the consolidation strength and toxicity are the drawbacks of the use of solvent (Selwitz 1992).

In this paper hybrid curable formulations were prepared by adding TEOS to two different epoxy resins without the inclusion of water. The curing of the organic resins was achieved in the presence of the ytterbium triflate as acid catalyst (Penczek 2000). Under acid conditions, the alkoxy groups of TEOS can react with atmospheric moisture to generate silanol groups which can condense to form siloxane crosslinking (Sangermano et al. 2007). In this way, TEOS plays a dual role, increasing the film mechanical properties and reducing the formulation viscosity without the addition of solvents. Furthermore, the in situ generated hybrids show better homogeneity than the epoxy system filled with preformed silica nanoparticles (Pandey & Mishra 2011). The purpose of this study was to investigate the properties of the new materials and to evaluate their suitability as plasters consolidant respecting sustainability and green chemistry issues that are increasingly important in the field of conservation.

2 EXPERIMENTAL

2.1 *Materials*

Polysiloxane diepoxy resin (TEGO RC 1411, Degussa), 3,4-epoxyciclohexylmethyl-3,4-epoxyciclohexane carboxylate (CE, Sigma-Aldrich) and cyclohexene oxide (CY, Sigma-Aldrich) were used as epoxy monomer. glycidyl-propyl-triethoxysylane (GPTS, Sigma-Aldrich) was used as a coupling agent, and TEOS (Sigma Aldrich) was added to the formulations as precursor for the ceramic phase. Ytterbium III trifluoromethanesulphonate hydrate (Sigma-Aldrich) was employed as a curing agent. Finally, EP 2101 (Eurostac), was used to consolidate plasters sample useful as a reference for our formulations. This cycloalifatic epoxy resin is produced in the form of a 25% solution in toluene and isopropanol. The hardener is an aliphatic polyamine solution that is mixed with the resin in the proportion 1:5 in weight.

2.2 *Preparation method*

The polymerization of the epoxy silica resin TEGO RC 1411 and of the CE resin were obtained with the addition of different amounts of ytterbium catalyst, previously dissolved in propylencarbonate, in the proportion propylencarbonate: ytterbium = 2:1 by weight. In order to favor the silica deposition in the CE formulation, GPTS as a coupling agent was added in the proportion CE:GPTS 80:20. The inorganic precursor was added to both the epoxy resins in the range within 5–60 per hundred resin (phr). After the films characterization, the formulations were applied on the dry plaster samples, constituted of an aerial mortar of magnesian lime. Specimens were brushed until apparent refusal that was considered to be reached when the surface remains wet for two minutes.

2.3 *Characterization techniques*

Dynamic mechanical thermal analyses (DMTA) were performed with a Rheometric Scientific MK III instrument at a frequency of 1 Hz in tensile configuration. The morphological characterization of pristine resin and of the material cured in the presence of TEOS was carried out by means of a Field Emission-Scanning Electron Microscope (FE-SEM, Hitachi S-4000).

The morphology and texture of the samples were studied by means of a Scanning Electron Microscope (SEM, Hitachi S3200-D), acquiring an SE (Secondary Electron) signal. Colorimetric measurements were made using a spectrophotometer MINOLTA CM 700d, using the LAB system space, according to the Italian Normal Recommendation 43/93. The measurements were performed before and after ageing test, carried out by means of a QUV tester/SE Accelerated Weathering Tester (Q Panels Lab Product) producing UVA (310–400 nm).

3 RESULTS AND DISCUSSION

The first goal of this study was to define the correct percentage of thermal initiator and TEOS in order to obtain formulations with a useful pot-life that also allow the formation of the silica domains inside the organic matrix. After the TEOS addition, a reduction of the viscosity and an extension of the pot life were achieved. The high gel content value obtained (about 95%) indicates that the silica precursor did not significantly influence the polymerization process. As the transition temperature (T_g) of the CE is too high for this kind of application, the monofunctional monomer CY was added in order to reduce the cross-link density.

The flexibilization of the films has also been confirmed by DMTA analysis: the T_g value is reduced from 110°C to 70°C after the addition of 25% of CY, and also in this case without the use of any solvent. The morphology of the cured film was investigated by FE-SEM on the surface fracture. The inorganic in situ generated domains are well dispersed within the organic network and have an average size of around 60–80 nm. Thanks to these properties, both the hybrid films are transparent to visible light and furthermore an increase of hardness, adhesion properties and thermal behavior was verified (Tulliani et al. 2011).

The studied formulations were applied by brush on the plaster sample until refusal. SEM observations were performed to evaluate the penetration depth of the hybrid materials in the plaster samples and the morphological changes of the treated surfaces (see examples in Fig. 1). These parameters are strongly influenced by the viscosity of the resin and consequently are related to the TEOS amount added to the pristine resin. In fact, the best results were achieved when 40–60% phr of TEOS were added to the resins. It was observed that a penetration depth of about 1.5 cm was reached, the grains appeared more aggregated, porosity was maintained and film coating was not observed on the surfaces, as also demonstrated by mercury intrusion porosimetry measurements (Tulliani et al. 2011). The hydrophobic behavior of the two studied formulations is different. On one hand, the application of the epoxy resin TEGO, which has a siloxane backbone, increased the contact angle of the plaster's surface that became hydrophobic even in the presence of an important quantity of TEOS. On the other hand, the epoxy resin CE does not provide water repellency properties, even if water drops were not immediately absorbed by the treated surface of the plaster. In this way the water can slide down on the treated vertical surfaces of plaster. In both cases the capillary rise of water was reduced and a good water vapor transmission was maintained. The samples were exposed to a UV lamp for 1000 hrs to simulate a photo oxidative degradation and the total color difference (ΔE), as well as the changes in the yellow index (YI) were calculated. In accordance with the literature, we considered the treatment acceptable if the ΔE value is lower than 5 and compatible if it is lower than 3 (Delgado Rodrigues & Grossi 2007).

As expected, thanks to the reduction of the viscosity and the silica deposition, TEGO resin + 60% TEOS have a ΔE value lower than 3 that slightly increases after the UV light exposition. As highlighted in the introduction, the cycloaliphatic resins were chosen for their good behavior after artificial aging. For this reason the performances of CE formulations were compared with the commercial product EP 2101. In fact, the plasters treated with both resins showed a ΔE value lower than 3 which decreased further after aging due to the reduction of the Δa value (Fig. 2a). The YI rose slightly after the aging and it can be considered equivalent for the two treatments.

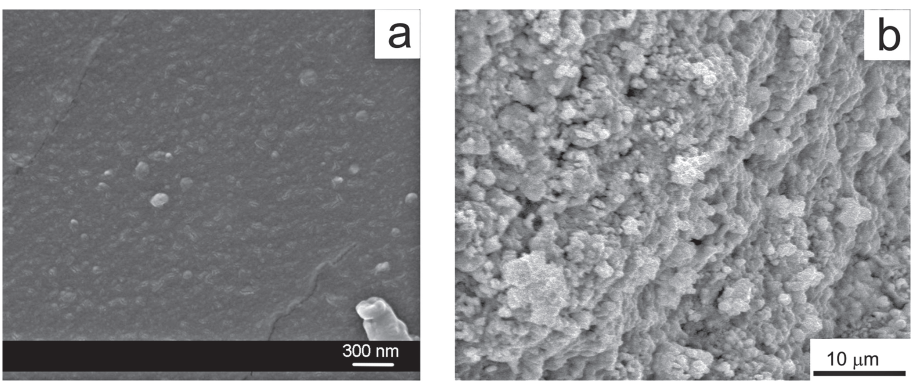

Figure 1. FE-SEM micrographs of cured TEGO + 40% TEOS (a) and of consolidated plaster cross-sections with CE + CY + GPTS + 40% TEOS at 2 cm in depth (b).

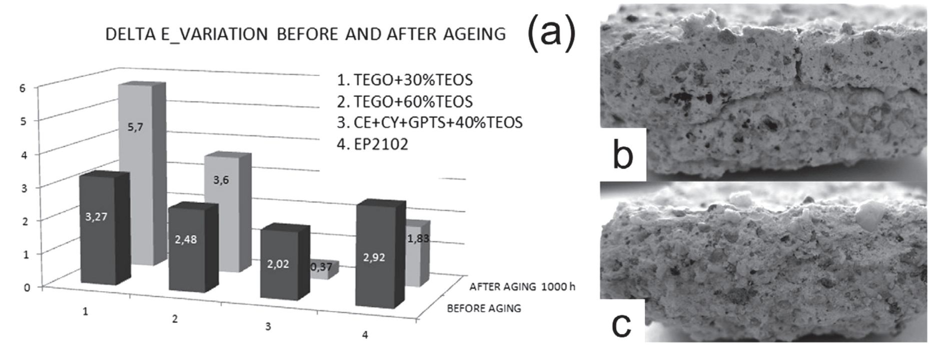

Figure 2. Colour evolution of treated plasters before and after artificial ageing (a) and images of two consolidated specimens after the 10th cycle, treated with EP2101 (b) and with CE (c).

Salt crystallization tests by total immersion were carried out according to the UNI EN 12370 recommendations, by using a 14 wt% solution of sodium sulphate decahydrate. The samples ($4 \times 4 \times 3$ cm^3) were consolidated with CE + CY + 40% TEOS, TEGO + 60% TEOS and EP 2101 by brush. In this way it was possible to evaluate the behavior at the interface between the treated and untreated surface. Comparing the trend of the sample's weight loss in relation to the aging cycle, it was noted that the worst behavior occurred for the untreated plaster (–45% of the initial weight) while the best one was reached by the sample treated with the CE + CY + 40% TEOS (–35%). After 15 cycles no salt efflorescence was found and it was observed that degradation occurs by pulverization of the binder and detachment of large flakes of plaster parallel to the main surface, so the samples are disintegrated at the corners and thinned. The consolidated samples show a predominant degradation on the untreated side, while the treated side appears more compact for about 1 cm that is the depth achieved by the consolidants. The degradation of the plaster is due both to the salt crystallization and to the thermal expansion to which the specimens are subjected every cycle. Even if the T_g of the formulation CE + CY + 40% TEOS is quite high for the consolidation treatment, as reported before, degradation phenomena related to its glass transition temperature were not observed. On the contrary, the plaster treated with EP 2101 showed a deep crack in the interface area (Fig. 2b).

4 CONCLUSIONS

New solvent free organic-inorganic materials as consolidants for lime plaster have been studied. In order to reduce the viscosity TEOS was added instead of a solvent. Moreover, thanks to the cationic polymerization, the in situ deposition of silica particles was obtained, avoiding the direct contact with nanometric materials and the resin was cured without amine. After that, the best formulations were applied to a plaster surface and good results in accordance with the requirements of a consolidant were obtained, in particular after the artificial aging carried out in the presence of salts and under UV light. We are now applying these formulations on an exposed wall in order to evaluate their behavior during a natural ageing process.

ACKNOWLEDGEMENTS

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Consolidation treatments for conservation of concrete sculptures

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ABSTRACT: Since the mid-twentieth century many artists have used cementitious materials in their projects. Currently, some of these works show evidence of decohesion which requires an adapted response to each case. This paper analyzed the behavior of two consolidants, tetraethyl orthosilicate (Estel 1000®) alone and blended with $Ca(OH)_2$ nanoparticles (Nanorestore®), on Portland cement mortars, following international recommendations for cultural interventions. The results obtained show that these products reduce significantly the hydric properties of the material and increase its mechanical strength. The color and gloss variations generated by the action of these treatments are near or below the limits of human perception. The interaction between the products and the cement resulted in the formation of a new C-S-H gel, with a longer chain length. Portlandite record is reduced with both products.

1 INTRODUCTION

The growing number of works of art from the twentieth and twenty-first centuries based on experimentation with new materials, which generate pathologies different than those already known in traditional heritage, has promoted the study of the decay and the search for solutions for their adequate conservation.

The conservation of cement sculptures is of great interest, because despite their supposed durability, some of these cultural properties have begun to show decay, either caused by intrinsic factors related to its execution or by extrinsic ones relative to its location and maintenance.

The lack of cohesion of the cement mortar or concrete can start the corrosion of the metallic armor or cause the complete disintegration of the good. However, the proposal and validation for consolidation of these materials, adapted to international recommendations on conservation and restoration of heritage, have been little discussed in the literature, mainly focused on stone heritage conservation.

Markets offer many products with consolidant properties developed for both construction industry and conservation of stone heritage. For this latter use, products must follow certain requirements such as not modifying the aesthetics, compatibility with the constituent materials of the piece and maximum long-term stability (Alcalde et al. 1990, Martínez 1996, Esbert et al. 1997, Esbert & Losada 2003, Villegas et al. 2003, Ferreira & Delgado 2008, Fort 2012).

Based on the mentioned requirements, this study aims to validate the consolidant effectiveness of the tetraethyl orthosilicate alone and blended with calcium hydroxide nanoparticles on Portland cement mortars.

2 METHODOLOGY

For the development of this study cement paste and mortar specimens were prepared. Cement mortar specimens measuring 70 × 60 × 10 mm and 10 × 10 × 60 mm were elaborated with a cement CEM I 42.5 N/SR, a cement: sand ratio of 1:5, and a water content specified by the standard UNE EN 1015-3 (2000). The standard sand was sieved in order to obtain fine-free sand ($\Phi \geq 1$ mm) which helps to increase the mortar porosity.

The specimens were cured in a moist chamber (>95% RH) for 28 days. With the same cement and curing conditions cement pastes were also prepared.

The chosen consolidants, tetraethyl orthosilicate (Estel 1000®) (A) and additivated with $Ca(OH)_2$ nanoparticles (Nanorestore®) (B) in 4:1 ratio, were deposited on to the mortars by brushing (until saturation for 1 minute). The treated samples were cured for three weeks at 21ºC and 45% (±3%) of RH.

Changes in mortars color and gloss induced by the two consolidants were determined as recommended by the NORMAL 43/93 (1994).

Porosity and pore size distribution of the cement mortar before and after coating were studied with a Micromeritics Autopore IV 9500 V1.05. Water vapor permeability coefficient, nowadays considered as one of the properties with most influence on mortars durability (Alexander & Magee 1999, Claisse et al. 2009, Claisse 2005, Aguilar 2007) and water absorption under low pressure were also found, as recommended by RILEM (RILEM II.2 and II.3 1980).

To evaluate the effect of the products on mortars mechanical properties (UNE-EN 196-1:2005), compressive and flexural strength tests were carried out in prismatic specimens (10 × 10 × 60 mm) and elastic modulus were determined by Acoustic Resonance spectroscopy (ARS).

The interaction between the consolidation treatments and the hydrated cement paste was studied on cement paste specimens which were crushed and impregnated with A and B products. The resulted mixtures were subjected to different relative humidity conditions (45 ± 3% and >90%) for three weeks, after which they were characterized by FTIR (Nicolet 6700-FT-IR) and ^{29}Si NMR (Bruker Advance-400 (9.4 T).

3 RESULTS AND DISCUSSION

3.1 *Physical and hydric characterization of the consolidated mortar*

Table 1 shows some of the physical and hydric properties of the mortar before and after being treated with the consolidants.

Table 1. Some physical and hydric properties of the cement mortar specimens before and after being coated with the two consolidants.

	Uncoated	A (Estel 1000®)	B (Estel 1000® + Nanorestore®)
Decline in water vapour permeability (%)	*	54.2	63.1
Decline in water absorption under low pressure (%)	**	40.68	80.23
Hg porosity			
Total (%)	12.9	9.47	8.80
$\Phi \leq 1$ µm (%)	7.76	7.57	6.64
Color			
L*	73.75 ± 1.26	68.88 ± 1.17	73.36 ± 0.12
a*	0.40 ± 0.03	0.50 ± 0.06	0.06 ± 0.12
b*	5.65 ± 0.25	6.78 ± 0.55	5.87 ± 1.54
ΔE*	–	5.03 ± 1.01	3.35 ± 0.20
Gloss units (85º)	0.17 ± 0.07	0.30 ± 0.05	0.40 ± 0.1
Compressive strength (MPa)	37.71 ± 4.56	55.15 ± 4.00	51.17 ± 6.62
Flexural strength (MPa)	7.88 ± 0.78	10.72 ± 0.89	10.65 ± 0.55
Increase in elastic modulus (%)	***	15.11	12.62

* $1.901715 \cdot 10^{-12}$ kg/ms Pa; ** 1.77 kg/m^{2}h; ΔE* (total color variation) = $(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$; *** 31.51 GPa.

The mortars coated with ethyl silicate and calcium hydroxide nanoparticles (4:1) (B) showed a higher decrease on the hydric properties than those treated only with ethyl silicate (A). The water vapor permeability was reduced by 54.2% with A and by 63.1% with B. The amount of water absorbed under low pressure decreased by 80.23% after the application of B and 40.68% with the consolidant A.

Neither of the treatments significantly modified the color and gloss of the mortar surfaces; treatment A darkened the surface more slightly than B, while the latter increased a little more the gloss. In both cases the color variations are within a range ($\Delta E^* < 5$) not perceptible to the human eye (Sasse & Snethlage 1996).

Both products noticeable increased the mechanical strength of the mortar; the compressive strength by 36 to 46% and the flexural around 35%. The elastic modulus determined by ARS, increased accordingly and was consistent with the reduction undergone by total porosity (26% with consolidant A and 32% with B), especially by the pores with a diameter over one micron.

3.2 *Chemical interaction of hydrated cement paste and A and B consolidant treatments*

FTIR spectra revealed a drastic decrease in intensity of O-H stretching vibrations of portlandite in pastes impregnated with treatment A, cured at both environments, but not in those treated with B at dry conditions.

Hydrolysis of ethyl silicate was accelerated in the presence of a higher relative humidity. So, S-O (1115 cm^{-1}) and Si-O (986 cm^{-1}) asymmetric stretching bands of sulfoaluminates and C-S-H gel (Fig. 1a), respectively, were extensively modified by the application of the two treatments: the increase in the intensity of the latter and its widening towards higher wavenumbers which overlapped the sulfoaluminates band were observed. In dry cured samples bands of ethyl silicate were just superimposed to the ones of cement paste.

^{29}Si NMR spectra (Fig. 1b) confirmed the interactions cement paste and consolidants in wet conditions (> 90%) as the relative increase in Q^2 (Si) (≈ –85 ppm) signals from the C-S-H gel regarding the ones of Q^0 (Si) (≈ –70 a –75 ppm) from the silicates in the anhydrous cement showed.

No bands were observed at –90, –100 or –110 ppm, that would indicate that ethyl silicate failed to produce polymerized Q^3 (Si) (planar structure) or Q^4 (Si) (three dimensional structures) units however it interacted with the silicates from the C-S-H gel increasing the number of units of silicates in the middle of the chain (Q^2 (Si)) and, therefore, the average length of the chain. When the consolidant also included calcium hydroxide nanoparticles, the structure of the C-S-H gel was modified once again, suggesting the participation of these nanoparticles on

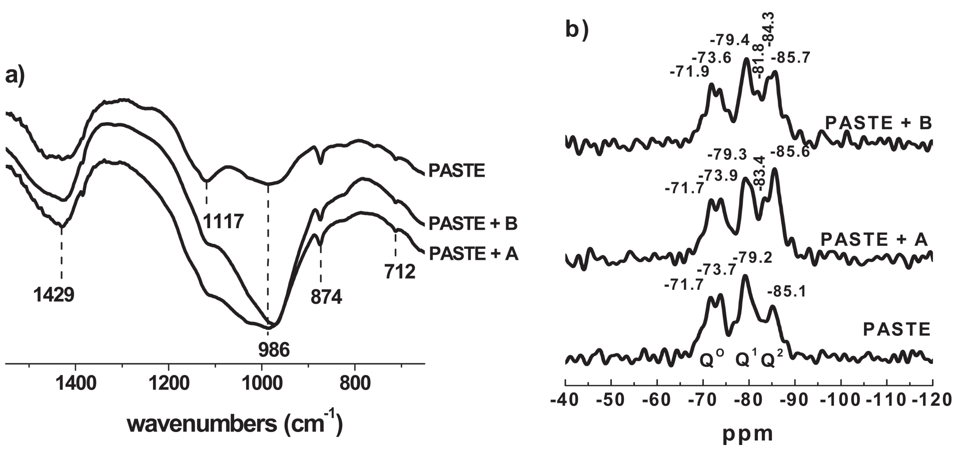

Figure 1. FTIR (a) and ^{29}Si NMR (b) spectra of the untreated and treated cement pastes with consolidants A and B cured in moist environment (>95% RH).

the C-S-H gel structure. The formation of this new C-S-H gel justifies the improvement of the mechanical performance, the decrease in porosity and permeability of the cement mortar.

4 CONCLUSIONS

The use of ethyl silicate or ethyl silicate with calcium hydroxide nanoparticles on cement mortars opens the possibility of particular investigations for its use in heritage since they generate related products. The formation of a new C-S-H gel justifies the improvement of the mechanical performance, the decrease in porosity and permeability of the cement mortar. It is necessary to note that these products modify the water vapor permeability, a factor that is of great importance for mortar future conservation.

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Thaumasite formation in hydraulic mortars: Thermodynamic studies

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ABSTRACT: Thaumasite is formed as a result of the reaction between sulfates, carbonates, and the calcium silicate hydrates present in old and new hydraulic mortars. Thaumasite formation is more prevalent in mortars exposed to low temperatures, high humidity and environments with high sulfate content. The present study aimed at ascertaining whether pH, type of aggressive solution and mortar composition may increase thaumasite formation. Thermodynamic modelling results (PHREEQCI program) have been considered for the evaluation of the potential risk of different ligands with less aluminates and silica fume addition causing thaumasite formation. Samples were immersed for 1 year in: $CaSO_4$, $MgSO_4$ and Na_2SO_4 (1500 ppm of sulphates). Thermodynamic results indicated that all solutions were in equilibrium with thaumasite. Samples immersed in $MgSO_4$ solutions were also in equilibrium with magnesium silicate, silico-aluminate, and carbonates. Thaumasite only formed over the surface of the sample exposed 1 year to $MgSO_4$ and $CaSO_4$ solutions.

1 INTRODUCTION

Thaumasite is formed as a result of the reaction between sulfates and carbonates and the calcium silicate hydrates present in old and new hydraulic mortars. It is well known that thaumasite formation is more prevalent in mortars exposed to low temperatures, high humidity, and environments with high sulfate contents, as well as mortars made with limestone aggregate (Blanco-Varela 2006, Nobst 2003).

There are a number of studies showing that pozzolanic cements has a superior resistance against thaumasite formation, however it is difficult to generalize the results. Some authors attributed this effect due to portlandite decreases from the pozzolanic reaction (Bellman 2003).

Compositions of aggressive solution can play an important role in thaumasite formation. The cation type (Ca^{2+}; Na^{+} or Mg^{2+}) associated with sulfate ions significantly influences concrete deterioration due to sulphate attack (Dehwah 2007). Then European Standards describe an accelerating test taking into account the solution composition, i.e., magnesium, ammonium, sulphate and pH. Pore solution composition in cement pastes changes drastically with pH, i.e in $MgSO_4$ solutions produces insoluble $Mg(OH)_2$ that decreases pH until 7. However in Na_2SO_4 solutions, portlandite is formed and pH increases until 12 (Cao 2008, Zhou 2006, Hoobs 2000].

The present study aimed to ascertain whether, pH, type of aggressive solution and mortar composition may further thaumasite formation. Thermodynamic modelling results (PHREEQCI program) have been faced to evaluate the potential risk of type of solution in thaumasite formation in cement mortar. In order to avoid sulphate attack through ettringite formation, ligands with less aluminates (CEM I SR) as well as 10% addition of puzzolanic materials (Silica Fume) have been used in mortars preparation, plane OPC (CEM I) was used as reference. Samples were immersed for 1 year in the following aggressive solutions: $CaSO_4$, $MgSO_4$ and Na_2SO_4 with 1500 ppm of sulphates.

2 EXPERIMENTAL

Two commercial cements were used CEM I 42,5 as reference and CEM I 42,5 SR. Silica fume (SF) was selected as pozzolanic material. Cements were analysed mineralogically by XRD (Siemens D500 diffractometer, monochromatic CuKα1 radiation only, selected with an incident beam germanium monochromator; 2θ recording range, 5–110º; count time per step, 0.5 s; step size, 0.019º). Pastes samples were prepared with an effective water to cement ratio of 0.25 and 0.27 for the cement samples and with SF respectively (UNE EN 196-3). Both cements were mixed with 10% of SF and placed in moulds of 10x10x60 mm. After casting the samples were allowed to cure 24 hours at 25ºC and 99% R.H. They were then demoulded and cured 28-days at 25ºC and 99% R.H. After this curing period the specimens were immersed in plastic containers with aggressive solutions: a) Na_2SO_4; b) $MgSO_4$ and c) $CaSO_4$ with 1500 ppm of SO_4^{2-} at 5ºC for 1 year. Water/aggressive solution ratio was 3/1.

The concentration of Na^+, Ca^{2+}; Si^{4+}; Al^{3+}; Mg^{2+} in solution in contact with samples were determined using inductively coupled plasma spectrometry (ICP Varian 725-ES); carbonate was determined as total inorganic carbon (TIC, Shimazdu TOC VCSH); and SO_4^{2-} by ionic chromatography (I.C., Dionex LC20). Finally the pH of the solution was determined with a pH electrode.

The PHREEQCI program (version 2) was run to determine the saturation and speciation rate of the different phases of the systems studied using solution concentration and pH. Thermodynamic data for aqueous species as well as for many solids were taken from previous papers (Martinez-Ramirez 2007).

3 RESULTS AND DISCUSSION

Mineralogical characterization of the anhydrous cements by XRD identified in both samples main clinker phases C_2S, C_3S, C_3 A, C_4AF, gypsum and $CaCO_3$.

Thermodynamic modelling is used to calculate the composition of the stable hydrate cement phases and of the surrounding solution assuming thermodynamic equilibrium. Thermodynamic data for aqueous solutions as well solubility products for cement minerals were taken from previous works (Stronach, 1996; Martinez-Ramirez 2007). Figure 1 shows composition of the solutions after 1 year of immersion of the specimens used as input to the calculations in the PHREEQCI program.

Table 1 summarized experimental pH solution after 1 year of immersion in the sulphate system. It was observed that pH solution is always lower than 10, then no portlandite is present in the aggressive medium and then instability of C-S-H is possible. Species with saturation index (S.I.) higher that solubility constant (K_s) can be considered as solid precipitate when the aggressive solution will be in equilibrium with the specimens. Thus S.I.values have been calculated with the PHREEQCI program and precipitate phases have been calculated (Table 1).

Figure 2 shows S.I. of thaumasite and ettringite in the aggressive solutions and it is clear that, in the equilibrium, aggressive solution will be oversaturated with thaumasite and undersaturated with ettringitte.

Thaumasite is, from thermodynamically point of view, stable in all the aggressive solutions as well as for any of the cement compositions studied. It is interesting to note that thermodynamic modelling indicates that solution becomes undersaturated of portlandite (and or brucite) in the studied conditions.

Pipilikaki (2009) indicates that thaumasite formation is a process that happens in two stages: in the first stage carbonation of the mortars surface occurs and the mortar becomes rich in calcite and in the second stage sulphates attack the C-S-H of the cement in the carbonated zone to form thaumasite. For the samples immersed in $MgSO_4$ solution no calcite is formed as different magnesium carbonate phases are thermodynamically stables.

From the experimental point of view only thaumasite was observed over the surface of the samples exposed 1 year to $MgSO_4$ and $CaSO_4$ solution. Figure 3 shows deposits of thau-

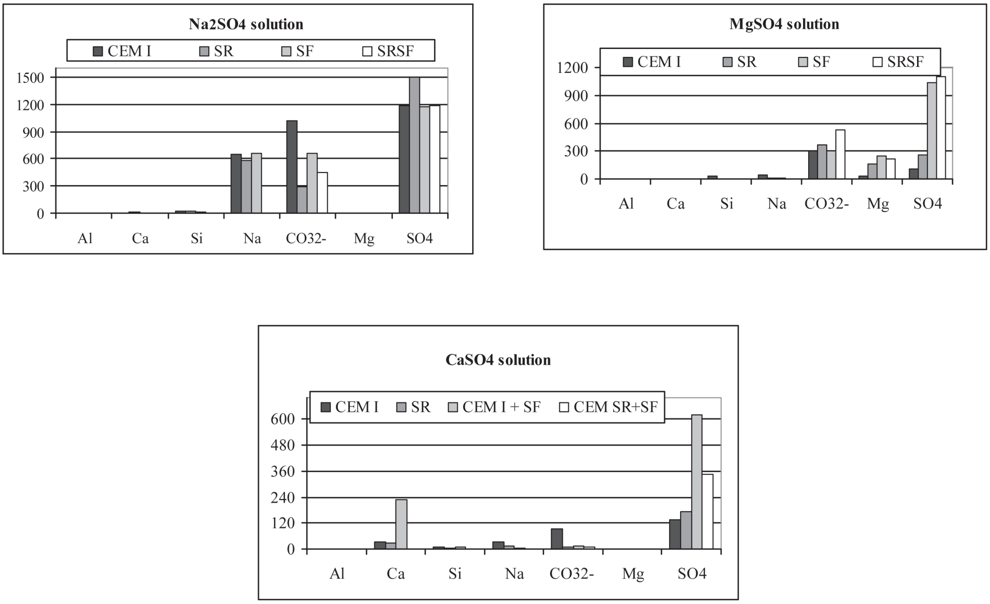

Figure 1. Solution composition after 1 year of specimens immersion. SR = CEM I SR; SF = CEMI + 10% SF; SRSF = CEM I SR + 10% SF.

Table 1. Experimental pore solution pH and phases with saturated index (S.I.) higher that solubility constant (K_s).

	Solution					
	$CaSO_4$		$MgSO_4$		Na_2SO_4	
Sample	pH	Phases	pH	Phases	pH	Phases
CEM I	8.5	Th	9.4	Th/A	9.6	Th/C
CEM I SR	8.9	Th	9.5	Th/B, M, D	9.0	Th/C
CEM I + 10% SF	8.6	Th	9.3	Th/M, D	9.6	Th/C
CEM I SR + 10% SF	8.4	Th	9.2	Th/A	9.2	Th/C

Th = thaumasite; A = magnesium silicate and magnesium silico aluminate; B = $MgCO_3 \cdot Mg(OH)_2 \cdot 3H_2O$; M = $MgCO_3$; C = $CaCO_3$ and D = $CaMg_3(CO_4)_3$.

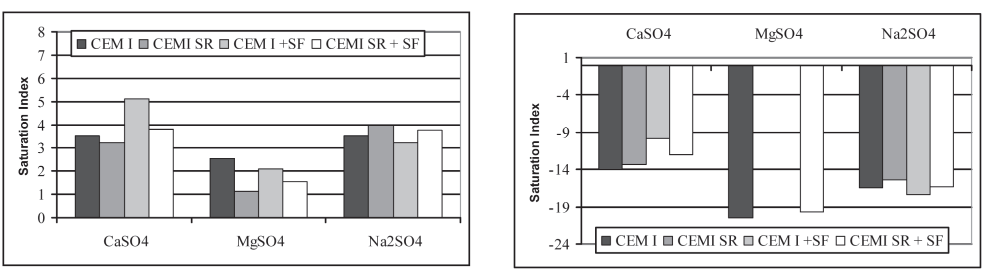

Figure 2. Saturation Index of thaumasite (left) and ettringite (right) for the specimens immersed in $CaSO_4$, $MgSO_4$ and Na_2SO_4 aggressive solutions.

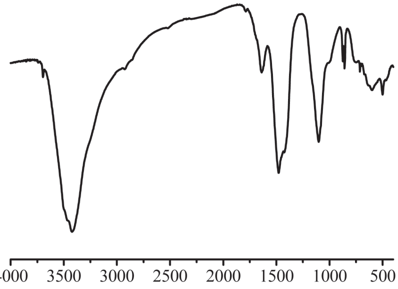

Figure 3. Sample CEM ISR immersed 1 year in $MgSO_4$ (1500 ppm) solution. FTIR analysis of the formed salt.

masite in the sample CEM I + SR immersed in $MgSO_4$ solution. Irassar 2009 indicates that surface damage on specimens exposed to $MgSO_4$, increases at low temperature. It could be due to the development of thin or null protective layer of $Mg(OH)_2/MgCO_3$ that accelerates the attack on the surface of specimens and the thaumasite formation.

4 CONCLUSIONS

Thermodynamic modelling indicates that thaumasite can be formed in sulphoresistent cement and in cements with pozzolanic additions. However, the experimental results further show that thaumasite formation occurs only in sulphoresistent and pozzolanic cement immersed 1 year in $MgSO_4$ and $CaSO_4$ solutions. Thermodynamically was calculated that calcite can be stable in cement systems in contact with Na_2SO_4 solutions (1500 ppm of sulfates). Portlandite consumption produces pH lowering and C-S-H instability.

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Permanent anti-graffiti for artificial construction materials: Lime mortar and brick

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ABSTRACT: The effectiveness of two permanent anti-graffiti treatments, a commercial fluoroalkyl siloxane and an organically modified silicate (Ormosil), in two artificial building materials, brick and lime mortar, was analyzed. The research was based on the assessment of the physical properties, cleaning efficiency and durability of the coated construction materials. The results showed that both treatments induced minimal chromatic variations in the materials surface. Ormosil was a better water repellent for its greater capacity to fill the pore systems that enhanced materials resistance to freeze-thaw cycles while lowering their water vapour permeability. Graffiti (alkyd spray paint) cleaning was satisfactory for the brick, after 4 cycles, particularly with the commercial anti-graffiti. On the other hand, lime mortar resisted only one cleaning episode, which removed not only the paint, but part of the material surface.

1 INTRODUCTION

The damage caused by the traditional agents of construction materials decay, namely water, air pollutants, biological agents and so on, is accentuated by direct human action in the form of graffiti and soiling. While graffiti can be found on nearly any surface, their effects—visual impact and deterioration—are especially pernicious in historic masonries: such as brick and stone walls.

Lime mortar, a traditional pointing and rendering material that fell into disuse when Portland cement started to be produced, is nowadays regaining attention thanks to the restoration of some of these historic masonry works (Maravelaki-Kalaitzaki et al. 2005, Myrin & Balksten 2006, Pavía & Caro 2006), and therefore it is susceptible, like other materials, to graffiti attacks.

Anti-graffiti coatings have been developed to protect the surface of construction materials by preventing paint from penetrating their pore systems or from adhering to the surface, since the removal of graffiti with traditional (chemical or mechanical) methods is not always successful and/or inevitably entails altering surface characteristics of the materials. These protective treatments at the same time that facilitate cleaning operations (with pressurized water, chemical products and so on) when applied to historic masonries must respect their aesthetic integrity (minimum changes in their gloss and colour) and not induce undesirable changes in superficial energy, permeability and so on.

This study aimed at assessing the effectiveness of two of these protective treatments a fluorinated commercial product (fluoralkyl siloxane) and an organically modified silicate (Ormosil), both known as permanent anti-graffiti, in two different materials, lime mortar and brick, which can be easily found in historic walls (studies in stones and cement with these anti-graffiti treatments have been published elsewhere (Carmona-Quiroga et al. 2010a)), since so many little research has been conducted to test the suitability of these new protective treatments in conservation of Cultural Heritage (Segalini et al. 2001, Di Gennaro et al. 2002, 2003, García & Malaga 2012).

2 METHODOLOGY

Lime mortar specimens measuring 70 × 60 × 10 mm were prepared with commercial lime mortar (Calhidro, Guipúzcoa, Spain) and a binder+sand/water ratio of 4.6/1 and cured until complete carbonatation in a chamber with CO_2. An in-plant waterproofed brick (with methyl siliconate to avoid efflorescence; Hermanos Díaz Redondo, Toledo, Spain) was the second artificial building material selected for the present study. Two permanent anti-graffiti treatments: a commercial product (waterbased fluoroalkylsiloxane, Protectosil Antigraffiti by Degussa) and a organically modified silicate (Ormosil) (Oteo et al. 1999) were chosen.

Changes in construction materials porosity, saturation coefficient, water-vapour permeability, colour and gloss induced by the two anti-graffiti were determined as specified in Carmona-Quiroga et al. (2010a). Cleaning (spray paints) efficiency was assessed by repeating 4 times the procedure described in Carmona-Quiroga et al. (2010b). Durability tests which included up to 30 freeze-thaw cycles and 2000 hours of UVA radiation were also conducted. The photochemical stability after UV exposure was analyzed by FTIR. The treatments response to SO_2-polluted atmosphere has been previously studied in Carmona-Quiroga et al. (2010c).

3 RESULTS AND DISCUSSION

3.1 *Physical and hydric characterization of the coated brick and lime mortar*

Some of the physical and hydric properties of the lime mortar and brick before and after being impregnated with the two anti-graffiti products are given in Table 1. Mercury intrusion porosimetry revealed that the fluorinated anti-graffiti had no effect on the total porosity (accessible to mercury) of both construction materials, whereas Ormosil, by filling the pores primarily with a diameter of under one micron, lowered their porosity by 11 (brick) to 21% (lime mortar). The water-vapour permeability of both materials declined accordingly by only 7 to 8% with the fluorinated product, while Ormosil lowered their permeability by 13 to 15% (Table 1).

Saturation (48 hours at atmospheric pressure) values were similar for both substrates before and after being coated with the commercial anti-graffiti (between 13 to 16 wt.%). This finding is consistent with the null decline in their porosity accessible to mercury (Table 1). By contrast, in the Ormosil-coated samples, the amount of water freely absorbed by the materials declined very significantly (around 90%).

Table 1. Some physical and hydric properties of lime mortar and brick before (UT) and after being coated with two anti-graffiti (standard deviation).

	UT lime mortar	Fluorinated	Ormosil	UT brick	Fluorinated	Ormosil
Hg porosity (%)						
total	38(2)	38.5(0.4)	30(1)	32.9(0.4)	31.8(0.6)	29.4(2)
≤1 µm	6.4(0.5)	6(1)	0.3(0.2)	32(1)	31.4(0.8)	28(2)
Saturation coefficient (% mass)	14.9(0.3)	12.6(0.6)	1.4(0.2)	15.2(0.6)	15.9(0.3)	1.3(0.6)
Decline in permeability (%)	^	7(5)	15(4)	^^	8(2)	13(4)
Colour						
L*	87(1)	88.5(0.4)	87.3(0.7)	61.7(0.4)	59.8(0.4)	58.3(0.5)
a*	0.2(0.1)	0.02(0.05)	0.2(0.1)	16.4(0.1)	17.9(0.1)	18.3(0.4)
b*	3.1(0.1)	2.7(0.2)	3(0)	27.2(0.2)	31.2(0.1)	29.4(0.8)
ΔE*		1.2(0.4)	0.5(0.4)		4.7(0.2)	4.4(0.8)
Gloss units (85º)	6(5)	16(4)	3(2)	3.2(0.4)	7.3(0.6)	1.6(0.5)

^ 29(3) ∗ 10^{-12} kg/ms Pa; ^^ 7.8(0.8) ∗ 10^{-12} kg/ms Pa; ΔE* (total colour variation) = $(\Delta L^{*2} + \Delta a^{*2} + \Delta b^{*2})^{1/2}$, L* = luminosity, a* and b* = chromatic coordinates, red and yellow axes, respectively.

The two anti-graffiti coatings darkened (denoted by L* value) the brick surfaces slightly and generated weak yellowing (b* coordinate), with minor variations (almost unnoticeable: $\Delta E^* \approx 5$) (Di Gennaro et al. 2002) in the brick overall colour. In lime mortar, colour changes were not observed with the naked eye ($\Delta E^* << 5$). Surface gloss was slightly raised by the commercial anti-graffiti and insignificantly lowered by Ormosil in both building materials.

3.2 *Cleaning efficiency*

Permanent anti-graffiti treatments should be durable enough to withstand numerous cleaning cycles. The lime mortar and brick coated with the two treatments were subjected to a total of 4. After that, total colour variation of the surfaces was measured (Fig. 1). Lime mortar resisted only one cleaning episode, after that not only the paints were removed, but part of the treated material surface (the low energy barrier), turning the protection in ineffective. In brick, no traces of paint after 4 successive cleaning cycles were observed ($\Delta E^* < 5$; Fig. 1). The characteristics of the substrate, namely its scant roughness and prior, in-plant waterproofing, favoured these good results. Nonetheless, the post-cleaning chromatic values of untreated brick surfaces revealed the importance of the paint repellence of the two anti-graffiti treatments, particularly the commercial one, in achieving such effective cleaning.

Further to the measurements of the brick chromatic parameters, the elimination of the paints slightly darkened and yellowed the surfaces, the first in the specimens treated with Ormosil and the second in the ones impregnated with the commercial anti-graffiti.

3.3 *Durability*

The results of the freeze-thaw cycles revealed that Ormosil improved brick and lime mortar resistance to frost by inducing a decline in their saturation coefficient (Fig. 2a, c). Meanwhile, the fluorinated anti-graffiti accelerated their deterioration by obstructing the egress of water trapped in the pore systems during successive thawing episodes (Fig. 2a, b, d).

Neither of the treatments exhibited decay after exposure to UV radiation (2000 hours) according to FTIR analysis.

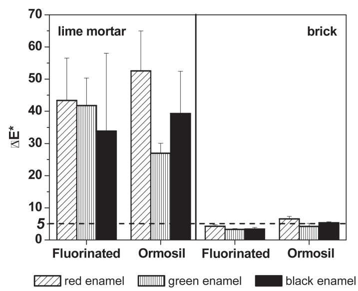

Figure 1. Total colour variation (ΔE^*) of the anti-graffiti coated brick and lime mortar after 4 successive painting-cleaning cycles.

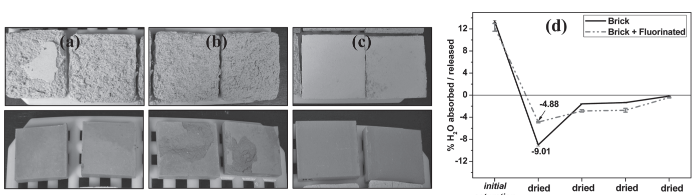

Figure 2. Pictures of lime mortar (above) and brick (below) uncoated (a); coated with the fluorinated anti-graffiti (b) and with Ormosil (c) after 30 freeze-thaw cycles. (d) Water desorption of brick untreated and treated with the fluorinated anti-graffiti.

4 CONCLUSIONS

The different behaviour of the two permanent anti-graffiti chosen, a commercial fluoralkyl siloxane and an organically modified silicate, reaffirms the necessity of their individualized testing prior to applying to historic masonry.

In bricks, cleaning was more satisfactory with the fluorinated treatment than with Ormosil; however the latter exhibited higher performance as a water repellent due to its capacity to fill the material pores, which translated into an improvement of brick resistance to frost and a high decline in material permeability. The fluorinated anti-graffiti, on the contrary, accelerated the weathering in freeze-thaw cycles by obstructing the egress of water trapped in the pore system.

In lime mortar cleaning was totally ineffective, with both treatments, due to its soft nature unable to withstand the several cleaning-painting cycles conducted. As it happened in brick, the Ormosil improved material resistance to frost and the fluorinated treatment worsened.

In spite of some of these drawbacks, both anti-graffiti seemed to fulfill the requirements of "invisibility" (minimum changes in gloss and colour) and "stability" (UV radiation) needed to be applied to built Heritage.

ACKNOWLEDGEMENTS

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Nanostructured products for the conservation of the wooden supports: Evaluation of their effectiveness and durability

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ABSTRACT: The present study is focused on both testing some commercial nanostructured products and measuring the effects on different wooden samples in order to evaluate their properties and their long-term effectiveness. Non-invasive and non-destructive analytical techniques have been utilized, suggesting a methodological approach for the control and monitoring of the nanocomposite coatings properties.

1 INTRODUCTION

The present study, developed within the University Master on "Nanostructured materials for Cultural Heritage", held at the University Centre of Agrigento (academic year 2010–2011), has the objective to evaluate the properties and the effectiveness of products, that offer water repellent properties, on different wooden samples, investigating the rate of water absorption into the treated wood after wetting processes and artificial ageing cycles. A specific methodological approach aimed to establish suitable procedures for systematic controls of wood samples, also used on works of art, has been proposed. As a matter of fact, the obtained data intend to offer a contribution to evaluate the potentiality of nanostructured materials in the conservation field.

2 MATERIALS AND METHODS

2.1 *Wooden samples*

The treatments have been performed on wood samples of spruce fir (*Picea abies, L.*), and of chestnut (*Castanea sativa, Mill.*) in order to compare the behaviour of the selected products, on a softwood and on a hardwood, respectively.

For each specie, 15 rectangular samples, (6 × 4 × 2 cm), without knots and cracks, have been cut tangentially from modern wooden board. Six blocks for each species have been selected for the application of each nanostructured product to have a representative number of data per treatment: three blocks have been treated before the artificial ageing and the other three after the ageing. Each sample has undergone a complete diagnostic procedure in order to assess and record the untreated sample properties and monitor their variations following the application of the coatings. The proposed protocol consists of different steps as listed below:

- preliminary characterisation of the untreated wooden samples, also at dried and wet state (static angle-contact, nuclear magnetic resonance (NMR) relaxometry and colorimetric measurements);
- artificial ageing of six samples per specie in an accelerated weathering chamber with pre-determined thermo-hygrometric cycles;
- characterisation of the aged samples (static angle-contact, NMR relaxometry after absorption of distilled water by capillarity for 48 h, colorimetric measurements);
- application of nanostructured products on the samples "as such" and analytical measurements (static angle-contact, NMR relaxometry after absorption of distilled water by capillarity for 48 h, colorimetric measurements);
- artificial ageing of the treated samples and analytical measurements (static angle-contact, NMR relaxometry after absorption of distilled water by capillarity for 48 h, colorimetric measurements).

Other characterisation measurements, aiming to evaluate the permanency and effectiveness of the products after ageing and their performances when applied on unaged or aged wooden surfaces, are currently in progress.

2.2 *Nanostructured products used for the treatments*

Two nanostructured products have been tested: Surfapore W®—NanoPhos (SWN) and MP NanoProtector®—Nanotech system, Multiproducts (MPN). SWN has a water based formulation, consisting of different nanoparticle sizes, intended to penetrate into the mass of wood and to bond with the hydroxyl groups of the cellulose content. A nano-emulsion of paraffin ensures a lasting surface protection. MPN is designed to penetrate deeply into the wood fibres, blocking the access to the water, oil, dust, etc. without occluding the porosity. Both products have been applied by brushing on all the sides of the samples to give them a uniform behaviour towards the experimental conditions and allow water to enter or leave the wood only through the coatings.

2.3 *Experimental techniques*

NMR relaxometry: an excellent tool to determine the wood moisture content of coated and uncoated wood samples following water absorption and to distinguish between bound and unbound water. The measurements of relaxation times were performed by a Bruker single-sided NMR at the UniNetLab. Transverse relaxation time T_2 was acquired using the CPMG pulse sequence. *Colorimetry*: a contact spectrophotometer (Minolta CM-2600d) records the spectral reflectance factor (SRF) curves that were used to calculate CIELAB colour coordinates in order to monitor eventual chromatic changes induced from different treatments. The integrated sphere allows colour determination in the d/8° geometry, based on spectral acquisitions from a 3 mm diameter circular spot. The spectra acquisition was performed in the 400–700 nm range at 10 nm intervals in specular excluded (SPEX) mode. The colour data were calculated under the D65 standard illuminant using the colour matching functions associated with 10° observer (Oleari 2008). *Static contact angle*: a First Ten Angstrom FTA1000C instrument was used at the Laboratory of Materials for the Conservation and Restoration of Cultural Heritage (DICAM-University of Palermo).

3 RESULTS AND DISCUSSION

3.1 *Samples of Spruce*

3.1.1 *Treatment with Surfapore W®*

Static contact angle measurement: The application of the product give to the sample surfaces hydrophobic properties: after about 90 s from the release of the droplet on the block, the value of the contact angle is around 90°.

NMR relaxometry: Three contributions due to different water molecules, i.e. constitution water, bound water and free water, may be identified in the samples, independently from the product application. As an effect of ageing, a lowering of the peak related to free water is clearly visible in both treated and untreated samples (Fig. 1).

Colorimetric measurements: The comparison from SRF curves of treated samples before and after the ageing evidences a lightness decrease in the visible range, except for a small residual in the red region (600–750 nm). The main effect of ageing is the increment of chromatic coordinates a* (+a* = red and –a* green) and b* (+b* = yellow and –b* = blue) with high (>2) Δa* and Δb* values (Fig. 2), which correspond to color changes visible by the human eye.

3.1.2 *Treatment with MP NanoProtector®*

Static contact angle measurements: The application of the product gives greater hydrophobic properties to the surface of the samples than those obtained with SurfaPore W®: after about 50 s, the value of the contact angle does not tend to decrease but remains constant at around 110°.

NMR relaxometry: A response similar to that obtained with the application of SurfaPore W® was observed.

Colorimetric measurements: The product induces effects similar to those previously discussed, and also in this case, the high values of Δa* and Δb* due to the effects of ageing, make the colour differences perceptible by the human eye.

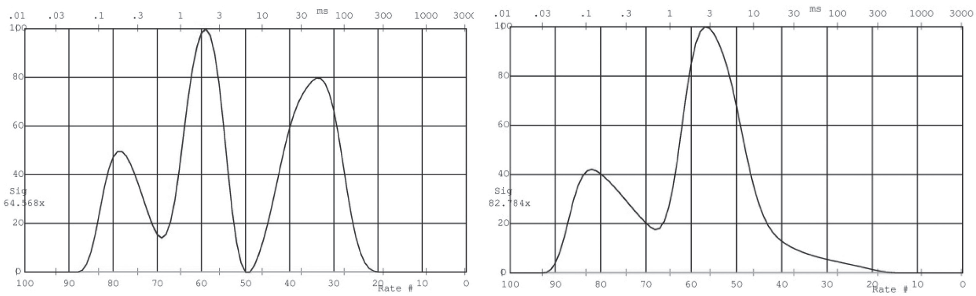

Figure 1. T_2 distribution for a treated sample (left side), where three contributions of water are visible, the constitution water (around 0.1 ms), bound water (around 1–3 ms) and free water (around 30–50 ms). T_2 distribution for the same sample after ageing (right side).

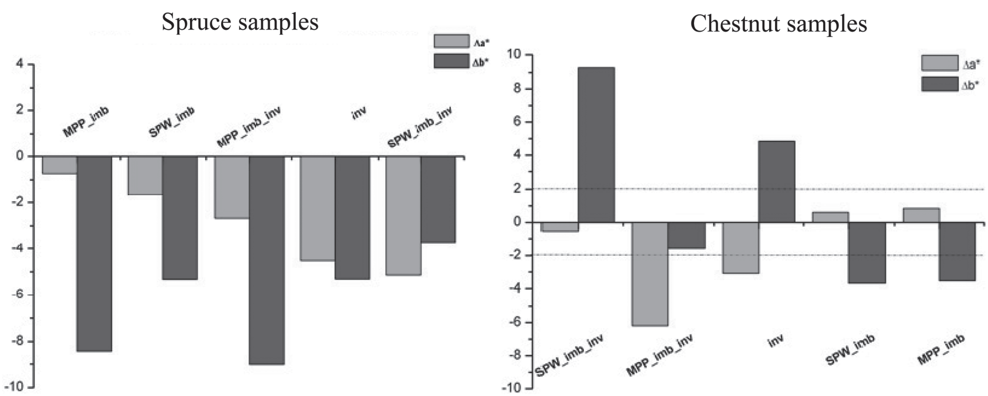

Figure 2. Chromatic differences Δa* and Δb* measured for Spruce and Chestnut samples, respectively.

3.2 *Samples of Chestnut*

3.2.1 *Treatment with Surfapore W®*

Static contact angle measurements: The treatment induces hydrophobic properties to the sample surfaces as after about 90 s, the contact angle is around 90°.

NMR relaxometry: The contribution of free water would seem to decrease due to the presence of the nanostructured coating. After ageing, the free water T_2 peak is quite intense.

Colorimetric measurements: The product induces the same variations noticed in the Spruce samples. The very high ΔE color differences can be mostly attributed to lightness (L*) variations caused by ageing. Unfortunately, after the ageing, the measurements have been affected by wood tannins, solubilized during the wetting, which have induced a significant surface blackening.

3.2.2 *Treatment with MP NanoProtector®*

Static contact angle measurements: The value of the contact angle is around 90° as in the chestnut samples treated with SurfaPoreW®.

Results of NMR relaxometry: All three contributions due to water are present in the wet samples, whereas after the accelerated ageing, the contribution of free water within the structure seems to be greater than that observed for the previous product.

Colorimetric measurements: The treatment determines the b* increase, while ageing causes its decrease with a simultaneous increase of a* values, greater than that obtained with Surfapore® (Fig. 2). Also in this case the values of ΔE are very high and attributable to L* changes due to ageing.

4 CONCLUSIONS

The decrease of the NMR peaks corresponding to free water molecules after ageing, found in the series of samples of Spruce coated with SurfaPoreW®, would suggest that the product succeeds in reducing the penetration of water into the system. This finding could also be related to the possible presence of paramagnetic species induced by the ageing process inside the samples. This hypothesis will be checked out through complementary diagnostic analysis, such as ESR and SEM.

As confirmed by static contact angle measurements, the treatments induce hydrorepellency. Furthermore, it was found that the treatments and artificial ageing gives rise to high chromatic variations. Unfortunately, in the case of Chestnut wood the colorimetric measurements are affected by the presence of wood tannins solubilized during the wetting and ageing processes.

The main aim of this ongoing research is to acquire data and experiences to give a real contribution to set up a methodological protocol for the control of wooden surfaces coated with nanostructured products, eventually also suitable for wooden materials of historical and artistic interest.

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Design of new gypsum-lime based mortars applied on the restoration of Mudejar heritage from Aragon (Spain)

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ABSTRACT: The region of Aragon is one of the most important centres of Mudejar architecture in Spain. It is characterised by the use of brick masonry with gypsum-lime based mortars-filled joints as the main building materials. Nowadays, these materials are continuously exposed to different causes of deterioration making it necessary to establish a restoration program. The main goal of this paper is to design new gypsum-lime repair mortars compatible with traditional building materials. Compatibility requirements for new repair mortars were defined based on the reproducibility of the original mortar characteristics. As a consequence, mortars were prepared by varying the binder proportions, the type of aggregates and the binder/aggregate ratios and were characterized by means of physico-mechanical analysis. Since they were prepared following a systematic procedure and observing standards, the results indicated their suitability to be used in building restoration plans. Knowledge obtained provides practical information to establish a fitting mortar mixture for restoration repairs on Mudejar monuments.

1 INTRODUCTION

Gypsum based mortars were very frequently used during the Mudejar artistic period in Spain from the 12th to 16th century, not only for joints in exterior walls but also for rendering and the plaster decoration of historical buildings.

During the last century, these mortars were replaced with other incompatible materials, which caused even further damage to the masonry structures. Nowadays, it is a known fact that both old and new materials must display similar characteristics. According to Rossi-Doria (1986), compatibility between the new repair mortar for restoration purposes and the original components must be based on the reproducibility of its main characteristics such as mineralogical and chemical composition, physical and mechanical properties.

As a consequence of increasing interest and recommendations to use gypsum based mortars for restoration, new gypsum-lime repair mortars compatible with traditional building materials were elaborated in this research. Different mortars were prepared according to the composition variability of the ancient materials themselves which had been previously characterized (Igea et al. 2010, 2012). This meant varying the binder proportions (gypsum/lime), the type of aggregates (siliceous or alabaster gypsum), the binder/aggregate ratios and different curing periods.

The aim of this paper was to characterize the physico-mechanical behaviour of the different gypsum-lime mortars as a function of curing time in order to compare with ancient mortar characteristics. Mechanical strength and porosity measurements were performed after curing periods of 1, 28 and 90 days. The knowledge obtained from the studied mortars provides practical information to establish a suitable mortar mixture for restoration works on historic buildings and modern architecture where gypsum-lime based mortars are used.

2 METHODOLOGY

2.1 *Materials*

Compatible gypsum-lime mortars for restoration were prepared using different commercial raw materials. A preliminary thermal analysis by means of DTA-TG of the binders and aggregates was carried out to determine their composition.

The mortars were made up with two different binders based on the compatibility of the materials with old Mudejar mortars; calcium sulphate hemihydrate and air lime of class CL90-S. Both binders displayed >75% in bassanite and portlandite, respectively and low proportions of calcite (<10%) were also presented in the thermal analysis. Quartzitic sand (angle-shape siliceous aggregates (99%, SiO_2)) and alabaster aggregates (rounded-shape gypsum aggregates (95%, $CaSO_4 \cdot 2H_2O$)) were selected as both had been detected in ancient mortars. To improve the workability of the mixtures, tartaric acid (0.1% by weight of binder) was added as a retardant in the blending process of the binders.

2.2 *Mortar preparation*

Different restoration mortars were prepared manually according to European standard (UNE-EN 13279-2, 2004) and following the patterns of ancient gypsum-lime mortars previously analysed.

In the first step, three types of binder mixtures (calcium sulphate hemihydrate/air lime) were proposed: 1:1; 1:0.4 and 1:0.2 by weight, establishing two kinds of mortars according to the aggregate used: gypsum-lime with quartzitic sand aggregates (GL-QS) and gypsum-lime with alabaster gypsum aggregates (GL-AG). In the second step, three different binder/aggregate ratios were prepared: 1/1; 1/2 and 1/3 by weight, with a total of nine different mixtures made up for each type of aggregate (Table 1).

Both dry binders were thoroughly mixed for 15 min. Admixture (solid tartaric acid, 0.1% in weight) was then added to the mixing process for 1 h. The mortar pastes were obtained using the amount of water required to achieve normal consistency and a good workability measured by the flow table test. Binder was manually mixed together with the water for 1 min. Aggregate was then added and mixed for 1 min at low speed using an Ibertest automatic mixer. The mortars were cast in prismatic 40 × 40 × 160 mm casts. They were then

Table 1. Characteristics of the nine different mortar mixtures prepared with a total of 54 samples.

Mortar	Binder*	Aggregate	Csh**: Air lime ratio	Binder/Aggregate ratio		
GL-QS	Csh:Air lime	Quartizitic	1:1	1:1/3	1:0.4/3	1:0.2/3
			1:0.4	1:1/2	1:0.4/2	1:0.2/2
			1:0.2	1:1/1	1:0.4/1	1:0.2/1
GL-AG		Alabaster	1:1	1:1/3	1:0.4/3	1:0.2/3
			1:0.4	1:1/2	1:0.4/2	1:0.2/2
			1:0.2	1:1/1	1:0.4/1	1:0.2/1

Binder*: Admixture: Tartaric acid (0.1% by weight).
Csh**: Calcium sulphate hemyhidrate.

slightly pressed to free any air bubbles and released from the mould after 24 h. Three prismatic specimens of each of the nine mortar mixtures prepared were obtained with a total of 54 samples (Table 1). A forced carbonation chamber was used to subject samples to a CO_2-saturated atmosphere at a temperature of 20 ± 5°C and a relative humidity of 65% to accelerate the carbonation process until the test day.

2.3 *Analytical methodology*

Compressive and flexural strength were measured according to European standard (UNE-EN 13279-2, 2004). Three samples of each mortar mixture were tested to ensure the validity of the results after curing times of 1, 28 and 90 days with a total of 162 specimens. Samples were previously dried at 40ºC up to constant weight. The flexural test was performed on the mortar specimens using a Netzsch tester. Compression strength test was measured on the two fragments of each resulting specimen from the previous flexural test with Ibertest-Autotest 200/10 equipment.

The open porosity was determined by Mercury Intrusion Porosimetry (MIP) using a Micromeritics Autopore IV 9500 porosimeter. Irregular fragments from samples with 10 × 10 × 10 mm dimensions were taken to characterize the evolution of the mortar porosity and its relation to other properties during the curing time (1, 28 and 90 days).

3 RESULTS

3.1 *Mechanical behaviour*

Figure 1 shows the measured compressive strength of the samples versus curing time (1, 28 and 90 days). The results obtained confirm an increase in mechanical resistance of all the mortar mixtures after the tested curing time as a consequence of the development of the carbonation process in each mortar. Samples with lower lime binder and aggregate amounts show the most significant results in both mortars (Fig. 1).

Concerning the evolution of resistance versus curing time, all the mortars analysed reach 65% of their maximum strength value at 28 days and close to 90% after 90 days of curing. In several specimens with 1:0.4 and 1:0.2 binder ratios, similar resistance at both 28 days and 90 days can be observed. On the contrary, it can be emphasized that only the mixtures with the lowest aggregate proportions (1:1/1, 1:0.4/1, 1:0.2/1) show a high rise in strength after up to 28 days of curing (Fig. 1).

The compressive values shown by GL-AG mortars are always lower than the results obtained in GL-QS mortars (Fig. 1). Flexural strength indicates a similar trend to that of the compressive values in both mortars. GL-QS mortars again display a much higher resistance

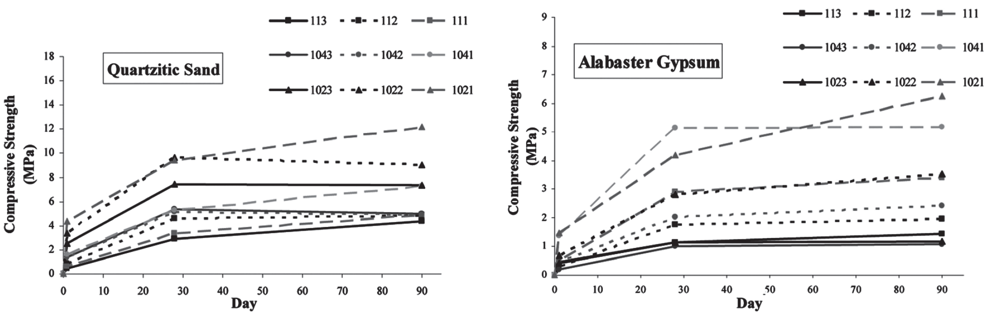

Figure 1. Compressive strength results in all the mortar mixtures vs. curing time. GL-QS mortars (left); GL-AG mortars (right).

Table 2. Comparative results of compressive strength and open porosity between ancient and repair mortars (90 days of curing time).

Mortar	Sample (*)	Compressive Strength (MPa)	S.D**	Open porosity (%)	S.D**
Repair	GL-QS (54)	6.6	2.6	29.4	2.5
Repair	GL-AG (54)	3.0	1.8	32.2	2.1
Ancient	Mudejar (30)	3.8	1.7	30.3	2.2

* Total samples analysed.
** Standard deviation.

Table 3. Open porosity (%) of mortars prepared at different curing times (1, 28 and 90 days).

		Binder/Aggregate ratio								
Mortar	Day	1:1/3	1:1/2	1:1/1	1:0.4/3	1:0.4/2	1:0.4/1	1:0.2/3	1:0.2/2	1:0.2/1
GL-QS	1	29.0	30.6	50.7	27.3	34.1	26.4	28.4	35.6	29.0
	28	28.5	29.7	48.7	25.7	30.2	32.3	25.5	27.3	32.5
	90	30.9	32.2	30.3	26.9	30.6	30.7	24.6	27.3	30.7
GL-AG	1	30.5	29.7	42.7	29.1	29.0	38.3	28.8	30.8	34.8
	28	30.9	35.0	41.1	30.8	30.6	33.6	33.9	28.9	34.6
	90	30.0	30.7	34.5	30.6	33.2	35.9	30.5	31.3	33.1

than that obtained for GL-AG mixtures. The inclusion of angle-shape siliceous aggregates with a suitable grain size distribution made it possible to develop faster and more complete carbonation and greater strength in GL-QS mortars.

Table 2 shows comparative results of compressive strength between Mudejar and restoration mortars. GL-AG mortars display similar mechanical resistance than ancient mortars whereas GL-QS mortars show higher resistance obtaining the best results after 90 days of curing time.

3.2 *Porosity*

The results of open porosity of both mortars versus curing time (1, 28 and 90 days) obtained by means of MIP are given in Table 3. From these results, it can be seen that the porosity values show significant differences between the prepared mixtures of each type of mortars. Comparing the samples with the same binder amounts at early ages (from 1–28 days), it can be observed that porosity increases due to the small amounts of aggregate. In general, at long-term curing time (90 days), the porosity values are very similar to the results obtained at 28 days and the porosity ranges from 25 to 36% for all the mortar mixtures prepared (Table 3). These values are compatible with the results obtained in other gypsum based historic mortars (Table 2).

In the GL-QS mortars, only the mixtures with lower aggregate amounts and different lime proportions (1:1/1, 1:0.4/1, 1:0.2/1), show a reduction in porosity values from 28 days of curing time (Table 3). A higher early porosity allows a faster carbonation in these samples, reducing the porosity values at long-term curing time and improving the strength (Fig. 1). No significant changes were identified in the porosity values at the different curing times in GL-AG mortars, only specimen 1:1/1 shows a significant reduction over the curing period (Table 3).

4 CONCLUSIONS

Gypsum-lime based mortars prepared are suitable for restoration purposes and are compatible with the traditional building materials of Mudejar Heritage. GL-QS mortars, in particular specimens with less quantity of lime binder and also particular aggregate contents (1:1/1; 1:0.4/1 and 1:0.2/1 samples), achieved the best results in the development of physico-mechanical properties over the curing times. The knowledge obtained from the studied mortars must been taken into account to establish a fitting mortar mixture for restoration works and to avoid mortar decay after applying it to masonry.

ACKNOWLEDGEMENTS

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

Old materials, new solutions

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ABSTRACT: The contribution of this paper in the Conference is to present the first results collected at the first phase of the documental study R & D & I project "*Materiales y métodos en los tratamientos de refuerzo de pintura sobre lienzo mediante entelados a la gacha: documentación, función y conservación*", supported by the Ministerio de Economía y Competitividad (MINECO). One of the aims of the project is the compilation and evaluation of the recipes, methodologies and tendencies developed during centuries through documental and experimental studies, to prove their behaviour physical-chemical and stability, in addition to propose improvements and preventive conservation guidelines.

1 INTRODUCTION

In this Conference, we present the first results of the documental study conducted in the 1st phase of the R + D + i project "Materials and methods of pasta linings for the reinforcement of canvas paintings: documentation, functionality and conservation", supported by the Ministerio de Ciencia e Innovación (MICINN) and led by the Complutense University of Madrid (UCM). A multidisciplinary team of international experts in this area has been meeting representing the countries where pasta linings have been usually carried out, as the Mediterranean basin (Spain, Portugal, France and Italy) and northern Europe (Denmark, Netherlands and the UK).

Ana Macarrón (IP) (UCM) and Ana Calvo, UCM and Research Center for Science and Technology in art (CITAR), Laura Fuster and Sofía Vicente, Polytechnic University of Valencia (UPV), Paul Ackroyd (National Gallery, London), Marion F. Mecklenburg (Smithsonian Institution), Joan Reyfsneyder, (The Florence Conservation Resource Center), Mikkel Scharff and Cecil Krarup, (Royal Danish Academy of Fine Arts, School of Conservation), Matteo Rossi (Laboratorio Torrimprieta), Aurealia Chevalier (Université Paris I Panthéon Sorbone, Atélier Chevalier), Kate Seymour (Stichting Restauratie Atelier Limburg, SRAL), Erminio Signorini (Cesmar 7).

The Museo Thyssen-Bornemisza, Museo Nacional del Prado and Patrimonio Nacional, from Spain, also collaborate in the project. As Promoters Contributors (EPO) takes part the companies CTS and Productos de Conservación. The research is integrated into the activities of "Research Group UCM (930420): Documentation Techniques, Heritage Conservation and Restoration", Facultad de Bellas Artes, UCM. One of the aims of the project is to compare and evaluate the various recipes, methodologies and tendencies developed over centuries, beginning with the documental study conducted during the first phase of the research.

It is tried to study from an experimental point of view, their physicochemical behavior, and its stability against environmental factors (RH, T, light), mechanical traction, and its compatibility related to the materials of the artwork paintings, taking into account the technical characteristics of the works of art, the mutations of the materials, and the environmental conditions of each country. The Smithsonian Institution (USA) also participates in the project advising on the structural tests to be performed.

Trying to determine the possible effectiveness and current convenience of a reinforcement treatment that has evolved over more than 300 years in Europe, whose materials are very

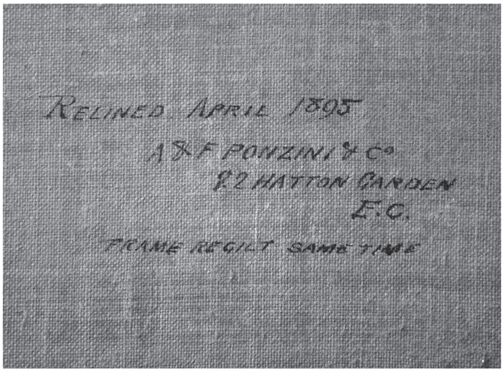


Figure 1. Signature of a lining intervention. (Photo: José Mendes. CITAR-Universidade Católica Portuguesa, Porto).

homogeneous and compatible with most canvas paintings, barely toxic, cheap and sustainable comparing them with the existing synthetic adhesives that has certain advantages, but also some drawbacks, and to suggest improvements and preventive conservation guidelines.

2 METHODOLOGY AND FIRST RESULTS OF THE PROJECT

2.1 *Phase 1: Documental study*

The structure of the project goes in three phases: documental, experimental and informative. In the first phase of the research collection of old and new recipe has been made, from the consultation of archives, treaties, invoices of materials, reports of restoration and information/data provided by restores through two inquiries developed for the old and currently lining research. These inquiries, translated into English and French, have been sent directly to official institutions and private restorers from Spain and Europe and published on the website of the Spanish Group of the International Institute of Conservation (GE-IIC).

The purpose of these questions is to establish a unified approach for issues concerning linings performed with this procedure previously and nowadays, in which wondered different aspects such as the terminology used to describe the procedure, details of the paintings, institutions, restorers and dates of intervention. Additionally, materials and proportions of the recipes, tools and methodology used, observation of the lining results (formation and correction of deformities, reversibility, stability, etc.) current conservation status of the painting (if the painting preserves the lining, or if it was necessary a later intervention due to this, etc.), environmental conditions of the exhibition and storage; and documentary sources from which the information has been extracted.

2.2 *Selection of case studies*

Amongst the documented artworks, a selection of paintings treated with this procedure has been examined in order to verify its current conservation status. It should be mentioned the following cases studies: the equestrian portraits of Felipe III and Margarita de Austria by Velázquez, "La fiesta del vino" by Brueghel, and "El sueño del Patricio" by Murillo, all of them in the Prado Museum; and "Cristo crucificado" by José Ribera, in the Diputación Foral de Álava.

2.3 *Development of database*

Moreover a relational Access Database has been designed to manage all the information collected, allows consulting and searching from different approaches and compare the vari-

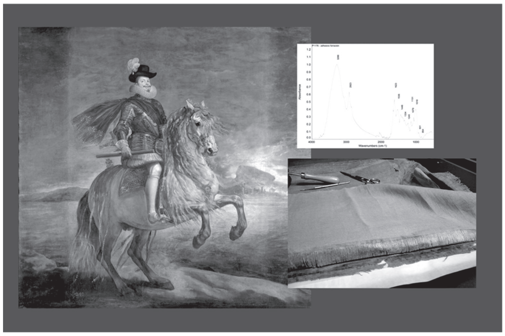


Figure 2. Case study: "Felipe III a caballo" by Velázquez. Museo del Prado. Restored by Andrés de la Calleja in the eighteenth century. FTIR spectrum of a sample lining adhesive. Removing the additions, process of reinforcement and protection of edges.

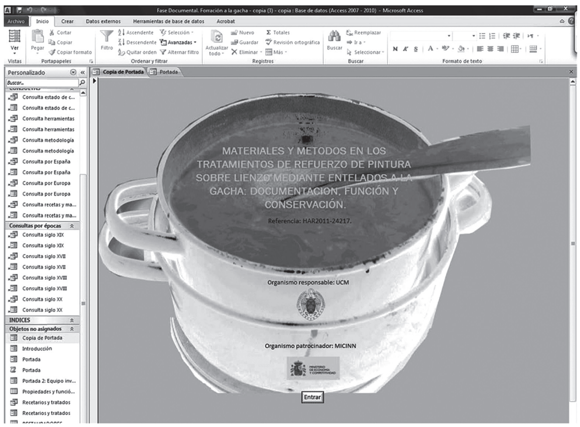


Figure 3. Screenshot of Database Access on lining.

ous recipes and procedures. The information of interventions can be consulted by periods, regions, materials, restorers, recipes books, treaties, among other bibliographies.

2.4 *Phase 2: Experimental study*

At this phase a study of adhesive qualities, dimensional and mechanical behavior will be performed (tensing and peeling tests), before and after the accelerate aging cycles on the testers that had been prepared with selected recipes and techniques to evaluate their stability, safety and innocuous properties and mechanical behavior.

Besides it will be done the chemical analysis of the samples that can be extracted from the original art work, in order to carry out the identification of the main components and different additives which have in their composition.

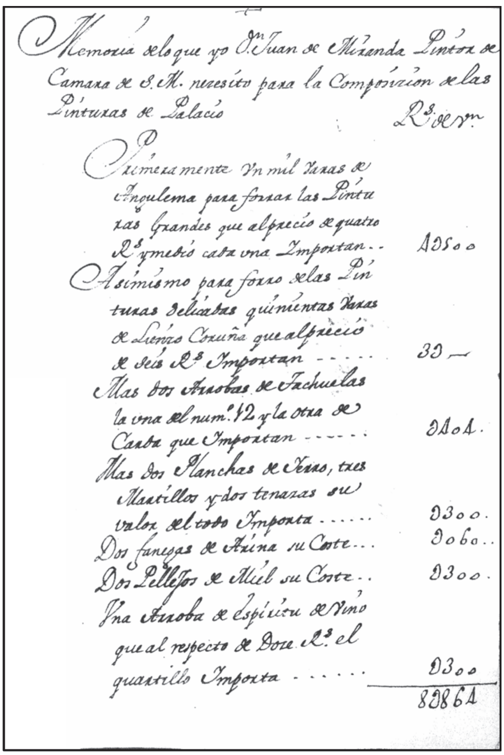
At this moment the only information that we have is about the adhesive from some of the selected works of art.

3 PROVISIONAL RESULTS

The results achieved are:

- Historical documentation of the procedure, by compiling recipes and processes used, throughout history until the present time.

- Valuable information about unknown cases and recipes have been collected, as those of Juan García de Miranda, who was an initiator of the procedure in the 17th century in Spain and many others until the 21st century, from recipe books and reports in Portugal, Denmark, UK, Italy and France as well as the signatures of the restorer on the back of some works, common practice since the late eighteenth and early nineteenth centuries.
- Creation of a library of images of the works of art studied and of the analysis performed.
- Elaboration of an interactive database.
- Analysis has been made on the adhesive of three paintings from the Prado Museum by Velázquez, Murillo and Brueghel. The first two are oils on linen canvas, and the third is glue-tempera. On all three, it was found starch + animal glue, which are the main ingredients of the glue paste. The analysis also presents traces of pine resin, corresponding perhaps to Venice turpentine present in most recipes, and traces of grease (information provided for this project by Mª Dolores Gayo, Head of the Analysis Laboratory at Prado Museum). "Grease", perhaps linseed and nut oil, appears in some lining material orders in 18th and 19th century. There are references to the oleaginous cover that was given to the painting and iron to prevent sticking.
- Regarding the objective of dissemination of the project, we can now point out the presentation of the first results in this Congress, and the organization of a One-day Seminar (October 15th, 2012) in the Thyssen-Bornemisza Museum, partner on the project on linings titled "Reinforcement treatments of canvas paintings: Studio cases, evolution and behavior".



Memoria de lo que yo Dn. Juan de Miranda Pintor de Camara de S. M. necesito para la Composizion de las Pinturas de Palacio — Rs. de vn.

Primeramente Vn mil Varas de Angulema para forrar las Pinturas Grandes que al precio de quatro Rs. y medio cada vna Importan .. — 4U500

Asimismo para forro de las Pinturas delicadas quinientas Varas de Lienzo Coruña que al precio de seis Rs. Importan ..... — 3U—

Mas dos Arrobas de Tachuelas la vna del num.º 12 y la otra de Canba que Importan ...... — U404.

Mas dos Planchas de Yerro, tres Martillos y dos tenazas su valor del todo Importa ..... — U300.

Dos fanegas de Arina su Coste... — U060..

Dos Pellejos de Miel su Coste.. — U300.

Vna Arroba de Espiritu de Vino que al respecto de Doze Rs. el quartillo Importa ...... — U300

8U864

Figure 4. Invoice of lining material by Juan de Miranda, in 1735. (Archivo de Palacio Real, Patrimonio Nacional).

Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

Application of the double layer system as preventive method in the moulding process of sculptures and ornaments

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ABSTRACT: The physicochemical properties of artworks of the Cultural Heritage are modified by degradative environmental agents and biodeterioration. In many cases, the most effective intervention is the replacement of the work of art by a copy, and, often the preventive conservation solution considers the moulding of the original and its reproduction by restoration mortars. In this regard, the analysis and optimization of various reagents substances used in a bilayer system during the moulding process on two different types of stone have been studied: one macro porous travertine and a micro porous biocalcarenite. This novel, innocuous system is based on the superposition of several layers, one directly on the stone with a nonpolar character the alkane hydrocarbon cyclododecane and another, polar, above it (funori or latex). All specimens were tested after accelerated aging by UV light and colour changes have been controlled by spectrophotometry and light microscopy (LM).

1 INTRODUCTION

The reproduction of historical materials and artwork has been since antiquity a form of conservation and dissemination of art. In many cases (historic) outdoor work of art is highly damaged, and it is essential to carry out a copy and to keep the original under controlled conditions, i.e., in a museum. The restorers are faced with the problem of protecting the work of art from the moulding materials when a copy has to be produced. In this sense, it requires the study of a separator which prevents adhesion of any moulding material on the surface of the work, which at the same time forms a thin film allowing to keeps the details of the surface, non-staining and, of course, allowing subsequent easy removal.

This last feature is of great importance in very porous stone supports, as the interest lies in investigating substances that do not require a removal phase and therefore avoiding the application of chemical or physical means on the work. Until now, only a few scientific-technical studies attempted to solve this kind of persuasive performance through the use of easily reversible film-forming materials (Mas et al. 2006). Thus, the bilayer system presented is based on the use of an nonpolar substance (the alkane hydrocarbon cyclododecane CDD) and a polar substance (Fig. 1). The use of cyclododecane origins back to the middle of the 1990s, successfully applied to various aspects of the conservation and restoration of cultural assets as a temporary consolidating material (Hangleiter et al. 1995, Cagna & Riggiardi 2006, Hiby 2008, Riggiardi et al. 2010). However, scientific studies related to this substance in conservation and restoration of stone as a support are rare (Stein et al. 2000, Maish & Risser 2002).

The objective of this bilayer technique is to solve the problem faced by restorers when making a mould of a sculptural or ornamental object with micro and/or macropores, since the use of inadequate mould release substances is a focus of waste and unpredictable colour changes.

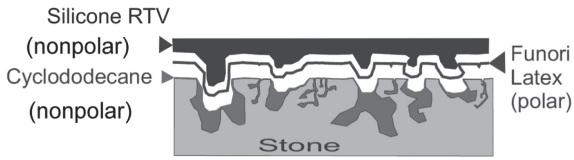

Figure 1. Sketch of the polar-nonpolar bilayer system applied on the porous stone.

2 EXPERIMENTAL METHODOLOGY

2.1 *Stony support*

The stone *Novelda Bateig cream* is a biocalcarenite rock with a high porosity and an average pore size of 0.12 microns, extracted from the Vinalopó Medio area (Novelda-Alicante, Spain). Remnants of shells or other type benthic organisms can be observed, presenting a structure of a very cemented sandstone with carbonate. The *Tosca de Rocafort* is a travertinic limestone with a macroporous structure, extracted from the quarries of *Rocafort* (Valencia, Spain). The stone is composed by sparitic microcrystalline aggregates and due to its formation environment developed an intense macropore porosity, mostly interconnected. Both types of stone are present in the vast Monumental Heritage of Valencia.

2.2 *Reagents*

- The cyclododecane CDD (nonpolar barrier, $C_{12}H_{24}$), unsaturated and chemically stable, seals the pores of the stone material and prevents the penetration of the silicone elastomer. Solvent: xylene.
- *Látex de goma* 602 (polar barrier, natural rubber) is a transparent copolymer in aqueous dispersion. Creates a polar film between the CDD and silicone elastomer.
- *Laitex ME-10* (polar barrier) is a milky fluid based on natural rubber. Laicril EA-1323 is a high viscosity acrylic thickener, creating a polar film between the CDD and silicone elastomer.
- *Funori* (polar barrier, polysaccharide, non-toxic): transparent natural product produced from seaweed. The polysaccharide product is a pure mixture of two kinds of red algae (3.6-anhydro-galactose Agar-xL and carrageenanos sulphation). Creates a polar film between CDD and silicone elastomer.
- *Silastic* 3483 is a white thixotropic RTV silicone elastomer with excellent mechanical properties, resistant and high fluidity. Copies the surface details of the moulded material or work.

2.3 *Methodology*

For this study, stone samples of the *Tosca Rocafort* and *Novelda Bateig crema* were cut (dimensions: 6 × 5 × 3 cm). Likewise, different CDD solutions (40%, 60%, 80%, 95%) in xylene have been prepared (Mas et al. 2008). The three substances used as a polar interface layer between the nonpolar CDD layers and the silicone elastomers were *Laitex ME-10*, the *Látex de goma* 602 and the polysaccharide *Funori*. All layers, both polar and nonpolar, were applied by brush bristles creating a uniform film. Experimental methodology as follows:

(a) Colorimetric measurement of all the specimens before applying CDD. (b) Applying different CDD solutions in a water bath and afterwards application by brush. (c) Application of different polar separator 90 min. after the CDD. (d) Application of the *SILASTIC* 3483 silicone after the drying of the polar interface layer-ca. 120 min. (e) Separation of the silicone after 24 hours. (f) Removal of the interface layer by mechanical means. (g) Application of specimens by UV, 720 h. (h) Colorimetric measurement of the specimens after removal and sublimation of CDD.

2.4 *Instrumentation*

- Spectrophotometer Minolta CM-2600D. Measurement settings: D_{65}; 6500 °K and standard observer at 10°; specular component included (SCI) and with 100% UV; wavelength

400–700 nm. The colour space CIELAB has been adopted. Chromaticity coordinates of the specimens with various separators have been measured before and after the accelerated ageing tests by UV irradiation.
- Optical microscope *Leica MZ APO* (LM, 8–80x zoom). Employed to observe the surface of the specimens and the evolution of the sublimation of the CDD and the presence of residue or stains.
- Accelerated ageing chamber by irradiation (720 hours) with UV light *QUV/Basic*, with 8 UVB lamps (313EL, radiance of 0.77 W/m/nm). It was used to determine the deterioration effect of ultraviolet radiation on the samples prepared with various separators.

3 RESULTS AND DISCUSSION

3.1 *Optical microscope*

In general, absence of surface residues in both types of test specimen, *Tosca de Rocafort* and *Novelda Bateig crema*, was observed where the polar separators (*Laitex ME-10*, *Látex de goma* ex 602 and *Funori*) and *Silastic* 3483 RTV silicone were applied. This was corroborated by the results of the colorimetric study, where total colour variation are virtually nil in all analysed samples, especially in the *Bateig Novelda crema*. Furthermore, CCD shows its suitability as a barrier and insulating agent during moulding of micro and macroporous supports (Fig. 2). In this sense, the nonpolar-polar bilayer system ensures that the SILASTIC 3483 RTV silicone elastomer does not act negatively causing irreversible stains and residues. However, in the case of *Funori* a mechanical removal of a substance is required due to its fixative and adhesive properties.

3.2 *Spectrophotometry*

This technique allows quantifying the colour difference between two or more colours with high accuracy. The measurement of key points of the samples was performed before the application of CCD and after removal of the silicon, with the goal of evaluating the chromatic variations. The measurements were repeated three times and the mean and standard deviation were calculated. The only sample that shows values of total colour change (ΔE*) above 4 points (and hence

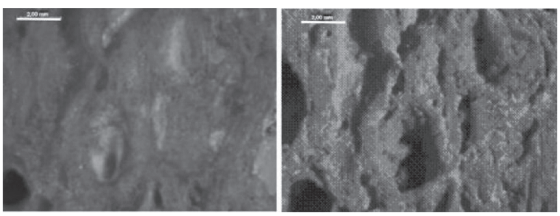

Figure 2. Detail of the macroporous structure of the *Tosca de Rocafort* stone with the nonpolar cyclododecane layer before (left) and after the sublimation (right). Note the absence of polar residue (8x).

Table 1. Colour differences between the different samples.

Name	DL (UV-before)	Dd	Da (UV-before)	Dd	Db (UV-before)	Dd	DEab* (UV-1)
UTC 5	–0,42	0,07	0,24	0,01	–0,10	0,01	0,50
UTL 5	–2,95	0,37	0,64	0,25	0,43	0,46	**3,05**
UTF 2	2,68	0,25	–0,31	0,09	–3,63	0,92	**4,52**
UBC 3	0,36	0,14	–0,05	0,00	–0,29	0,01	0,47
UBF 2	0,41	0,77	–0,10	0,00	–0,01	0,08	0,42
UBL 3	0,79	0,07	–0,07	0,06	–0,35	0,01	0,87

U: UV, T: *Tosca de Rocafort*, B: *Bateig crema*, L: *Laitex ME-10*, C: *Látex de goma 602*, F: *Funori*.

observable by the human eye) was the UTF 2, while the remaining samples have experienced not appreciable colour changes, which supports the suitability of the method (Table 1).

4 CONCLUSIONS

This method based on a system of layers with different polarities allowed to isolate and protect the porous stone materials from the silicone elastomer, which is the cause of irreversible stains on stone substrate. Likewise, removal of the silicone in all specimens were satisfactory showing that the three polar separators (*Laitex ME-10*, *Latex Rubber 602* and *Funori*) complete their function as a barrier and protection from the migration of silicone oils. With regard to colour, we can conclude that the method works especially well with the *Bateig* stone, since the maximum total colour change (ΔE^*) was 1.57 CIELAB units. Regarding the *Tosca de Rocafort* stone, very good results have been obtained in the UTC5 specimen. In all other cases the ΔE^* ranges between 2 and 3 units, excluding UTF2 exceeding 4 units. In addition, this system has a number of advantages for the moulding process of porous materials that makes it appropriate for the conservation and restoration work (good film-forming properties, almost no toxicity in pure, reversibility due to its ability to sublimate, intervening in very altered art pieces without removal of the separator, and, the applied films remain long enough so that the silicone can get vulcanized). However, some inconvenient drawbacks like the labour-intensive preparation and application of different materials, and the affinity of cyclododecane to the silicone elastomer, obliges to insert an additional polar layer, which is very time consuming.

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Effectiveness of a new nanostructured consolidant on the biocalcarenite from Agrigento Temples Valley

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ABSTRACT: This study presents the effectiveness evaluation of two crack-free nanomaterials with consolidant and consolidant/hydrophobic properties, respectively, developed at the University of Cadiz, in the context of the Master in "Nanotechnology and Nanomaterials for Cultural Heritage" of the University of Palermo. The consolidant product was obtained from a silica oligomer in the presence of a surfactant, whereas in the case of the consolidant/hydrophobic product, an organic component, i.e. polydimethilsiloxane, was also added to the starting sol. The effectiveness of the two products was evaluated on biocalcareous stone from Agrigento Temples Valley (Italy).

1 INTRODUCTION

The object of the present study is to evaluate the effectiveness of two new nanomaterials on the stone of the Temples Valley. This stone is a biocalcareous shellstone belonging to the so called "formation of Agrigento", composed of a succession of clays, sandy clays, sands and calcareous shell stones in heterotopy, sometimes in form of biocalcareoudites, with cross stratification levels constituted by fossil fauna, lower Pleistocene aged (Brai et al. 2004, Cotecchia et al. 1995). It is extremely porous and hydrophilic, with a size of rock grains from 0.2 to 8 mm, and an open porosity around 27%. This characteristic, added to a high presence of soluble salts, often causes strong erosion on the block surfaces, with irregular cavities on the surface, frequently covered by stone detached grains (Rossi Manaresi & Ghezzo 1978). After these considerations, we can state that the decayed stone has to be treated by a consolidant in order to restore the original intergranular cohesion. Moreover, since water infiltration is at the base of all the decay phenomena, it would be avoided by applying a hydrophobic product on the stone surfaces. The research project here presented, developed through the cooperation between the University of Palermo and the TEP-243 Nanomaterials group from the University of Cadiz, aims at synthesizing two nanostructured products with consolidant and consolidant/hydrophobic properties, and testing them on some stone samples collected directly on the archaeological site of Agrigento.

The products were obtained by mixing a silica oligomer and a surfactant (n-octylamine) acting as a pore-structure directing agent. In the hydrophobic product, an organosiloxane (PDMS) was also added to the starting sol in order to reduce superficial energy of the material. We performed colorimetric tests, drilling resistance evaluation and contact angle test before and after the application of the coatings on the stones, in order to verify if the products had modified the stone characteristics.

2 MATERIALS AND METHODS

The consolidant was prepared by mixing a commercial silica oligomer (Dynasylan by Evonik) and a surfactant (n-octylamine by Aldrich) acting as a pore-structure directing agent. It was prepared by the addition of two different proportions of n-octylamine in the sol: respectively, 0.075 v/v% and 0.15 v/v%. The formulations tested have been designated as UCAD (Dynasilan/n-octylamine) via the procedure devised at the University of Cadiz.

The consolidant/hydrophobic product, designated as UCAD10P2O (Dynasilan/PDMS/n-octylamine) via the procedure devised at the University of Cadiz, was prepared by mixing the commercial silica oligomer in the presence of the surfactant, with an organosiloxane (PDMS). The PDMS was used in the proportion of 10 v/v%, while the proportion of n-octylamine in the sol was 0.15 v/v%.

The treatments were performed by spraying until saturation the synthesized products on some 4 cm-cube stone samples. In comparison, other stone specimens were treated, under the same conditions, with three commercial consolidants: Tegovakon V100 (Degussa), a mono-component system based on silicon acid esters, Compatt (Vilo) an ethyl silicate in ethanol, and Nanoestel (CTS) a water dispersion of nanometric silica, stabilized in sodium hydroxide.

After the complete drying, we measured the uptake and the dry matter, and evaluated color changes produced after treatment. The measurements were performed using a colorimeter Colorflex by Hunterlab (illuminant C, observer 10°, CIEL*a*b* color space).

We also evaluated the adherence of the products on the stone samples by scanning electron microscope (SEM) using a FEI Sirion.

The effectiveness of the products in consolidating the stone was evaluated by comparing changes in drilling resistance using a drilling resistance measure system (DRMS) by Sint Technology (rotation speed 600 rpm, penetration rate 5 mm/min).

The effectiveness of the hydrophobic nanomaterial was evaluated by measuring dynamic and static contact angles, using a commercial video-based software-controlled contact angle analyzer, OCA 15 plus by Dataphysics Instruments.

3 RESULTS AND DISCUSSION

Uptake of the products under study and dry matter are shown in Table 1. The UCA products had, in general, higher uptake and dry matter than corresponding commercial products.

The evaluated color changes after treatment revealed a value slightly above the standard perception during the first monitoring period, but progressively this value has drawn near to the standard value ($\Delta E^* < 5$).

SEM images are presented in Figure 1. UCA products produced mesoporous crack-free coatings showing a good adhesion to the stone. In the case of the commercial product, a completely cracking coating was observed.

The effectiveness in consolidating was evaluated comparing changes in drilling resistance (drilling profiles are shown in Fig. 2). All the products significantly increased resistance of the stone.

The contact angle tests revealed a strong increase of hydrophobicity of the treated surfaces, compared to the untreated ones that were extremely hydrophilic. On the other hand, as expected for consolidant-only products, it has not been possible to measure the contact angle as they did not increase the hydrophobicity of the surface.

Table 1. Measurement of uptake and dry matter.

Product	UCADO	UCAD2O	UCAD10P2O	Compatt	NanoESTEL	TV100
Uptake (%w/w)	0.58 ± 0.13	0.34 ± 0.19	0.38 ± 0.07	0.19 ± 0.17	0.27 ± 0.008	0.28 ± 0.13
Drymatter (%w/w)	0.57 ± 0.12	0.16 ± 0.27	0.27 ± 0.18	0.15 ± 0.003	0.05 ± 0.02	0.10 ± 0.08

Data correspond to average values. Standard deviations are also included.

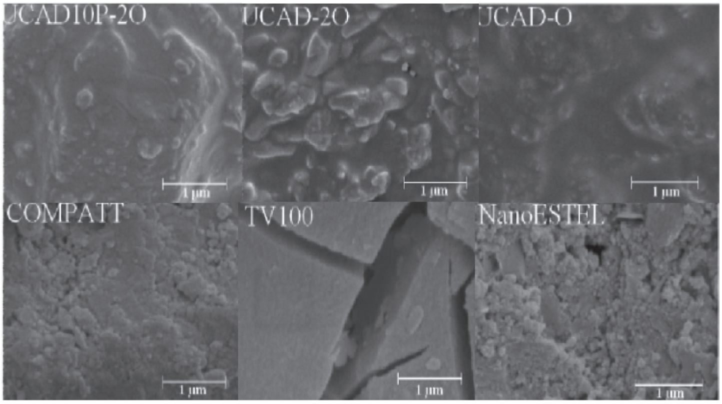

Figure 1. SEM images of the treated stone surfaces. The scale bar is 1 μm.

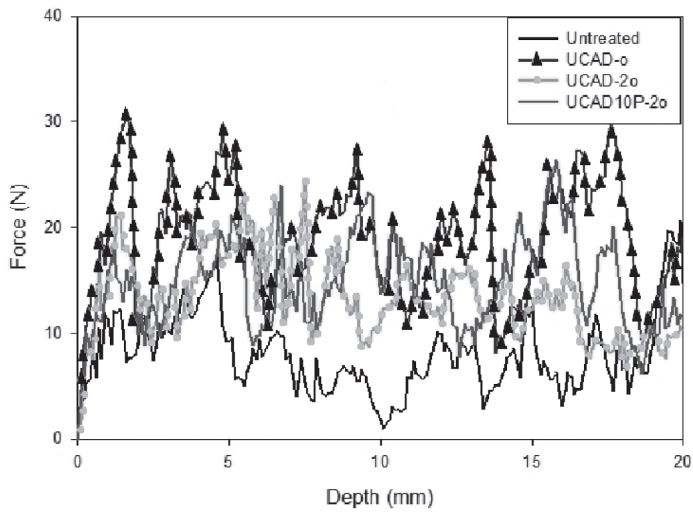

Figure 2. Drilling resistance vs. testing depth of treated biocalcarenites and its untreated counterpart.

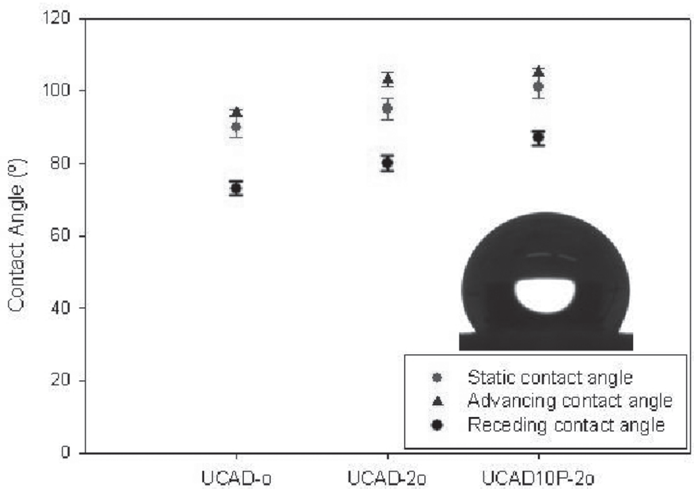

Figure 3. Contact angle measurements.

4 CONCLUSIONS

Crack-free nanomaterials containing PDMS and silica have been prepared by a simple sol-gel method in the presence of a surfactant.

These products, applied on the Agrigento biocalcareous shellstone, have been shown to improve stone cohesion, robustness, hydrophobicity and water repellence.

By comparing our materials with the available commercial products, we observed that UCA materials had a higher effectiveness. As demonstrated by drilling test, the stone treated with UCA products became more resistant to mechanical perforation and showed a higher cohesion, while the contact angle measurement demonstrated that the new materials improved the hydrophobic and the hydro-repellent properties of the stone.

Moreover, the presence of the surfactant, still more in combination with PDMS, prevented gel cracking.

The project is still in progress: the next phase is to test the persistence of the synthesized products through artificial ageing processes, in order to evaluate if the characteristics added to the stone by the treatments could be able to withstand the severe environmental conditions of the archaeological site.

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Technical studies for the restoration of the Immaculate Conception monument, Seville

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ABSTRACT: In 2010, the Immaculate Conception monument in Seville was completely restored to resolve several pathologies, including extensive material loss requiring stone replacement. The technical study presented in this work was undertaken to find a similar stone to the original in the monument and to assess the effect of two treatments (a consolidant and a water repellent). The first step was a petrographic study of the two types of stone slated for intervention and of rocks from local quarries in Alicante (cited in sources as the origin) to identify the best suited for replacing losses. Once we identified the two stones for use, treated specimens from the quarry and the monument were studied to determine changes in several physical properties to verify whether the treatments were effective.

1 INTRODUCTION

The monument was built in 1917–18 (Espiau Eizaguirre 1984) by using four types of stone. The Immaculate group is made of Carrara marble, the base of Sierra Elvira stone, the table, pillars, and four statues (Murillo, Martínez Montañés, Miguel del Cid, and Juan de Pineda) in the base of "Murcia blue stone", and the pedestal of "Almorquí" stone. The last two types are not currently in use and the location of their quarries is unknown. The sculptures in the base (especially that of Martínez Montañés) (Fig. 1) had lost large fragments that needed to be replaced. Indeed, two stones as similar as possible to the originals had to be found (Fort et al., 2002).

In addition, due to the monument's exposure (completely exposed in the centre of the plaza) to environmental agents (especially S-SW wind and rain), the stone had to be protected from rainwater and its cohesion had to be improved. A consolidant (CON) and a water repellent (WR) were applied, the latter to both the original stone and the replacement fragments.

The specific objectives of the technical studies herewith presented were identifying the two types of stone to be used for reconstruction of missing fragments of the sculptures, and evaluating the effect of the consolidant and the water repellent treatments on both stones.

2 EXPERIMENTAL

2.1 *Stone materials*

Samples from the two unidentified stones of the building were taken to determine their characteristics. To obtain replacement material various samples of stones currently sold from quarries in Alicante were investigated. Between them, two were selected due to their similarity to the monument's original stones and used in the restoration (Table 1).

Figure 1. Inmaculate Conception monument (left); Martínez Montañez sculpture before and after restoration (center and right).

Table 1. Name, designation, origin and open porosity of samples.

Name (designation)	Origin	H_2O porosity	Hg porosity Untreated	Hg porosity Treated
Immaculate grey (IG)	Monument's statue	18.14	15.15	17.14
Immaculate yellow (IA)	Monument's step	24.08	24.01	20.69
Bateig blue (BA)	Alicante quarry sample	14.23	15.85	14.47
Bateig flat (BLL)	Alicante quarry sample	20.97	19.30	19.38

2.2 *Treatments*

Estel 1000 (CON) and Estel 1000 + Silo 111 were applied to the monument samples, and only Silo 111 (WR) was applied to the quarry samples. Test stone samples (3 cm cubic) were submerged in the products for 10 minutes then dried in a well-ventilated area at about 20ºC to a constant weight. The samples from the monument were first impregnated with the consolidant and then, once they reached a constant weight, were treated with the water repellent 14 days later.

2.3 *Instrumentation and tests*

The four stone samples were characterized by microscopy of the thin-section with a microscope Nikon Optiphot-Pol and by XRD with a Bruker-AXS D8 Advance difractometer.

After complete drying of treated samples, porosity, pore size distribution, colour, and surface hardness were measured. The total porosity was determined by vacuum water absorption of the untreated samples in accordance with the UNE-EN 1936 (AENOR, 2007) standard, and mercury intrusion porosimetry on the treated and untreated samples with a Micromeritics AutoPore IV equipment. The sample colour was measured with the CIELab colour system using a Neurtek Dr Lange model colorimeter. For each group, the average values were calculated, as well as the colour differences between treated and untreated test specimens for each type of stone, and the colour difference between the treated quarry stone (BA WR, BLL WR) and the treated monument stone (IG C + WR, IA C + WR), for each of the following pairs: grey stone, IG with BA, and yellow stone, IA with BLL. These differences are calculated with the following expression:

$$\Delta E = \sqrt{(L_1 - L_2)^2 + (a_1 - a_2)^2 + (b_1 - b_2)^2} \quad (1)$$

The hardness of the test specimens has been measured by means of a Brinell hardness test, using a 5 mm ball and applying an initial force of 10 kg and a total force of 30 kg. The hardness (0–130 Brinell hardness units) is inversely related to penetration of the durometer. On each specimen, four measurements were made on each of the three perpendicular faces, totalling 12 measurements. The average values were calculated per test specimen and per treatment.

3 RESULTS AND DISCUSSION

3.1 *Stone for reconstruction*

All stone were characterized as biocalcarenites, essentially comprising abundant mid–late Miocene foraminifer remains and terrigenous fragments (quartz, feldspars, colourless mica, calcite) cemented by micrite.

XRD studies show that the major mineral is calcite, mainly micrite (microcrystalline calcite cement). The terrigenous minerals also include quartz and potassium feldspar (microcline), and the authigenic minerals comprise dolomite and traces of ankerite $Ca(Fe^{2+}, Mg, Mn)(CO_3)_2$. Finally, samples IG and BA have traces of paracoquimbite $Fe_2(SO_4)_3 \cdot 9H_2O$, perhaps accounting for their greyish-blue colour. While samples IG and BA are extremely similar in mineralogy and texture, there are greater differences between samples IA and BLL: sample IA has no feldspar, dolomite, or ankerite, and porosity and grain size are greater than in sample BLL.

3.2 *Porosity and pore size distribution*

The total porosity of the four types is shown in Table 1. Pore size distribution is very similar in all of them. The quarry samples have a slightly lower total porosity than those of the monument, visible in both the porosity accessible to water and in the mercury intrusion porosimetry.

Treatment application produces only a slight decrease in the total volume of pores without appreciably altering size distribution. Only the IG sample shows a slight change in distribution, although it is probably due to the original distribution in the sample before treatment being a little different than in the untreated sample, since the total porosity is greater in the treated sample than in the untreated one (Villegas et al. 2009).

3.3 *Colour*

For each group, the average values of L, a, b are shown in Table 2. Also the colour differences between treated and untreated samples (ΔE) are included, as well as the colour difference between the treated quarry stone (BA WR, BLL WR) and the treated monument stone (IG C + WR, IA C + WR. The difference between the quarry stone and the monument stone is very small for the grey stone and rather larger for the yellow stone. It was noted that WR application (1) produced a colour more similar to the original than when only the CON was applied (2). It may be that application of the WR partially dissolves the consolidant, slightly modifying its effect. Following Delgado-Rodrigues & Grossi (2007), these changes are not discernible by human eye.

3.4 *Surface hardness*

Two aspects should be noted (Fig. 2). First, the effect of the CON is quite significant in both stone types used in the monument. On both cases a slight decrease in hardness is produced when the WR is applied, that is, a weakening of the consolidant's effect similar to the colour change.

Second, it must be noted that the hardness values of the monument stone with both treatments (IG C + WR, IA C + WR) and of the quarry stone with the WR (BA WR, BLL WR) are very similar. That is to say, the characteristics after the restoration of both the original stones and the new stones will be very similar.

Table 2. Average colour of each group of test specimens

	Sample	L	a	b	ΔE	Dif. E
Grey stone	IG	77.9	–0.1	6.7		
	IG C + WR (1)	73.0	0.2	7.7	3.38 (1)	
	IG Cons	74.6	0.0	7.4	5.06 (2)	
	BA	74.3	–0.5	6.8		
	BA + WR	73.7	–0.5	6.9	0.59	1.32
Yellow stone	IA	79.9	1.2	15.2		
	IA C + WR (1)	74.9	1.9	18.2	3.02 (1)	
	IA Cons	77.1	1.5	16.4	5.85 (2)	
	BLL	79.6	0.5	12.2		
	BLL + WR (2)	78.8	0.6	12.2	0.73	7.27

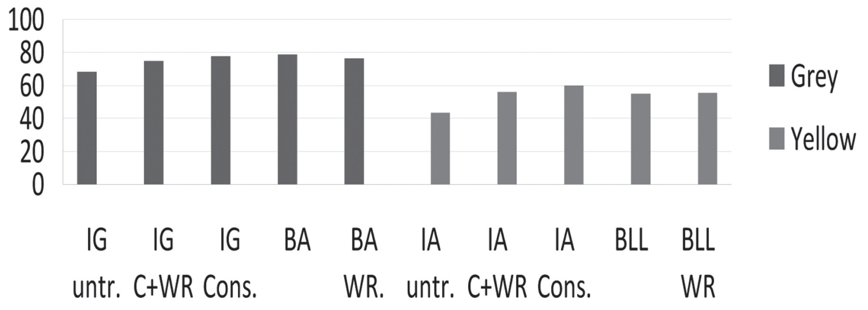

Figure 2. Average surface hardness of each type of test specimen.

4 CONCLUSIONS

The treatments provide a suitable effect as the changes in the stone properties are not marked.

The replacement stones have a composition and physical characteristics that are very similar to the monument stones. Once treated, the properties are also very similar, and therefore their evolution over time should be comparable as well.

Overall, the materials and treatments proposed for the restoration are shown to be quite suitable and have a satisfactory behaviour.

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Materials made from polyolefins used in tasks of preventive conservation: A comparative study of their long-term behavior

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ABSTRACT: In this paper, the results corresponding to the study of different materials used in the field of Preventive Conservation have been presented. All of them are polyolefins, but show differences related to the type of polyolefin and the nature of additives. Their long-term behaviour has been evaluated by performing accelerated artificial aging (arc-xenon aging) and changes in their original composition and properties have been determined. The analytical techniques used have been: FTIR-ATR, Py-GC-MS, DSC, TGA, and GPC.

1 INTRODUCTION

The use of synthetic polymers is widely widespread in the Conservation of Cultural Heritage and their presence is usual in the field of Contemporary Art. Thanks to the great advances developed by chemical industry, it has emerged a great range of products that can be used in the shape of sheet, supports, foams, etc. into the tasks of Preventive Conservation (handling, packing, storage and exhibition). Usually, these products have been initially developed for other industrial uses and the information available concerning their composition is quite limited and, in some cases, inaccurate. However, all the materials used in artworks or in their conservation treatments should have the appropriate characteristics to ensure their long-term behavior. For these reasons, a research Project is being developed in order to study the synthetic polymers used in the field of conservation of Cultural Heritage and in Contemporary Art. This research arises from the collaboration between the Chemistry Laboratory of Painting and Restoration Department of the UCM, the Materials Laboratory of the IPCE and the Polymer Technology Laboratory of the URJC. The objectives of this research are to identify the composition of some materials, by means of using several analytical techniques, to study changes promoted by accelerated aging process and the establishment of the relationship between these changes and material's composition. All the materials investigated have been previously selected by conservators of different areas (painting, sculpture, graphic document, archaeology, textile, etc.).

In this paper, the results corresponding to the study of three materials used in the field of Preventive Conservation have been presented. They can be used as supports in storage, exhibition and movement of pieces, dust barriers, packing and insolation of artworks. In figure 1 are shown the commercial products investigated (Cellaire®, Propore® and Lampraseal®). All of them are polyolefins, but show differences related to the type of polyolefin, the nature of additives and their processing. Their long-term behaviour has been evaluated by performing accelerated artificial aging (arc-xenon aging) and changes in their original composition and properties have been determined. The analytical techniques used have been: FTIR-ATR, Py-GC-MS, DSC, TGA, and GPC. All of them are very useful to investigate the composition of polymeric

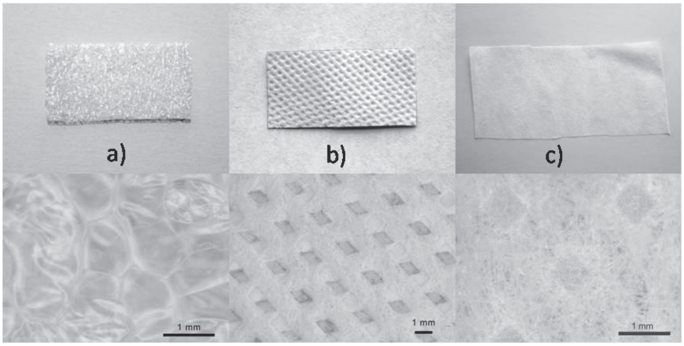

Figure 1. Photographs of: a) Cellaire®. Laminated foam-film used for protection and packaging of artworks; b) Propore®. Multilayer material (tissue and pressure sensitive material) used in lining support for objects; c) Lampraseal®. Multilayer material (laminated film and tissue) for protection and packaging artworks.

materials and to identify changes promoted by aging (D'Orazio et al. ,2001, Stuart & Thomas 2000, Forrest 2002, Chércoles et al., 2009, Lazzari et al., 2011).

2 METHODOLOGY

The selected materials have been analyzed by different analytical techniques. FTIR spectra were recorded with a Thermo Nicolet spectrometer (model 380) equipped with an attenuated total reflection diamond crystal accessory (ATR), and having a DTGS detector (4000–400 cm^{-1}), working at 64 scans and a nominal resolution of 4 cm^{-1}. The differential thermogravimetric analysis (DTGA) were carried out with a Mettler-Toledo SDTA/851e working at a heating rate of 5ºC · min^{-1}, from 40 to 800ºC, under atmosphere of N_2 (100 ml · min^{-1}). DSC analysis were performed in Mettler-Toledo DSC822e, under atmosphere of N_2 (30 ml · min^{-1}), using heating rate of 10ºC · min^{-1} and three heating scans, heat from –70 to 220ºC, cooled to –70ºC and reheat to 220ºC. After each scan, sample remained for five minutes at the final temperature achieved. Size Exclusion Chromatography (SEC) measurements were carried out to estimate the molecular weight distribution of the samples, using a Waters Alliance GPCV 2000 equipped with refractive index and viscometer detectors. The molecular exclusion were made by three columns, two Plgel 10 μm Mixed-B and one 10 μm 10^6Å. 1,2,4-trichlorobenzene was used as solvent at 145ºC and the flow rate was 1.0 ml · min^{-1}. The instrument was previously calibrated using narrow standard polystyrene samples, and the molecular weights were obtained by universal calibration. The Py-GC-MS analysis were carried out with an integrated system composed of a Pyroprobe CDS 520 pyrolizer, an Agilent 7890 A gas chromatograph equipped with a HP-5MS 5% Phenyl Methyl Siloxane capillary column (30 m × 250 μm × 0.25 μm) and an Agilent 5975C mass spectrometer (MS) with a quadrupole mass analyser. The pyrolyser transfer line was set at 290ºC, and the injector at 280ºC. The GC/MS experiment were carried out by split injection and detected in the range m/z (29 to 550).

These analyses have been made before and after artificial aging. The aging procedure has been performed in an arc Xenon Chamber (Suntest XLS+) equipped with a light source filtered for 295 nm, 765 W · m^{-2} irradiation constant and maximum temperature into the chamber is 45ºC. Aging protocol has been applied attending test standard ISO 4892 (Methods of Exposure to Laboratory Light Sources Using Xenon-arc Lamps).

3 RESULTS AND DISCUSSION

Figure 2a shows the FTIR-ATR spectrum corresponding to Cellaire®. It presents characteristic bands of poly(ethylene) and more specifically of LDPE. The results obtained by DTGA confirm this result, as the main decomposition stage is at 469ºC (Table 1). However in this diagram could be appreciated a weight lost in the initial region (<200ºC) not expected in PE. This result can be attributed to the presence of some additive, possibly a plasticizer. This hypothesis has been confirmed by Py-GC-MS, where a derivative of phtalic acid, may be a phthalate, has been identified. This type of compounds is usually used as plasticizer of plastic materials. With regard to DSC analysis, the diagram obtained shows two peaks at 69ºC and 107ºC (Table 1). The former corresponds to a PE of less crystallinity than the second one. The total crystallinity of this material is around 48%.

FTIR-ATR spectrum of aged Cellaire® showed some structural changes that may be related to an oxidation process. After 1800 h of accelerated aging, bands corresponding to oxidized groups have been identified: γ-lactone (1782 cm^{-1}), aldehyde (1747 cm^{-1}), ester (1732 cm^{-1}), ketone (1711 cm^{-1}), carboxylic acid (1698 cm^{-1}) and vinyl group (1647 cm^{-1}) (Fig. 2a). This process is associated to a significant decrease in the molecular size. The results obtained by SEC analysis shows up that the molecular weight distribution is around ten times reduced (Table 2), possibly as an effect of molecular excision promoted by photo-oxidation. The thermal analysis by DSC does not show important differences and the total crystallinity and main lamellar thickness are very similar. On the other hand the low thickness lamellar species disappear when the material is aged. So, stiffness will be similar but the brittleness and elongation ability will be reduced with aging, mainly due to the molecular weight reduction. With regard to DTGA, in the analysis of aged material significant changes are not detected (Table 1).

Propore® is a multilayer material composed by a tissue of poly(propylene) and a pressure sensitive adhesive (PSA), likely a poly(acrylate). Both polymers have been identified by FTIR (Fig. 2b). In the TGA analysis two decomposition temperatures have been detected at 388ºC and 450ºC (Table 1), attributed to PSA and PP decompositions, respectively.

The aged Propore® shows important changes. The higher presence of tertiary carbons in the chemical structure of polypropylene, induce a rapid and sudden oxidation in comparison with polyethylene (Fig. 2b). In the TGA diagram the T_1 remains constant and not affected by the age process, however there is a displacement of the PP degradation temperature (Table 1). Thermal analysis by DSC show clear difference between both samples tested (unaged and aged). Melting temperature and crystallinity sharply decrease in the aged sample (Table 1).

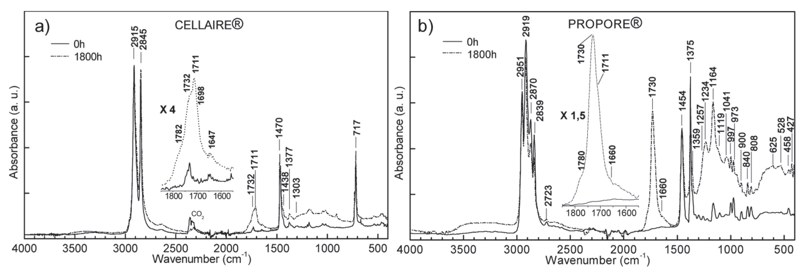

Figure 2. FTIR-ATR spectra of polyolefins before and after having been exposed to arc-xenon aging for 1800 hours: a) Cellaire® (LDPE); b) Propore® (PP).

Table 1. Values of relevant thermodynamic parameters determined by TGA and DSC.

	Cellaire® (LDPE)	Cellaire® (1800 h)	Propore® (PP)	Propore® (1800 h)	Lampraseal® (LDPE + PP)	Lampraseal® (900 h)
$T_{decomposition}$ (ºC)	469	468	388 (PSA) 450 (PP)	392 (PSA) T2??(PP)?	459	459
$T_{melting}$ (ºC)	69 (T_1) 107 (T_2)	109	159	147	108 (LDPE) 162 (PP)	101 (LDPE) 132 (PP)
Cristallinity (%)	47.9	50.6	45	15	47 (LDPE) 50 (PP)	? (LDPE) ? (PP)

Table 2. Molecular weight distribution analysis before and after arc-xenon aging.

	Cellaire® (LDPE)	Cellaire® (1800 h)	Propore® (PP)	Propore® (1800 h)	Lampraseal® (LDPE + PP)	Lampraseal® (900 h)
M_n ($kg \cdot mol^{-1}$)	15.1	1.9	4.4	1.6	12.7	2.4
M_w ($kg \cdot mol^{-1}$)	243.5	25.4	308.5	129.6	181.7	7.2
M_w/M_n	16.1	13.6	69.7	82.7	14.9	2.9

Finally SEC analysis confirms a molecular excision as the main degradation process promoted by photo-oxidation. The PP molecular weight is around three times reduced but the PSA molecular weight remains almost constant (Table 2).

Lampraseal® is another multilayer material which is composed by a laminated film of PE and a tissue of PP. The results corresponding to aged material are similar to those obtained in Cellaire® (LDPE) and tissue side of Propore® (PP). Both polymers show a significant oxidation process accompanied by an important decrease of molecular size. Attending to the results of molecular weight distribution analysis, this property is reduced around twenty five times (Table 2). This result confirms that the molecular excision is the main degradation process. So, mechanical properties will dramatically fail. Thermal analysis by DSC points out that PP layer thermal properties are significantly more affected than those of the PE one. However, the decomposition temperature is not affected (Table 1).

4 CONCLUSIONS

Synthetic polymers are used not only as constituents in contemporary artwoks, but also as materials used in conservation tasks. Some commercial products contain additives and they should be detected and taken into account due to possible interaction with the artwork. The main degradation mechanism in PE and PP is the chain excision process promoted by photooxidation. Its progress will depend on the type of material, molecular weight and morphology. Although both polyolefines experiment changes, polyethylene shows higher stability and better thermal properties to the aging process. FTIR, Py-GC-MS, GPC, TGA and DSC techniques offer good possibilities in the evaluation of aging mechanisms and changes in the polymer properties.

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Critical and technical aspects for safeguarding, enhancing and the recovery of local architectural heritage: An emblematic example of rural buildings between Ossola (Italy) and Ticino (Switzerland)

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ABSTRACT: Public interest in the preservation of Val d'Ossola and Ticino rural buildings is now universally accepted. As a result, a common research program has been started up in order to promote, support and lead actions for the recovery and preservation of this heritage. This paper firstly outlines the main preservation requisites, within the current performance and functional requisites. The method proposed considers how they could be harmonized, in order to plan every intervention according to the building's particular nature. The ongoing research will seek to achieve two main outcomes: a) to promote a wider sensibility for the conservation and recovery of local traditional houses; b) to draft handbooks, designed as *open documents*, which must converge in binding rules and regulations for local governments as a mandatory administrative tool. During the research, outcomes will be applied to recovery interventions on some public buildings, in order to test the method and main results.

1 INTRODUCTION

The paper deals with the research programme, *Interreg Italia Svizzera 2007-20013*, *ID 27462783. mis. 3.1 (so called "Interreg")*, recently started up (January, 2012) and leaded by the District Council of Verbano Cusio Ossola. It concerns diffused rural stone architecture, between the areas of Val d'Ossola (Italy) and Ticino (Switzerland), in the central alpine arch. Since local diffused architecture is currently universally recognized as cultural heritage, the specific aim of the "Interreg" is direct to recover and enhance rural buildings which can later be used for tourist accommodation. In this way the program encourages sustainable tourism through the architectural heritage and its natural context (Conti & Oneto 2002) (*ambitus*) (see Fig. 1a).

The survey of the state of the art, the rules and acts corpus and the critical analysis of numerous specific studies (Simonis 1983, 2008, De Matteis 1985) has shown a wide knowledge and interpretation of historical values and architectural handcraft testimonies. However, this approach, which focuses on pure conservation, is difficult to reconcile with the quantity of ancient buildings to be recovered (and, with their future maintenance). Thus, it is observed that the increasing interest in recovering buildings for new uses and the related new initiatives to be encouraged by public offices are then hindered by conservative and restrictive current regulatory requirements. Nowadays the number of unsuitable refurbishment interventions (or new interventions) is increasing. Their causes and consequences can be divided into the following groups: a) mistakes due to lack of either knowledge in traditional building techniques or interpretation of the original elements; b) errors due to an apparent reduction of costs as a consequence of the application of different materials from the original ones; c) a combination of the two previous groups; d) lack of method and of local planning rules can induce erroneous interventions; e) errors due to lack in mechanical characteristics of traditional materials used in build traditional elements: in these cases mistakes can be increased by the lack of specific technical standards.

Figure 1. Views of: significant alpine hamlet at Durogna (a), characteristic stone modillions (b), example of traditional stone roof in contrast with an unsuitable result of a recovery intervention (c) and wooden structure of a traditional stone roof (d).

Therefore, final aim of the *Interreg* research is to promote a diffused sensibility through "reappropriation" of culture for conservation and recovery of traditional houses in Ossola and Ticino. The criteria (related to the widely shared assumptions of conservation debate) are based on the concept that every preservation, recovery or refurbishment intervention must be *CONGENIAL, COMPATIBLE* and *VIVIFYING* (Scarzella & Zerbinatti 2009). The critical issue consists in give a sample instrument, useful for: a) public offices and technicians, to regulate and evaluate both proposal and results of interventions; b) owners and designers, to direct interpretation of traditional architectural values. These results will be achieved by preparing a handbook, which will be composed by different sections, concerning a certain number of buildings studied during the present program: it will be accompanied by encoded language and graphics and taken by local governments as a mandatory administrative tool, in order to be increased over time, by every new intervention (or proposal of it). The content of each section of sheets has been defined as consequence of the different aims, and is related to the sequence of steps necessary for the recovery interventions: "Knowledge sheets", "Technical Sheets", and "Control Sheets". Above all, the handbook must be a guide to improve knowledge of rural buildings, through the identification of characteristic building elements that feature the significant and stratified image of local traditional architecture; secondly, it must support projects, directing technical choices; finally, it must represent an evaluation instrument, to qualify interventions. Following paragraphs describe method and expected results.

2 THE INTERREG RESEARCH

Reversibility, environmental sustainability, energy costs reduction and increasing local production by innovation into production cycles, are only some of the current requirements in refurbishment and recovery projects. We must also consider requirements connected to current habits, which are generally different from those of ancient buildings. A third series of requirements is connected to preservation: primarily, the use of traditional building techniques and local materials. Every recovery intervention must achieve a harmonization of these requirements, and this result is possible only if every critical issue is taken into consideration. Thus, the research will be developed through different steps, each one of which ideally represents a step of a correct intervention project.

The first step is represented by the critical approach of knowledge: since every building is unique, it must be surveyed carefully (Scarzella 1968), in order to interpret each traditional element that characterizes it; for this, a good traditional building construction culture is needed. This action will be directed by the first section of sheets, which will be planned taken from state of the art surveys, collection and critical analysis of local planning rules. The analysis of a certain number of traditional rural buildings will increase knowledge of heritage and represent a significant anthology for analysis and cataloging each type of existing building. These sheets also introduce references to three different areas: lakelands, high and low mountain terrains, in order to identify specific elements of buildings related to their natural context.

A second step is represented by a thorough analysis of maintenance, attitude to recovery and a first draft of technical intervention for the existing buildings (in accordance with original materials, of course). This action will be directed by the second section of sheets, the draft of which is being supported by two different steps of the research programme. A direct survey of critical and virtuous emblematic examples of intervention in recovery of historical buildings and some experimental tests carried out in the laboratory.

The direct survey of intervention is useful for the identification of major types of errors occurring and their correspondent main causes. Sometimes, mistakes are the consequence of a lack of knowledge in traditional building techniques, or no interpretation of the original elements. As regards to thatched roofs (e.g.) since there are no original coverings, the main error generally consists in modifying the slope of the wooden structure, and geometry of the eave: as a consequence, it is often impossible to interpret characteristics of historical roofing. Other times, errors are due to apparent reduction of costs as a consequence of applying different materials to the original ones. In the recovery of stone roofs (e.g.) major errors may concern characteristics and the laying of stone slabs (reduced thickness and overlap of stone slabs, regular dimensions, reduced workmanship on sites) (see Fig. 1c). Often, both errors are present (as in the introduction of a ridge in wooden structures), thus the slope of the roof is modified and unsuitable stone slabs are laid (Fasana & Nelva 2011). In addition, in a lot of refurbishment interventions we have observed a great superficiality in the method and contents of local planning rules: Figure 1c is an emblematic result of the textual application of a general rule by erroneous methodological and technical approaches, worsened by the use of improper materials. Finally, a great critical issue is represented by errors due to poor mechanical characteristics of the local materials used in building traditional elements; these mistakes can be connected both with a poor and superficial construction culture, and to a lack of specific technical standards which designers can refer to. The set of experimental tests, planned in the research program, is related to the characterization of the mechanical behavior of stone materials (locally extracted), in order to qualify them and subsequently to project elements with improved performances. Finally materials are still considered in terms of image which should be coherent with the tradition. An example is represented by the cited case of stone modillions supporting stone balconies (see Fig. 1b). These elements are often replaced with reinforced concrete ones; this action is necessary due to fractures and the collapse of a great number of modillions in historical buildings, and result in major damage to the original architectural image. A particular purpose of the research is to identify a series of techniques to ensure mechanical resistance of stone modillions (also by the insertion of reinforcing elements), without modifying their traditional image (e.g. geometry and local stone material). Obtained results will be useful to regulate interventions not only in traditional contexts, like the "Interreg" area under investigation, but also more generally, since there is a current lack of specific technical standards. A relevant contribution to achieve expected results, will be given by the realization of exemplary pilot yards. The ongoing outcomes are applied in recovery interventions on some public buildings, chosen because of their emblematic image. Firstly, this will permits us to test the method and the main results and it will represent a significant improvement to produce emblematic examples, which must begin a virtuous way of intervention. Secondly, it represents an efficient way to directly involve experienced workers, in order to codify their knowledge in traditional techniques and to diffuse it to young craftsmen; these will be achieved by specific workshops. Evaluation of recovery interventions will be supported by a third section of sheets, the drafting of which, at the present time, is still in progress.

3 CONCLUSIONS

With regard to the valorisation and recovery of local architectural heritage, the paper focuses on primary critical issues in current refurbishment projects whose requirements are often in antithesis, and explains the method, which is largely acquired. According to this, within the emblematic example of rural buildings in the considered alpine area, the ongoing drafting of a set of handbooks is presented. The different sheets that compose the handbooks correspond to the different phases of an ideal recovery project, and their adoption by local planning offices can contribute significantly to attaining the two main objectives of the *Interreg* research program:

– to promote a wider sensibility through reappropriation of the local culture in order to lead suitable conservation and recovery interventions on traditional houses in Ossola and Ticino,
– to harmonize existing studies, rules, standards through this *open document*, in order to make owners, designers, building constructors and craftsmen converge to a new way of recovering historical rural architecture, not only for its conservation but, particularly, for its suitable recovery.

The whole documents resulting from the research programme will be taken by local public administrations (like the District Council and Environment Restricted Areas) as mandatory planning and regulation tools.

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The protection of the *baserri* as a system for organising rural landscapes in the context of the urban sprawl processes: The "SLaM" model versus the Utopia of "smart cities"

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ABSTRACT: The *baserri* is a vernacular efficient agricultural productive system that has shaped the Basque landscape. As industry was undergoing mass expansion, many *baserris* were abandoned. After the industrial crisis, the value of these bucolic farms increased, but not as agricultural undertakings and forestry exploitations. This landscape has begun to be perceived as a continuous metropolis that needs a different model of consumption and performance.

The neoliberal concept of "smart cities" gives priority to immediate economic profitability and technology, which are only applied to the fastest-growing neighbourhoods in metropolitan areas with the highest financial capability, dispossessing them of their identity.

In contrast, we regard 'smart landscapes of memory' (SLaM) as heritage districts of a high cultural level and generators of a feeling of identity and belonging. They are subject to coordinated management and urban planning in order to achieve the sustainable development of the territory and, above all, of its inhabitant.

1 CONTEXTUALIZATION OF THE *BASERRI* AS A PRODUCTIVE AND HABITATIVE MICROCYSTEM THAT STRUCTURES A TERRITORY

The population in the rural landscape in the Basque Country's Atlantic valleys remains disaggregated (not dispersed, in the strictest sense), following the productive patterns of traditional agricultural and livestock undertakings.

The production units that have moulded the Basque landscape have remained family-owned and self-sufficient since the middle ages, despite important structural changes, in a humid, mid-mountain setting.

Since the 16th century, the building used for agricultural purposes are compact, with living quarters for humans and animals, and areas for storing and processing farm products all under one roof. The houses (called *caseríos,* or hamlets, when they were grouped into isolated neighbourhoods) sought to optimize the surrounding resources, such as the available sunlight, work areas (e.g. *larrain* or threshing floors) and farmlands. Therefore, the system goes beyond the idea of a building to encompass the Basque word *baserri* (which probably comes from *baso*—forest—and *herri*, in the sense of earth).

The proliferation of *baserri*, with their houses, threshing floors, vegetable gardens, orchards and forests, formed a highly characteristic anthropogenic landscape that, with few variations, stretched from the Adour to the Zadorra and Arga Rivers, and from the Encartaciones Orientales region to the headwaters of the river Erro, an area 200 Km long and barely 80 Km wide.

2 SPRAWL AND SUSTAINABLE REGIONAL PLANNING IN THE CULTURAL LANDSCAPE OF THE *BASERRI*

The *baserri*'s profitability declined sharply in the mid-20th century with the industrialization of many of the valleys surrounding the capital cities, particularly Bilbao, Donostia-San

Sebastián and Bayonne. Hectares of pastures, woodlands and forests were neglected and invaded by undergrowth, while the newcomers' demands for comfort and urban sprawl turned the outlying hamlets into residential areas and satellites of the big cities.

The downturn in the real estate sector put an end to the suburban expansion which, in fact, had thrived in the Basque Country less than elsewhere in Spain. A return to agriculture, animal husbandry, organic farming and food processing (to make cheese and *txakoli*, for instance), regional plans for sustainable transport, improvements in conventional transport and environmental concerns pointed to a positive rururbanization process that would replace invasive, unsustainable urban sprawl.

3 SMART CITY

In 2050, 75% of the population will probably be concentrated in big cities, rendering the current model of consumption and operation obsolete. Many of those who defend the new method for building cities based on the 'smart' concept begin their arguments with this Manichean prediction.

The adjective 'smart' has a connotation of 'belonging to a common project'. Obviously, like the term 'bioclimatic', it is sometimes tinged with opportunism and marketing strategies, but the definition includes aspects that are essential for interventions in landscapes and regional planning.

The whole concept of cities has undergone a profound revision in the 21st century. When the adjective 'smart' is added to the word 'city', it leads to the powerful, versatile concept of 'smart cities', accurately described by the Dutch economist Peter Jijkamp and other authors as a city in which "investments in human and social capital, and in conventional communication infrastructures (transport) and modern communications (ICT, information and communication technology) promote sustainable economic development and high quality of life, in which participative government leads to wise management of natural resources" (Caragliu et al. 2009)

The most recurrent aspect of this definition is associated with the technification of infrastructures, in line with the research conducted by the Mitchell team at MIT. This approach is interesting owing to an organic perception of territory organised into strata: "cities have all the sub-systems that are needed by living organisms: structural skeletons, various layers of protective skins and artificial nervous systems" (Mitchell 2007). His development of 'mobility on demand' mechanisms that bring urban solutions based on new ideas in transport systems, such as the ones in Singapore, Brisbane, Stockholm and Maastricht, are another seminal contribution.However, his decision to rely on energy saving and his management of a combination of "software with digital telecommunication networks, the ubiquitously integrated intelligence, sensors and identifiers" (Mitchell 2007), as in the case of Malaga (Málaga Smartcity. Un modelo de gestión energética sostenible para las ciudades del future. http://portalsmartcity.sadiel.es) and Amsterdam (Smart Amsterdam, http://amsterdamsmartcity.com/#/nl/home), seems more debatable owing to their restricted and circumstantial usefulness.

The socio-economic and cultural approach that has emerged from such interesting experiences as the Distrito22@Barcelona project, a new model of compact city in which highly innovative companies are set up in the same area as centres for research, education and technology transfers, as well as houses (4,000 new subsidized housing units), facilities (145,000 sqm of land) and garden areas (114,000 sqm).

From a neo-liberal standpoint, however, the economic aspect has been over-emphasized as the only basis for urban development, which implies the risks indicated by Hollands: "the 'spatial fix' inevitably means that mobile capital can often 'write its own deals' to come to town, only to move on when it receives a better deal elsewhere. This is no less true for the smart city than it was for the industrial, [or] manufacturing city" (Hollands 2008: 303–320).

On the basis of giving priority to economic profit and applied technology, it is logical that only the cities with the highest financial capability are taken into consideration when planning projects and actions to add intelligence to their infrastructures.

Nonetheless, urban sprawl (Berry 1976), in the more precise definitions of expolis, metapolis, generic city or dispersed city, have systematically gone beyond the harmonious areas to which smart cities apply, normally in a spontaneous and disorderly fashion.

Some authors settle the matter by ignoring the edge city phenomenon, considering it to be undesirable and that "urban sprawl is an enemy of sustainable cities" (Vegara & de las Rivas 2004: 4). As a solution, they extend the city's scope to include the territory defined in the smart places concept. Yet such definitions do not always manage to distance themselves from the conventional meaning of metropolis: "they are innovative cities that are capable of attaining a balance between economic competitiveness; social cohesion and development; and ecological and cultural sustainability" (Vegara & de las Rivas 2004: 8).

The socio-economic reality of some European centres of development, particularly in the northwestern area (The Netherlands, Belgium and the German North-Rhine-Westphalia *lander*) have counterbalanced this negative view of sprawl with systems such as the 'polycentric metropolitan area' or 'city-region' (Franco & Etxebarria 2005).

4 SLAM

The cultural landscape of the *baserri* is liable to become a polycentric metropolitan region that is closely linked to medium-sized and small cities that complement them. In fact, there is a hypothetical approach to this (Calzada 2011) and it has materialized in the Basque Eurocity of Bayonne-Donostia, which has emerged from the agreements entered into between the cross-border administrations since 1993. Currently, the city includes 42 local entities in an area that covers 50 of the 200 Km that concern us here.

Planning the cultural landscape of the *baserri* and, above all, of the cities that are closely related to them, should not remain in the Manichean and conservative twin notions of 'old and new urban developments' as opposed to 'empty spaces in between' (Muñiz et al. 2002). We should progress from an 'urban approach' to a 'territorial approach' in every aspect, including cities, nature areas, cultural-heritage spaces and the unprotected intermediate spaces that "are the target for the intensive artificialization of Spain and, therefore, of the most invasive and unsustainable territorial changes" (Agudo 2007: 197).

Therefore, we need to go beyond the scope of cities and enter the broader area of landscape, which Art. 1.a of the European Convention of 2000 defines as "an area, as perceived by people, whose character is the result of the action and interaction of natural and/or human factors".

Putting what Lynch said more than fifty years ago into context, we could assert that landscape, "among its multiple roles, is also something that must be seen, remembered and cause delight" (Lynch 1998). In other words, landscapes are our memory.

Not all landscapes can be viewed as memory, however. Some do not manage to "give a feeling of connection with others and contribute to an understanding of the nature of the society we live in and a feeling of identity and place" (Thorsby 2001: 43).

The potential derived from a common yearning to belong arises from identification with a common project focusing on cultural heritage which, avoiding "exhaustive symbolism, disdaining cultural heterogeneity and the customs and periods to which accumulated assets belong" (Choay 2007: 222), manage landscape with a global vision adapted to local conditions, from 'glocalization' or *dochakuka* (from the Japanese term *dochaku*, 'one who lives in his own land').

Thus, perceived adequate connectivity and lively mobility contribute to the desired comfort in the use of a territory. "Connectivity breathes life into a city" (Dupuy 1998). In a space with a strong natural element, such as the one made up by the *baserri*, the connection must not only be fluid but ecologically sustainable.

The desired result should be the consolidation of a system we call SLaM (Smart Landscape of Memory). It could be defined as heritage districts generated by a feeling of identification and belonging, of a high cultural level, that are the objects of a common management and urban planning project for the physical, social, cultural, ecological and economic sustainability of the territory and, above all, of its inhabitants: "The places that are catalogued with the HC (high cultural level) distinction are artistic and cultural areas in which economic, non-economic and institutional stakeholders decide to use certain shared idiosyncratic resources (artistic, cultural, social and ecological) to develop a common project that is economic and, at the same time, a way of life" (Lazzeretti 2008).

In 2050, 25% of the population will probably be concentrated outside of the big cities, rendering the current model of consumption and operation obsolete.

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A petrological approach to the study of grinding mortars from the Roman gold mines of "Pino del Oro" (Zamora, Spain)

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ABSTRACT: This study shows how the petrological methods are useful for the characterization and interpretation of grinding mortars located in the Roman Gold-Mining Area of "Pino del Oro". Mortars were located in the most weathered and less hard granitic surfaces, finishing in depth, when the hardness of rock makes difficult continuing with the task.

1 INTRODUCTION

1.1 *Pino del Oro gold mines*

The Roman gold mines of Pino del Oro and its environment (Zamora, Spain) are mine workings developed in the Northwest of the Iberian Peninsula during the Early Empire (I-II AD) (Fig. 1a). They belong to the mining heritage of Roman Age preserved in the Iberian Peninsula. The fieldworks in this area have registered more than 70 sites associated with mining operations (Sánchez-Palencia et al., 2010). The archaeological work has allowed knowing the changes in the exploitation and territory between the Iron Age and Early Empire. However, the most significant are the mining structures that are found in Pino del Oro. The gold mineralization was exploited by various kinds of open works, mainly short trenches and opencasts. After the extraction of the ore it was treated as Pliny "The Elder" quoted in his Natural History: *"to obtain the gold from primary or rock deposits, ores must be subjected to special treatment of crushing, washing, firing and grinding to reduce them to the state of soft powder, like the flour"* (Plin. *HN XXXIII,* 69). The grinding process was made in singular bedrock saddle-quern mortars (Fig. 1b). These mortars are known with the name of "cazoletas" (here in after grinding mortars). They are known in other mining areas, like the Laurion's mines of silver, the gold mines of Egypt during the Ptolemaic era or the roman gold mines of Dolaucothi (Wales) and Tres Minas (Portugal) (Sánchez-Palencia & Currás 2010, Burnham & Burnham 2004: 281–284). All these mortars are movable, but the grinding mortars of Pino del Oro are made on the granite outcrops of the mining area where have been located more than one thousand of these mortars turning Pino del Oro in a singular gold mine in all the Empire.

1.2 *Geological setting*

Gold mineralization is associated with zones related to the different phases of Hercynian deformation that resulted in a network of fractures, with dykes and quartz veins. It relates in particular to the later stages in the formation of quartz veins with significant microcracking processes due to shear-type strain. The zones are altered. Gold values recorded in various surveys are between 0.01 and 16.08 ppm, with laws generally above 1 ppm (MG & MCyL 1997:136). The grinding mortars (Fig. 1b) are located on two kinds of outcrops. One of the outcrops is the so-called "Ricobayo" pluton formed by a granodiorite rock while the other outcrop is a monzogranitic pluton (IGME 1981, 1982). The "Ricobayo" pluton is the oldest one of both of them. Both

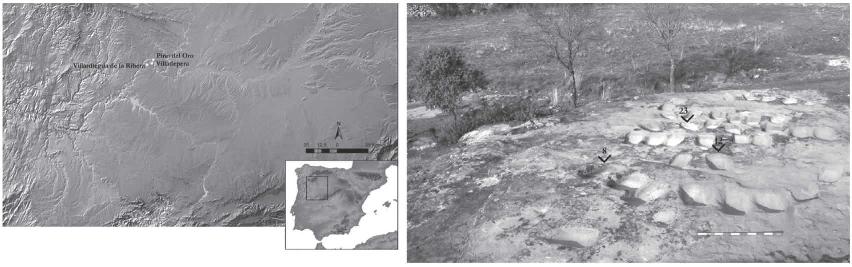

Figure 1. a) Situation of the study area b) Grinding mortars of “Pozo Serafín”.

kinds of rocks are mainly formed by quartz, K-feldspar, plagioclase, biotite and moscovite. The “Ricobayo” pluton appears oriented and deformed; it is a granular rock and has medium grain size. Its texture is holocrystalline and allotriomorphic. The monzogranitic rock form irregular outcrops and intrude the granodiorite. It is a granular and porphyritic rock. It has coarse grain size with K-feldspar phenocryst. Its texture is holocrystalline and hypidiomorphic.

1.3 *Aim*

The main aim of this study is to carry out a petrological characterization of several grinding mortars outcrops for determining its petrophysic and petrographic characteristics and for determine their state of deterioration in order to provide analytical information that may help to support various hypotheses related with the uses of the grinding mortars. In this article the aim is focused in the properties characterization of “Pozo Serafín” outcrop.

2 SAMPLING AND METHODS

Core specimens (4,5 in diameter, different cm long, up to 25 cm long) were extracted both inside the grinding mortars and outside them (Fig. 1b).

The research included the petrographical analysis of the samples and the petrophysical properties study of the stones, both “in situ” and in the laboratory. Polarized light optical microscope and a fluorescence microscope were used for the petrographical analysis allowing studying the fissuration rate of the samples in depth. The petrophysical characterization was done using ultrasonic wave propagation velocity (Vp)-taking into account the indirect transmission method (in the field) and the direct transmission method (in the laboratory)-, using the sclerometric method for the surface hardness measurement and a 3D optical roughness meter for the characterization of the rugosity. Other petrophysical properties determined included real and bulk densities, compactness, open porosity or porosity accessible to water and water saturation (RILEM 1980).

3 RESULTS AND DISCUSSION

“Pozo Serafín” outcrop is placed in the “Ricobayo” pluton. The field ultrasounds velocity and sclerometric data are lower in the areas were the grinding mortars are located (Vp: 2300 ± 600 m/s; sclerometric index: 33 ± 8) than in the granitic areas without grinding mortars (Vp: 2650 ± 500 m/s; sclerometric index: 39 ± 7). In Figure 2, it is possible to observe a core specimen extracted from the mortar outcrop area and the evolution of the different properties measured in the core specimen in depth. Porosity and compactness decrease in depth while ultrasound wave velocity increases; this fact is more clear 10 cm from the surface downward. These results show the better preservation state of the rock in depth. Another important factor is the influence of anisotropy in the rock (Fort et al., 2011). Total anisotropy (dM) of ultrasounds velocity is also show in Figure 2. Orthogonal direction measurements were determined through (1):

$$dM\% = [1 - (2Vp_1/(Vp_2 + Vp_3))] \times 100 \quad (1)$$

where Vp_1 is the minimum velocity, Vp_2 the highest and Vp_3 the intermediate. The results show also a change in the anisotropy of the material between 10 cm and 15 cm depth.

Sclerometric measurements were made in several grinding mortar across their longer length. Figure 3 shows and example of the hardness surface property of the grinding mortar, #12, which has a maximum depth of 9 cm. It points out that the maximum hardness is giving by the maximum depth and it is a direct relation between the hardness and the depth, increasing hardness with depth.

The results obtained by means of microscopy (Fig. 4) show the presence of most fissures in the outer parts of the core samples while the rate of fissures decrease towards the inner

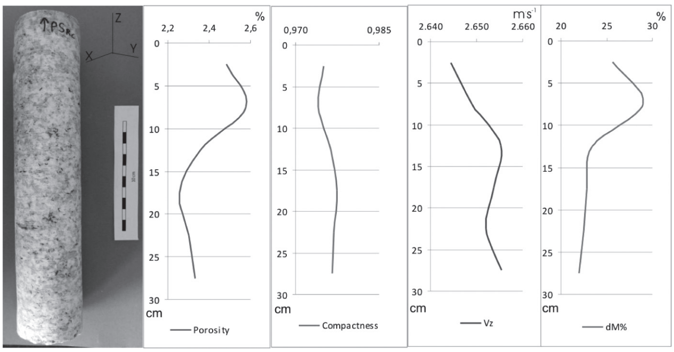

Figure 2. Left: core sample, from "Pozo Serafín" mortar outcrop. From left to right: graphics showing the evolution in depth of the open porosity, compactness, ultrasound velocity in Z direction and dM%.

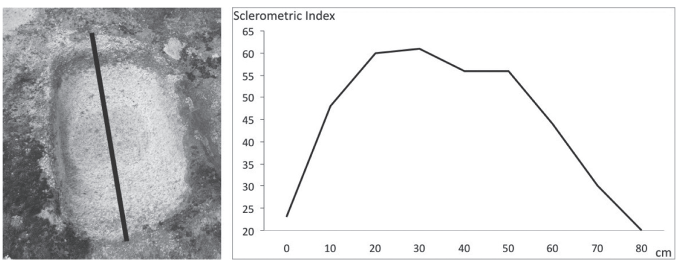

Figure 3. Sclerometric index results graphic across the maximum length of the grinding mortar #12 from "Pozo Serafín" outcroop. The black line of the left image shows were the measurements were made.

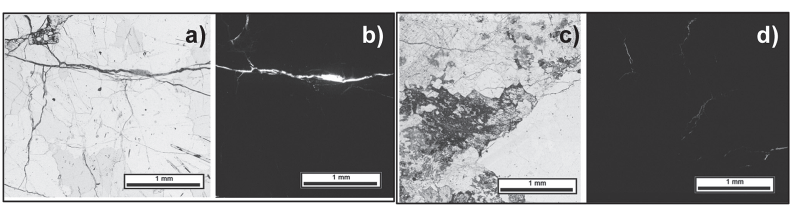

Figure 4. Some examples of the images obtained by means of the microscopic study; a) and b) shows a fissure across a quartz grain (depth from the surface: 1 cm); c) and d) shows the better state of conservation of the stone in a higher depth (24 cm). a) and c) are plane polarized images while b) and d) are images obtained with the fluorescence microscope (fissures: white, rock: black).

parts. The rock present some mica rich layers (parallel to the surface of the outcrop) that may be cause of the anisotropy of the rock. The fissures are also parallel to the surface of the outcrop and it could be thought that the fissures are associated to them. In fact, it happens in some cases but in others these fissures has been observed crossing a quartz grain. They are most probably caused with the tectonic stress that has suffered this area. Rugosimetry measurements (Rz parameter, which is is the sum of the vertical distances between the five highest peaks and five deepest valleys, was considered) were effectuated both at the bottom of the grinding mortars and in the corners of them. The mean of the bottom values is 27.2 while the mean of the corners is 22.3. However, the rugosity of each mortar grinding should be independently study in order to interpret in adequate form the obtained results.

4 CONCLUSIONS

The obtained results show how the different petrological methods are very useful for the characterization of the stone in which the mortars were excavated. These results provide a better knowledge of the decay rate of the outcrops and how it may have influenced the location, shape and depth of the mortars. It seems that in "Pozo Serafín" outcrop the grinding mortars are located in the most weathered and less hard granitic surfaces. It is possible that the use of each grinding mortar was stopped when the characteristics (higher hardness) in depth of the granite make difficult continuing with the task. However, the side by side arrangement of mortars suggests that the characteristics of that particular rock were sought by former miners, as their use can not be synchronous and have even documented examples of overlays. Although there are several sets like "Pozo Serafín", there are some places that have few mortars, 1–5, which could be interpreted by a type of granite as not suitable. Other circumstances have also to be considered: the results of closer mining, the time in which it was exploited, if it was a simply prospection or the proximity to water points needed to make the final washing process by panning. In any case, in future, these results will be compared with the results obtained in the rest of the study (taking into account both kinds of granites) obtaining scientific data for a better understanding and interpretation of the full area.

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Science and Technology for the Conservation of Cultural Heritage – Rogerio-Candelera, Lazzari & Cano (eds)

Origin and evolution of the agricultural landscape in Santiago de Compostela from the properties of a polycyclic terraced soil

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ABSTRACT: We analyzed with high vertical resolution a polycyclic terraced soil, looking for the imprints of ancient agricultural practices. Aluminum, Fe and Si fractionation was studied by selective dissolution techniques, and combined with elemental and isotopic composition, phosphate retention and pH in NaF. The aim was to identify signals of land-use change and infer the agricultural management techniques applied. The buried paleosol exemplifies the soil properties prior to the construction of the terrace and showed a strong andic character. But in the anthropogenic soil layers the soil components responsible for andic properties decrease. Variations in acidity, P and Ca content, and the $\delta^{15}N$ and $\delta^{13}C$, evidenced the use of fertilization and liming and/or new crop species. The 14C dating indicates that the intensification of the agricultural use and the strong anthropization started in the Early Middle Ages. The current agricultural landscape is mainly inherited from these early modifications.

The European Landscape Convention (2004) has defined the landscape as "part of the land, as perceived by local people or visitors, which evolves through time as a result of being acted upon by natural forces and human beings". Following this definition, the use transforms a specific territory in a landscape, which by definition is part of the Heritage. The land-use changes occur together with the cultural transformation and climate changes, which are an important factor in cultural evolution too.

However, past environments are not directly accessible. To reconstruct them we use superficial formations (soils, lake or ocean sediment, accumulation of peat, glacier ice, and other) that contain a record of environmental (including anthropically induced) changes, expressed as structural, textural, mineralogical, biological, and chemical signals. In particular soils, as substrate and livelihood, are affected by land-use. The imprints of the environmental and land-use changes on soils, can be read as signals of past conditions and human activities.

The change from forest to agricultural use and/or from early to more sophisticated technologies has been demonstrated to affect soil properties. In this sense, the change from forest to agricultural use may lead to a more than 50% decrease in soil organic matter (SOM) and organo-metal complexes (Verde et al. 2010). Also, the lack of vegetation during part of the year increases soil temperature enhancing mineralization of organic carbon (Haynes & Swift 1989). The extent of the impact of land-use in soil properties depends on the management technique and time of exposure. Before the Iron Ages agricultural practices are thought to have a non-severe, temporary effect on the soil, since tillage was very shallow and fertilization may have consisted only in the addition of the ashes from the burning of the shrub cover. Later, the adoption of new technologies involved deeper soil modifications. The correction of slopes implies the mixing of edaphic materials, modifies the surface runoff and the infiltration rate, and prevents significant erosion and colluvial movements, enhancing weathering processes (Camps & Macías 2000). Tillage increases soil aeration and destruction of aggregates, leading to losses of SOM and organometallic complexes by accelerated mineralization (Verde et al. 2010) and Fe oxidation. Fertilization intensifies mineralization and has an acidifying effect related to the nitrification (Verde et al. 2010) and liming produces soil alkalization. Both increased mineralization and organic amendments modify the isotopic signature of the soil C and N towards a higher δ^{15} N and δ^{13}C, because biological and chemical transformations of the SOM generally discriminate against the heavier isotope (Koerner et al. 1999). The detection of these modifications, combined with previous knowledge on paleoclimatic conditions, can be used to track ancient agricultural technologies and hypothesize about the cultural and social changes that led to their adoption.

We analyzed a sequence from an agricultural terraced system in Santiago de Compostela, aiming to get further insights into the processes of use and social construction of space throughout time. Data are read from the point of view of the landscape evolution, respect to the absolute chronology.

1 MATERIALS AND METHODOLOGY

The CC1 sequence is a thick polycyclic soil (300 cm) that was sampled at high resolution (samples of 10 or 5 cm in thickness) in 2002, in the context of the archaeological impact assessment and correction previous to the construction of the Galician City of Culture, in Santiago de Compostela (Galicia, NW Spain). Four different stratigraphic/soil units were distinguished: 1A, 2A, 3A, and 4A-4B-4C. The bottom unit (4A-4B-4C) is a buried paleosol that exemplifies the pre-terracing slope soil characteristics and the overlying soil layers have an anthropogenic origin. The samples were analyzed for pH in water (Guitián & Carballas 1976) and NaF solution (Fieldes & Perott 1966), phosphate retention (Blakemore et al. 1981), and total C, N and P content. Selective dissolution techniques were applied to assess the Al, Fe and Si in different fractions (see, for example, García-Rodeja et al. 2004). The ^{13}C and ^{15}N isotopic signatures were measured by isotopic ratio mass spectrometry. The mean values of these properties are summarized in the Table 1, grouped per horizons.

Four samples were dated by their ^{14}C content by accelerator mass spectrometry (AMS) at the radiocarbon facility of the Ångstrom Laboratory (Uppsala-Sweden). Conventional ages were calibrated using Calib 6.0.1 (Stuiver & Reimer 1993).

Table 1. Main values (standard deviation) per soil horizon of the chemical properties of CC1 soil.

Hor.	N[a]	pHw[b]	pHF[c]	Pret[d] (%)	C[e] (%)	N[f] (%)	P[g] (mg kg^{-1})	Alp[h] (g kg^{-1})	Fep[i] (g kg^{-1})	δ^{13}C[j] (‰)	δ^{15} N[k] (‰)
A	6	5.0 (0.16)	9.8 (0.30)	81.1 (0.47)	2.7 (0.53)	0.16 (0.03)	945.3 (111.0)	3,6 (0,52)	3,1 (0,47)	–25.7 (0.46)	8.22 (0.59)
2A	7	4.6 (0.08)	10.5 (0.24)	85.4 (3.64)	2.8 (0.28)	0.16 (0.01)	1238.0 (291.5)	5,2 (0,75)	3,4 (0,73)	–25.3 (0.08)	8.14 (0.74)
3A	10	4.6 (0.06)	11.0 (0.12)	92.9 (1.68)	4.2 (0.87)	0.22 (0.06)	1363.1 (276.0)	6,7 (1,39)	3,4 (0,81)	–25.6 (0.05)	5.96 (0.49)
4A	4	4.8 (0.05)	11.0 (0.37)	96.7 (2.88)	4.8 (2.96)	0.24 (0.16)	1021.7 (185.6)	8,3 (3,54)	5,1 (2,76)	–25.0 (0.33)	5.71 (0.58)
4B	5	5.0 (0.07)	10.1 (0.12)	91.4 (1.61)	0.9 (0.24)	0.04 (0.02)	87.5 (86.0)	2,7 (0,63)	1,4 (0,89)	–24.6 (0.08)	5.43 (0.51)

(a) Number of samples; (b) pH in water; (c) pH in NaF solution; (d) Phosphate retention; (e) Total C content; (f) Total N content; (g) Total P content; (h) Al forming organometallic complexes; (i) Amount of Fe in organometallic complexes; (j) relative amount of ^{13}C; (k) relative amount of ^{15}N.

The paleosol (4A) was dated in c. 430–270 BC, corresponding to the end of the Iron Age, although the development of this soil probably included also the Roman Period. The chronological gap between this layer and the bottom of the overlying one (530–660 cal AD) suggests the paleosol was truncated to some extent. Although, a large part of the original epipedon was preserved, as indicated by the presence of a 20 cm thick A horizon with andic properties. Soil properties are in agreement with the expected natural pedogenetic process (highly reactive material, with high contents of OM and Al-OM, and abundance of inorganic amorphous compounds) (García-Rodeja et al. 1987). During the Roman Period, environmental conditions in NW Spain were warm and humid (Warm Roman Period; Martínez Cortizas et al. 1999), which are favorable to agricultural productivity (Büntgen et al. 2011). This, together with the small population, made unnecessary a major adaptation of space devoted to subsistence activities.

The radiocarbon dating of the first terracing level indicates that it was built in a single deposition event dated c. 500–700 BC. Its OM content is markedly lower than that of the underlying paleosol. Different reasons may be responsible for this. Firstly, the abrupt decrease in OM content in the transition between 4A and 3A layers is probably due to the dilution of the OM of the surface horizon with inorganic materials in the construction of the terrace. Secondly, progressive decrease in OM and organometallic complexes in the 3A layer expresses the agriculture effects suggesting the use of tilling techniques (Verde et al. 2010) that enhances OM mineralization. Also, the increase in soil acidity, points to the use of N-fertilizers, which have the double effect of enhancing mineralization and acidifying the soil (Verde et al. 2010). P content increased compared to the paleosol, suggesting the addition of P-fertilizers to maintain agricultural production.

Both the isotopic ^{15}N and ^{13}C signatures of the 3A layer did not behave as expected: $\delta^{15}N$ is similar to that of the 4A horizon, and the $\delta^{13}C$ is lower. This may indicate an input of ^{15}N and ^{13}C depleted material that lowered the isotopic signature. We suggest the addition of plant biomass from N-fixating shrubs (e.g. Ulex spp.), as fertilizer by slash/mulch or slash/burn. These plants have a $\delta^{15}N$ close to 0‰ (Couto et al. 2011), and their ashes are ^{13}C depleted ($\delta^{13}C = -28$‰, Gómez-Rey et al. 2012) compared to the original slope soil (−24‰). Ulex shrubs would also contribute to increase P content since they have high P growing requirements (Gressel et al. 1996). In fact their key role in traditional agriculture to maintain soil fertility is well known (Bouhier 1979). Still, environmental causes would have also been involved in the depletion in ^{13}C and ^{15}N (drought, decreased temperature, nutrient (P) availability, Marriott et al. 1997) since layer 3A was built during the Cold Medieval Period (Martínez Cortizas et al. 1999). Therefore the data suggest an agricultural management based on tillage and the probable use of N-fixating species as fertilizer, either as green manure or ashes. The addition of amendments indicates an intensive and continuous soil use, agreeing with the few documentary references that we could find for this period, that reported the continuity of a settlement located nearby Monte Gaiás during the third and fourth centuries and the first stage of the Suevian era (Caamaño & Suárez 2003).

In the second terraced layer (2A) Al-OM complexes keep decreasing, probably due to strong mineralization. The increasing content in iron inorganic compounds indicates a higher pedogenic evolution despite this is a younger edaphic material. The $\delta^{15}N$ increases near a 4‰ in comparison to the 3A layer, suggesting a shift in land management to the application of ammonia rich amendments, as animal wastes, having a high $\delta^{15}N$ value. The low pH (4.5–4.6) would hinder the nitrification processes, favouring ammonium volatilization, which is a highly fractionating mechanism (Bedard-Haughn et al. 2003). The $\delta^{13}C$ values slightly increased (around 0.5‰), maybe as a result of an increased temperature (Marriott et al. 1997), since this terrace layer is dated in c. 800–1000 cal AD, during the Warm Medieval Period (Martínez Cortizas et al. 1999). All these data indicate a more intensive agricultural management, which is rather a result of demographic processes than forced by the environmental conditions. Indeed, the bibliographic sources report a population growth after the finding of the relics of the Apostol Santiago in the 9th century AD (Caamaño & Suárez 2003).

Nowadays the terracing system is still in use for agrarian production. The 1 A layer showed pH values and exchangeable Ca contents that suggest recent additions of lime. The increase in carbon content could be partially related to an organic amendment, together with the inputs from current vegetation. The amount of Fe-OM and Al-OM complexes is very low, pointing to slightly humified SOM that is coherent with a recent OM input. The $\delta^{13}C$ showed a marked decrease, probably as a result of the "Suess effect". The $\delta^{15}N$ continues to increase likely due to a more open N cycle with addition of inorganic N-fertilizers and appreciable N losses, probably by NO_3 leaching.

3 CONCLUDING REMARKS

Terraced soils can be used as environmental archives. Their multiproxy study offers a great potential for identifying and interpreting the impact of early agricultural activities, providing further information when archaeological artifacts are missing. We found important changes in the properties of the soil material following the construction of the Monte Gaiás terraces derived, firstly, from the constructive process that implies a mixing of surface and subsurface soil materials and a new topography. We also found clues about the kind and intensity of the past agricultural practices, including tilling, fertilizing and liming, in response to environmental and demographic changes. The landscape evolved towards an increased anthropization, albeit maintaining their main morphological features. This old agricultural landscape, built between the IV and X centuries AD, is still fully operational today and is part of our cultural Heritage.

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Possibilities of LASER conservation of metal objects from archaeological context

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ABSTRACT: Archaeological metal objects usually have a complicated state of conservation, characterized by the corrosion process that depends on the piece's nature, its technology and the burial context. In order to recover as much original *patina* as possible, usually hidden under a dense corrosion layer or even transformed into a layer of diverse nature, the restoration process requires an adjusted methodology, and the use of different tools and techniques. In this work we'll expose our good outcomes in metal cleaning with laser technology describing its efficiency in the treatment of four archaeological pieces of iron and copper with very specific problems, that couldn't be cleaned with traditional devices, such as ultrasonic piezoelectric spatula, micromotor and microsandblaster, scalpel, bamboo stick and brushes.

The aim is to understand the different results obtained with our laser device reducing the external deposits from the archaeological site and the corrosion products from iron and copper objects. Recognize the patterns from the objects depending on their nature and the fluency they received, and also how they get transformed and if the result is stable now and in the future.

The laser equipment used in this survey was a Nd:YAG (SFR) device, that works with 1064 nm, in a pulse length of 60 to 120 us; a pulse energy between 50 and 1000 mJ; a frequency range between 1 and 20 Hz and a spot diameter between 1.5 and 6 mm. All parameters can be modified except the pulse length. With the variation of spot and energy we can increase or decrease the fluency rate, which is the energy that the object receives per surface (J/cm^2) and by that we can favour an ablation cleaning or a photomechanical cleaning (Chamón et al. 2008).

The first possibility of laser ablation as part of the conservation treatment is the chance of cleaning extremely fragile objects. Metal objects from archaeological context whose advanced mineralization process has caused the structure's disintegration, cannot be treated with traditional cleaning techniques that imply vibration or pressure. That was the case of the Vaccean comb from Montealegre del Campo (Valladolid), made of iron (the teeth) and wood (the handle), but after the excavation only fibre marks remained and the teeth were corroded, with little metallic nucleus left and with external deposits adhered to the surface. The bad state of conservation and fragility didn't allow the use of microsandblaser, micromotor or ultrasonic piezoelectric device. Therefore, an alternative technique was necessary to carry out the cleaning, avoiding the vibration of these devices that threated the integrity of the damaged comb. The alternative was laser ablation that permitted the reduction of iron corrosion products and the recovery of the teeth's shape, ionizing the corrosion layer pulse by pulse, without harming the object.

The second improvement is the respect for the original surface, which is a great progress in comparison to traditional techniques. To illustrate it, we present two iron pieces from the Iberian necropolis El Salobral (Albacete): first, a falcata (Iberian sword) whose state of conservation was very delicate, due to the bending and cremation ritual, in addition to the hard burial conditions. The falcata was broken into many pieces; the surface was flaky and poorly adhered to the rest of the mineralized iron body. It had hydroxides corrosion, a magnetite patina and above it a dense layer of deposits from the archaeological context (carbonates, earths and silicates). The initial X-ray radiography revealed that the stable magnetite layer corresponded to the original surface, with signs of decoration. That layer was the cleaning limit; we had to recover it safely avoiding any artificial modification. Second, a falcata-style knife with its scabbard, that were better conserved, less fragile than the sword and maintained their original shape. The knife was complete except for its handle, probably from an organic material now lost. From the scabbard only the metallic areas remained. Here the challenge was to preserve the relief, rivets and structure details hidden under the corrosion and deposits.

The two traditional cleaning techniques for archaeological iron were dismissed because they would transform the original surface. The microsandblaster works smoothing down material by the impact of micro particles of aluminium oxide or glass microspheres. In any case, these particles don't distinguish between original layer, patina or corrosion product; they reduce first the soft areas, leaving the hard ones. That should be a problem if the corrosion layer is harder than the body and also in the case of decoration lines or applications that could be erased with the impact. On the other hand, the micromotor works reducing material by rotation and pressure, without differing between surfaces; the restorer takes the last decision about where and how much to clean, and could easily go too far and reach the nucleus, because usually the difference between what should be eliminated and left is not clear. Besides, this tool always creates the same type of surface: very smooth, plain, brilliant and "new", in the sense of reinvented. Therefore, neither of these devices (microsandblaster and micromotor) would be suitable to recover the magnetite layer, fuller, texture and relief. Like in the case of the fragile objects, the cleaning mechanism of laser ablation reduced gradually the corrosion crust until we reached the patina, where the impact didn't have the same ablation effect, because the nature of that surface was denser. That magnetite layer in the case of the falcata conserved the decorative lines engraved in it, as we can see on the picture (Fig. 1) and in the case of the knife and scabbard the structure's relief (Fig. 2). After applying laser technology to clean the surface and reach the magnetite, we used LIBS to characterize qualitatively the variation of the surface's composition on the scabbard (Fig. 3).

The third possibility of laser is the "cauterization" of copper chlorides, which are one of the biggest problems in archaeological copper conservation, since none of the methods developed until now can remove chlorides permanently. Most applied techniques involve application or immersion in chemical substances (silver oxide, alkaline solutions) which are quite aggressive treatments and their remains are difficult to remove. Besides, they're not always definitive and they can only be used when the archaeological object is well preserved,

Figure 1. Recovery of the fuller in the core of the falcata after treatment.

Figure 2. Falcata-style knife after laser restoration remaining the rivets from the handle.

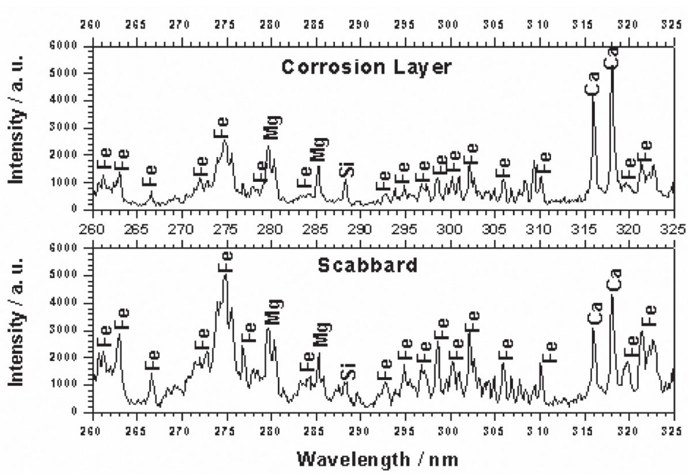

Figure 3. LIBS falcata spectra. The upper panel corresponds to the emission of the corrosion layer before the treatment and the lower to the emission after the cleaning process. The emission of calcium from the carbonates has decreased around 20% compared to the irons emission.

otherwise it's considered too risky. On the other hand, chlorides can also be reduced with mechanical techniques, but then scratches and marks can appear on the surface.

Our proposal was to take advantage of the lasers characteristics to "cauterize" chloride focus. When the beam reached the surface composed by copper (I) chloride, cuprite, atacamite and herbertsmithite, part of the material was ejected, atomized and ionized. This process seems faster for chlorine than for other elements. Amongst the compounds with chlorine, the copper (I) chloride is the most unstable and reactive (Orr et al. 1995). Therefore, this was removed almost completely, while atacamite and herbertsmithite were removed to a high degree from the surface. Meanwhile, cuprite was barely affected, turning partially into tenorite (CuO) (Kearns et al. 1998). So, by removing the problematic compound (copper (I) chloride) we delayed the corrosion process. It can be also stand out that the colour of the treated surface changed from green to black, and the texture became more compact and less porous than the previous chloride focus (Martí-López et al. 2009) what also reduced the corrosion. Even if this treatment was superficial, it's quite stable, particularly if the chloride focus has been reduced mechanically to a thin layer first and then treated with laser. Obviously, after the treatment, the objects should remain in an adequate environment with low and stable humidity. We used this method on copper alloy coins with historical restoration, where some chloride focus had appeared. We had excellent results removing the active compound of corrosion, transforming the typical green focus into a black surface very similar to the patina, and all that avoiding scratches, chemicals and aggressive treatments that could have risk the coins (Pardo et al. 2011).

The forth improvement is the possibility of treating heterogenic objects made of two or more materials thanks to the selectiveness and precision of laser. We present an iron lance tip decorated with silver threads, also from the Iberian necropolis El Salobral (Albacete). Like in the other cases, its conservation was very delicate: burnt, incomplete and mineralized, the iron nucleus was completely corrupted, remaining only a mixture of orange iron hydroxides. The silver threads were denaturalized, without shine, only adhered to the iron surface by corrosion products, and there were roots between the surface and the threads. In this case, the surface couldn't be cleaned with any other technique than laser, because under the irregular and thin surface, the orange hydroxides emerged with no end. That's why we didn't need to "clean" but to transform: it was the ability of laser to reduce the hydroxides what could stabilize that surface. Moreover, the property of focusing the light into tiny spots made it possible to clean the small zones around the silver threads, without risking them. Lacking this technique, especially helpful in the treatment of objects made of two or more materials, the lance tip would remain unrestored.

In conclusion, the research we've been carrying out validate the success on the use of laser in the treatment and cleaning of archaeological metal objects, always considering it part of a bigger procedure that should be used in common with other techniques, and improving the final result. Laser technology has given the chance to be treated to archaeological objects that were considered lost causes due to their fragility, complex composition or intricate structure that made impossible the access of traditional techniques and tools. The quick improvement of laser in conservation together with the evolution and versatility of the equipment and the results obtained make us very optimistic. One of our principal aims is keep studying and understanding chemical and physical process that occur when the laser impacts with our archaeological objects in order to guarantee the conservation.

ACKNOWLEDGEMENTS

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Geomatics applied to the monitoring of the damage and stability of the heritage

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ABSTRACT: This work discusses some relevant results obtained at the Laboratory of Geometric Documentation of Heritage -UPV/EHU- regarding the use of geomatics (surveying, photogrammetry, laser scanning, …) in order to define methodologies for detecting and monitoring the decay of historic elements.

Geomatic techniques are based on the acquisition of measures for the definition of shape, dimensions, visual appearance and spatial layout of objects. They can suit almost any need of size or accuracy. Therefore, they are most versatile and applicable in a great variety of cases.

To begin with, examples of 3D modeling of buildings at risk of collapse are shown. Secondly, we present some specific software created for the quantification of the loss of material on stone and the automatic detection of pathologies. To finish off, we deal with a case of how to optimize a recording methodology for the geometric monitoring of a historic building.

1 INTRODUCTION

Geomatic techniques comprise a set of methodologies based on the acquisition of measures for the definition of the shape, size and location of spaces and objects. Their current application to the measuring and monitoring of the decay of historic elements is evidenced by the wide variety of symposia organized by associations such as the International Federation of Surveyors (FIG), the International Association of Geodesy (IAG) or the International Society for Photogrammetry and Remote Sensing (ISPRS).

Some of the techniques involve to record images (photographs, infrared, etc.), with which the previous list of "shape", "size" and "location" can be expanded with the feature of "visual appearance". As a result, geomatic techniques allow the researcher to gather objective data about any of these four features and, by repeating the measures in two different times, also allow for the assessment of variation.

Many of the pathologies affecting historic elements (ICOMOS-ISCS, 2008) can be seen in changes in the features just mentioned and, hence, can be monitored in this way. In this work, some cases undertaken by the Laboratory of Geometric Documentation of Heritage (UPV/EHU) are presented as samples of their adaptability and potentiality as for the diversity than arises when dealing with heritage.

2 APPRAISAL OF THE CURRENT CONDITION

One of the main uses consist of recording the actual condition of a historic element at a given moment, for instance a building that runs the risk of crumbling. In these cases it is often advisable to resort to techniques, such as photogrammetry or laser scanning, which can capture very dense datasets quickly. The first case study (Gutiérrez Alonso 2007) shows a series of cross-sections taken by a three-dimensional laser scanner with a resolution close to 1 cm where the curving outwards at the bottom can be seen clearly (Fig. 1 Left).

Next case (Ibáñez de Elejalde Landa 2011) shows the documentation of a partially collapsed wall by means of photogrammetry. The geometric model has an accuracy of few centimetres and also reflects the visual appearance (plants, plaster, sort of materials, …) with a resolution of 5 mm (Fig. 1 Right).

3 OBJECTIVE VALUES AND AUTOMATIC PROCESSING

As said above, most of the pathologies that affect the heritage (cracks, erosion, moisture and so forth) are reflected by their shape and size. Therefore, they can be analysed by means of distances or coordinates. The following case (Moreno González 2011) quantifies the loss of material due to erosion in an oculus by comparing two digital models generated at different times (Fig. 2).

A similar situation can arise regarding visual appearance. The following case (Fernando de Fuentes 2010) shows the automatic detection of meaningful lines by visually processing both photographic pictures and range-images with a laser scanner device. The individual outputs are merged so as to obtain a refined result (Fig. 3).

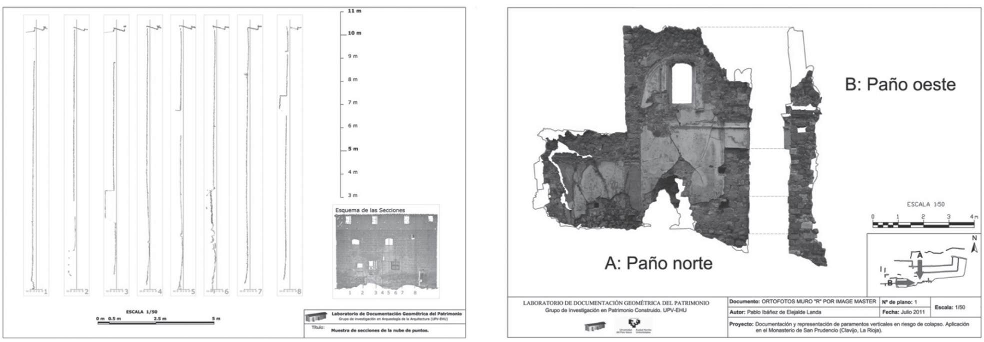

Figure 1. Left, set of cross-sections by laser scanning where the convexity of the walls is noticeable (Constables' Palace of Casalarreina, La Rioja). Right, elevation plan from photogrammetry which displays the condition of the coating layers (San Prudencio's Monastery of Mount Laturce, La Rioja).

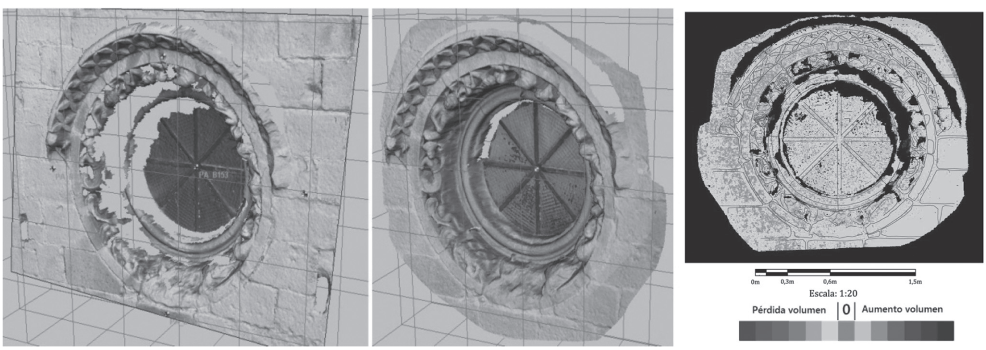

Figure 2. Two digital models from the circular window done at different epochs (left and centre) and the result of their comparison (right), detail of San Juan's church in Laguardia (Álava).

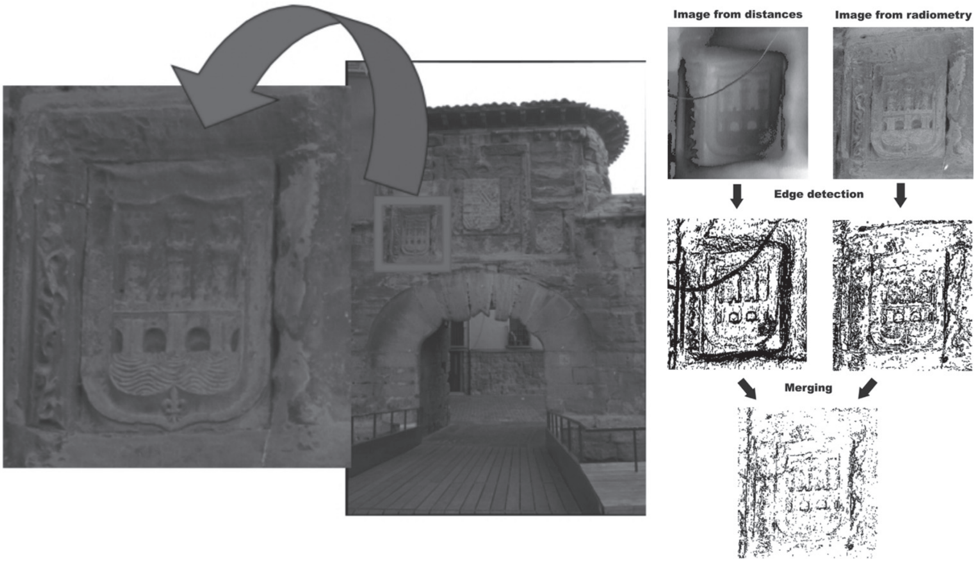

Figure 3. Left, stone relief representing a coat of arms. Right, edge detection from the merging of two processing over a photograph and a range-image (coat of arms on the wall of Logroño, La Rioja).

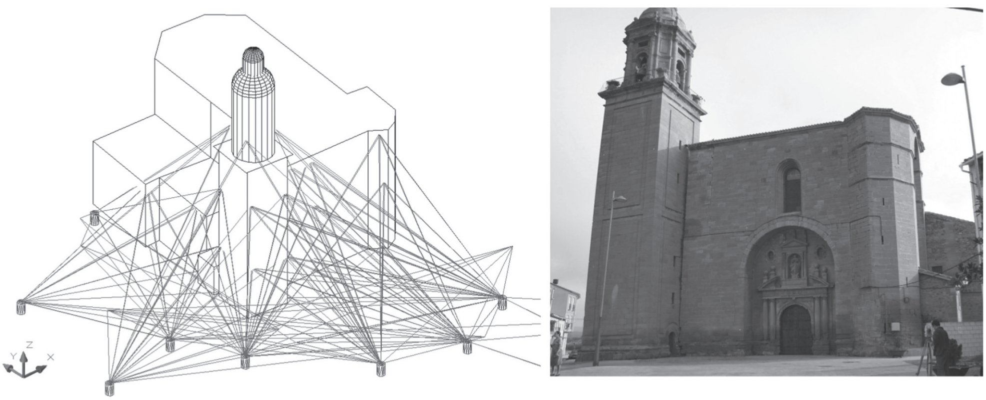

Figure 4. Sketch of the measures taken during the geometric monitoring of the church (left), picture during the data collection by land surveying (right). Geometric monitoring of Santa María la Blanca's church, La Rioja.

4 TUNING METHODOLOGIES UP

One step forward in the monitoring of heritage is to optimize the methodologies used. In the next case (Pérez Vidiella 2009) results are evaluated according to a set of variables: accuracy of the outputs, time, complexity, cost, etc. By means of simulation it is determined how these variables change if the data-collection procedure is modified. This kind of studies allows us to tune up different methodologies (Fig. 4).

5 CONCLUSIONS

The aim of discussing these cases was to show a sample of the possibilities given by geomatic techniques when applied to the study of decaying heritage.

Visual appearance and geometry can be recorded and, if done at successive times, the contrast can assess variations in a objective way and, thus, monitor the evolution of historic elements. Moreover, it is possible to create software and automatize the processes.

Since the results given by these techniques are dependent on many factors (time, equipment, etc.) it is possible to optimize the methodologies by means of simulation.

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Contribution of GIS and spatial analysis tools in the characterization of surface damage to paintings

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ABSTRACT: Geographic Information Systems (GIS) are computer applications conceived to edit, analyze and visualize spatial information. Their use in the graphic documentation and registry processes of canvas's damage allows to study in depth the condition of the painting surface through photographic records, providing qualitative data about all the represented elements. This makes it possible to precisely define the extent of the damage registered in the painting.

1 INTRODUCTION

The introduction of Geographic Information Systems in the field of conservation and restoration of cultural heritage, advance timidly and in an almost unknown way. So today, many of us remain oblivious to the great potential of these analysis and management tools of spatial information. Convinced of the need to raise awareness and to encourage the use of this new technology in our specific sphere of work, in the present article we want to spread one of its potential applications in the registry and graphic documentation process of a particular type of artwork, the paintings surfaces.

The main advantage of using GIS in the graphic documentation and registry field of paintings surfaces lies in their ability to merge spatial and alphanumeric information in order to analyze patterns, trends and relationships in a systematic way. Thanks to this, we are able to transform conventional damage maps into a real non-destructive analysis tool capable to provide metric characteristics about the extent and distribution patterns of the registered pathologies.

To illustrate the information provided by this new methodology of documentation, now we will show a GIS work of registration and diagnosis of an oil on canvas: *The Holy Family* of Gaspar de la Huerta.

2 METHODOLOGY

Geographic Information Systems are tools used mainly for the study of space projected onto a map. Therefore, the precision and reliability of their analysis depends on limiting, *a priori*, their scope to two-dimensional works of art. This is the reason why the present work focuses on the study and recording of a painting surface.

The Holy Family, an outsize painting located on the roofs of the Palau Ducal de Gandía's Galería Dorada, was restored in 2010 by the Instituto Universitario de Restauración del Patrimonio of Valencia (Spain). Its deterioration was marked by the dramatic consequences of an earlier intervention. It had been cut and fragmented into seventeen parts, being subsequently stuck and nailed to a plank. As a consequence of this new attachment, tensions appeared in the perimeter of the pieces, which caused abundant losses of the pictorial surface. Furthermore, multiple cracks and tears were generated because of the spiked. Finally, a large quantity of crude overpaintings invaded much of the original paint (Castell 2010).

In collaboration with the restoration project, we proposed to characterize the impact of this old restoration. To do this, using the software ArcGIS Desktop 9.3®, we generated a GIS damage map, in order to evaluate how far the missing areas and pictorial retouches was affecting *The Holy Family* surface.

To obtain quantitative data about this kind of deterioration, GIS technology used a simple vector-drawn damage map. However, unlike the graphics and image editing software used until now for graphic documentation, GIS permitted the projection of the true dimensions of the painting and its material alterations on its ortophotographic record (a planar projection) by a Cartesian coordinate system. Subsequently, in the editing tasks, GIS have provided automatically the area and the outline of each vector we were tracing, storing them in alphanumeric tables.

3 RESULTS

As a result, not only did we get a set of high-quality graphical representations, but also the losses and overpaints registered in our damage map could be calculated easily, as such their percentual reach. Additionally, after finishing the vectorization, SIG's analysis tools afforded us to manipulate the collected spatial information in order to interpret the relationship between these alterations.

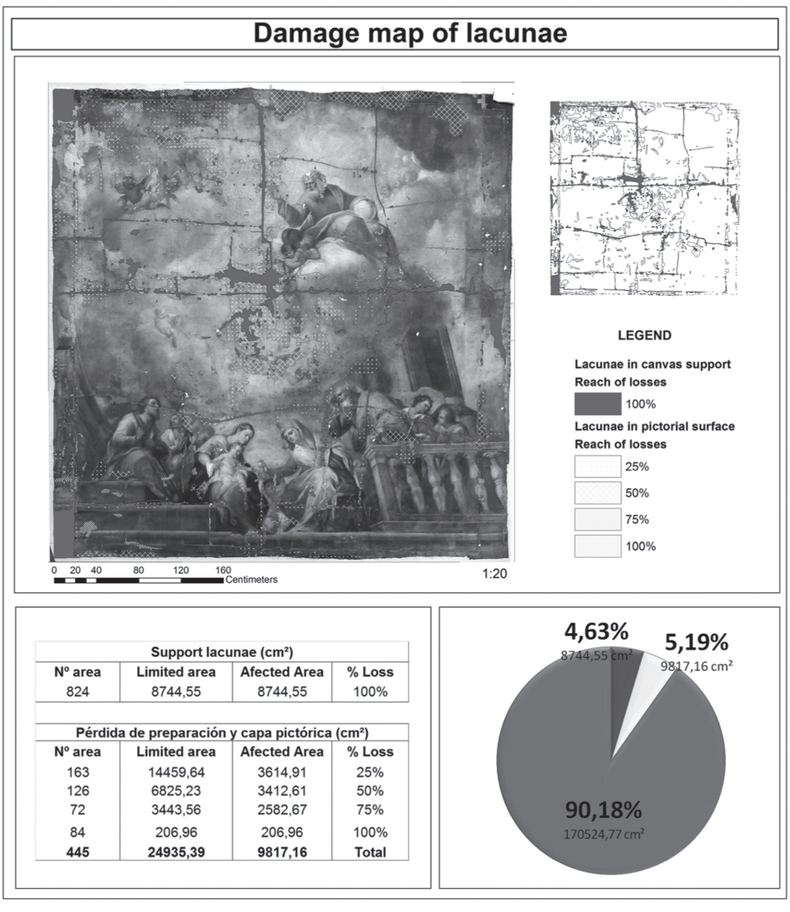

Figure 1. Distribution of *The Holy Family* missing areas according to the affected layer.

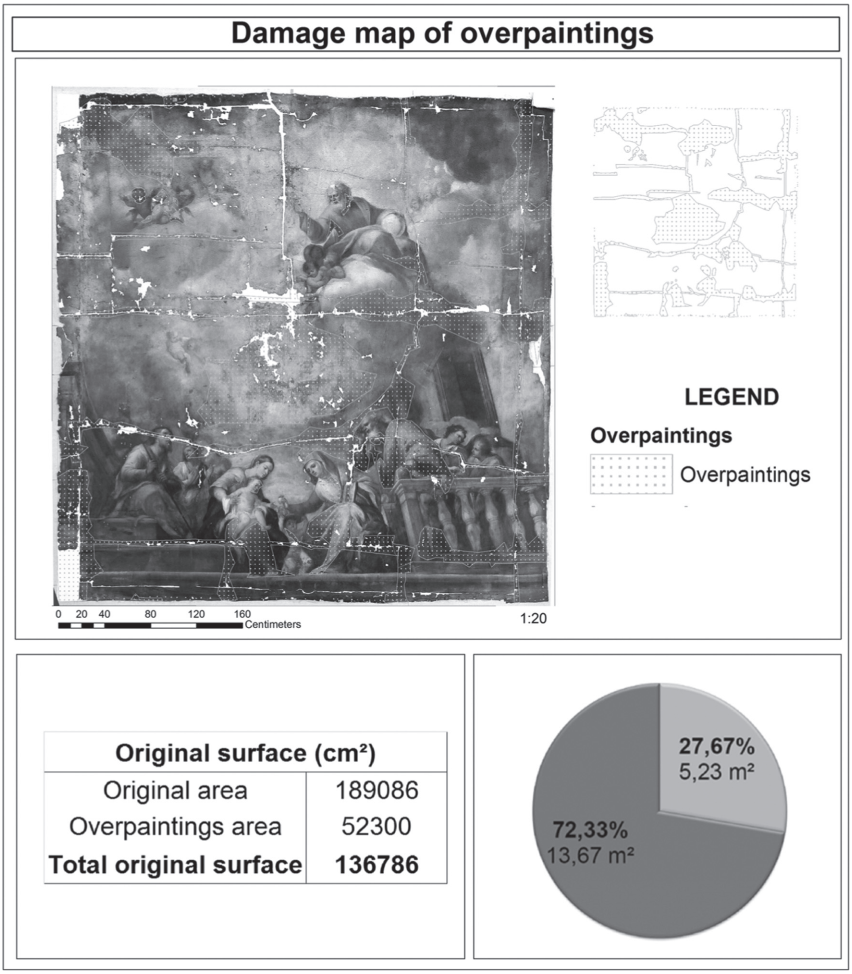

Figure 2. Description of the overpaintings reach.

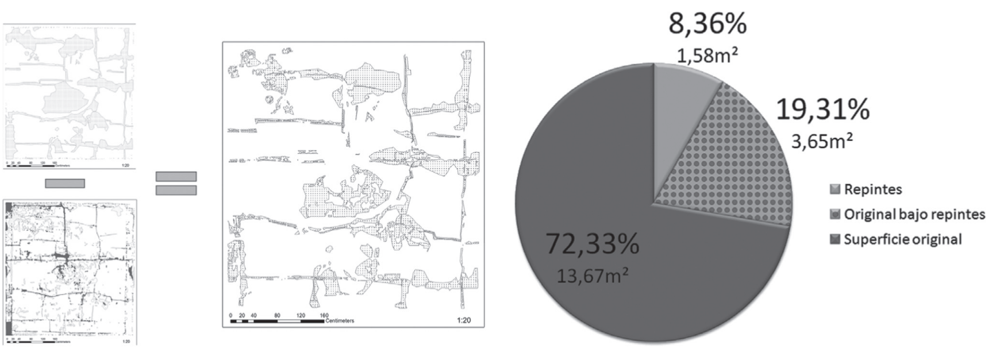

Figure 3. Spatial analysis of the relationship between lacunae and overpaint areas.

Thus, starting of the initial oil painting's outline, we could calculate that The Holy Family had originally an area of 18.90 m²; whereas the graphic representation of its lacunae added up to 1,85 m². This set its loss percentage at 9.82%, with 4.63% due to losses in the canvas support (0,87 m²) and the remaining 5.19% due to missing paint and gesso areas (0,98 m²).

Meanwhile, overpaintings reached a much larger area, 5.23 m², which meant the 27.67% of the total painting surface. This data evidenced that much of the overpaints were extended beyond the missing areas. To find out their exact proportion we simply had to cross the spatial information of these two kinds of deterioration, and subtract their intersection zones. This spatial analysis founded that 3.65 m² of overpaints were outside the lacunae, no more and no less than the 69.96% of their total area, which implied that the 19.31% of the original surface was hidden under these pictorial retouches.

4 CONCLUSIONS

GIS technology allowed us to deepen in the characterization of *The Holy Family* damage with very important quantitative information; among which are the metric characteristics and the reach percentage of its missing areas and overpaintings. This information, which has been until now out of reach of a restorer, is crucial to limit the subjective component of pathologic diagnoses enhancing their accuracy, and, therefore, to optimize the management planning of any restoration process.

The fact that a GIS provides so easily such information leads us to confirm that the use of these technologies is very efficient and may contribute to a significant improvement in documentation and registry processes; so we expect that in the future, GIS will be widely applied to painting documentation.

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Predictive model for the useful lifetime of a set of buildings of the Archdiocese of Seville

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ABSTRACT: Current predictive models related to the determination of the life of heritage buildings, including the recent norms, ISO TC59/SC14 "Design Life", and ISO 15686 Standards on Service Life Planning, fail to resolve the uncertainty associated with the various statistical methods involved.

In order to progress on this issue, in the proposed paper, the Fuzzy Building Service Life (FBSL) model is presented. This new model, implemented under XFUZZY 3.0 software, predicts the useful lifetime of a set of heritage buildings with homogeneous usage characteristics, and applies the theory of fuzzy logic to a hierarchy of factors provided by an interdisciplinary team.

This FBSL model has been applied to a sample of fifty buildings of the Archdiocese of Seville (Spain) to test its validity. The correlation demonstrated between the planning for the estimated lifetime of these buildings as developed from this application, and that generated from the direct assessment carried out by different experts, leads us to conclude that the presented model constitutes an evidently useful decision-making tool for competent authorities, inasmuch as its application to a wide range of buildings enables the evolution of their deterioration over time to be determined.

1 INTRODUCTION

Our research is focused on obtaining a predictive model of the useful lifetime of heritage buildings. Our field of work covers the buildings of the Archdiocese of Seville. For many years we have been developing methodologies that we have discussed at various conferences (Macías 2010a, b, c) and the interest raised by our proposals has been confirmed. Our model, called Fuzzy Building Service Life, FBSL, has recently been subjected to validation. The results are encouraging and hence further research along this line is being carried out which will enable us to continue improving this prediction model. The results are presented below.

It is assumed that the durability over time of a building is given by its vulnerability and by the risk of any type to which it is subjected. By finding a method that allows us to identify and measure potential key factors that affect vulnerability and risk, the useful lifetime of a building can be approximated and compared with that of other properties.

After studying various methodologies oriented towards the prediction of events (UNE-EN 31010-2011), we focus on the theory of Fuzzy sets (Zadeh 1965) as the most appropriate tool to address the problem we want to solve (Kosko 2010, Ponce 2011), whilst counting on the help of a group of experts for the definition of impact factors and their interrelationships (Cardona 2001). As a consequence of the application of this theory, we propose a model called FBSL (Fuzzy building service life) which offers us a result with reasonable margins of error, when fixing a specific date as the limit of the useful lifetime of a building.

The method is based on the validity of the factors proposed, which in turn are compared with various studies and reference standards (pr EN 16096-2011).

The scientific method requires us to prove or at least give sufficient reasons for the veracity of an experiment. To this end, the proposed model has been compared with three different proposals or systems in order to determine behaviour throughout the life of the buildings. The results of the application of our FBSL method are presented.

First, a tool, proposed in previous work is used, whereby the same factors are employed while applying neither the criteria of the experts, nor the theory of fuzzy sets, and the results of this method are then compared with those obtained by the FBSL method.

In the second approach, professional experts are asked to perform an estimation, with their own criteria, of the useful life of fourteen buildings they had previously studied, and then to apply the proposed predictive FBSL model, and the results are subsequently analyzed.

Thirdly, these fourteen buildings are subjected to estimation of their useful lifetime in accordance with ISO 15686-1.

Once all this data is analyzed, sufficient reasons are given, which prove that this research is on the right track and hence research of greater accuracy is justified in the future.

2 RESULTS OF THE APPLICATION OF THE PROPOSED METHOD

As initial data, the results, from applying FBSL, on fifty buildings of their estimated useful lifetimes are sorted into ascending order.

The estimations in the case studies range from twelve to fifty-two years of life, in the best case. For a total floor area of 36,065 meters square, the simple arithmetic mean gives a value of 28.5 years, with a standard deviation of 9.11, and hence are within perfectly normal limits. These results could be extrapolated to the entire property of the Archdiocese, thereby rendering an overall favourable view of the lifetime horizon of such buildings.

3 COMPARISON OF THE RESULTS OBTAINED BY ANOTHER METHOD

In the First National Congress of applied research to construction management, our first prediction model was presented. A comparison was made of the results obtained by each of the two methods. By applying the Pearson correlation coefficient, the value 0.66 is obtained which indicates a high correlation (Bisquerra 1989), between the two prediction models. This leads us to conclude that two tools with the same factors, but with different operating systems, offer us similar results, and therefore the reliability of these tools increases.

4 STUDY OF A SUBSAMPLE OF FOURTEEN BUILDINGS WITH THE CRITERIA OF PROFESSIONAL EXPERTS

Fourteen buildings of the Archdiocese have been selected. Professional experts have been asked to enter data for the FBSL model and to directly estimate the useful lifetime of each building. The following study has been made and the results are shown:

1st, Compare the useful lifetime as estimated by two experts, with the results of the application of the FBSL model on their data.

The correlations that are obtained by comparing the results are also high, except in the first case, which, as the estimation by expert 1, is more conservative than those obtained by the FBSL model. It can be observed how the criteria of the experts affect the final result, however when the same experts apply their data to the FBSL model, the correlations increase.

2nd, Compare the arithmetic mean of the useful lifetime as estimated by two experts with the results from the application of the FBSL model on our own data.

The arithmetic mean of the useful lifetimes as estimated by experts are compared with the results of applying the methodology used in our first predictive model, and then the results from the proposed FBSL model are compared with our data.

This result presents a very high correlation: when arithmetic means are applied and are compared with the expert model, then the results approach each other more and more. We conjecture that the expert model approaches the mean estimates of the experts.

3rd, Compare the arithmetic mean of the useful lifetime as estimated by the experts with the results from the application of the model set out in earlier work, on our own data.

It is observed how the Pearson correlation coefficient provides us with a greater correlation in the second case. As an illustration, it could be pointed out that the proposed FBSL model more closely follows the reasoning of the experts than that proposed in previous work.

4th, Comparison of the results with the ISO 15686–1standard (factor method)

We compared the results obtained with the estimation of the experts, and then with that of our FBSL model and obtained no significant correlation with the method proposed by the ISO 15686-1 standard.

We observe the following:

1. The ISO standard uses seven factors for the determination of the useful lifetime. In our case, the factors involved number seventeen.
2. In the ISO standard, each factor has the same representativeness in the final result. In our case, each factor is assessed in terms of the valuations of the other factors.
3. In the ISO standard, there is no hierarchy among the factors. In our model, following the advice of the experts, this hierarchy exists among the factors.

5 CONCLUSION

The proposed model is intended as an indicator of building evolution trends in the future, and to this end, three ways to make comparisons between different prediction systems have been employed.

Since a prediction table of durability had already been made available from previous work, it has been applied to the fifty buildings under study and compared with the results obtained with our model using the Pearson correlation coefficient, thereby obtaining a value of 0.65 which we interpret as meaning that the two methodologies point in the same direction.

The experts were asked for their opinion in relation to fourteen buildings also included in our study, whose data was used in an application of our methodology. It can be observed that the value of the useful lifetimes estimated by the two professionals, once the arithmetic mean of both sets of data and our model was calculated, the results also show strong affinity: an extremely high correlation of 0.90.

We employ the prediction model of ISO 15686-1 n accordance with the criteria of the Polytechnic of Milan which uses the Monte Carlo method, and the results obtained show no correlation with those analyzed hitherto. The reasons for this difference may include the following:

1. The ISO standard gives results based on statistical probability. It provides the reference service life (RSL) with a margin of error of between 25 and 30%.
2. With the ISO standard, we are not aware of any analyses applied to entire buildings having been performed. It constitutes a model aimed at building elements and not at building systems and, to even lesser extent, to the set of building systems.
3. The ISO standard is based on the premise of the estimation of the RSL at the time of the initial design of the project. In our case, since the majority of the buildings are antique, obviously the provision of this data has never been considered.

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Risk analysis in Historical cities: The cases of Carmona and Estepa (Seville, Spain)

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ABSTRACT: The degradation of monuments is mainly due to the deterioration effects caused by structural damages, weathering affection, pollution agents and anthropogenic factors. Intensity of degradation may be worsened by the vulnerability of each monument. RIVUPH is a project of the Andalusian government based on the analysis of environmental risk in Historical cities in order to develop conservation strategies and policies. With this purpose Risk and Hazard maps of different towns are being building with GIS software. The aim of this work is the application of this methodology to the cases of Carmona and Estepa (Seville, Spain). The conservation degree of monuments and the static-structural hazards, related to ground stability problems, set the main risks of the monuments in the Historical Cities of Carmona and Estepa. Analyzing the risks maps is a very useful tool to identify, evaluate and prioritize the restoration of Cultural Heritage.

1 INTRODUCTION

RIVUPH is a project of the Andalusian government based on multidisciplinary analysis of environmental risk in Historical Cities in order to develop global conservation strategies that can minimize the deterioration of Cultural Heritage Cities. These procedures provide protocols and policies for making decision when you have a huge monumental area to preserve.

Under these guidelines, a methodology based on procedures to analyze the vulnerability matrix has been carried out to study the conservation degree of 36 monuments and the influence of environmental risk factors.

2 METHODOLOGY

The vulnerability has been studied with a double entrance matrix adapted to the nature of heritage conservation problems of the Historical Town following the methodology developed by Galán et al. (2006). This procedure has been developed according to the methodology for assessment of environmental impacts.

The study of weathering forms has been made according to the glossary of ICOMOS (2008) and the standard 1/88 (1990). The diagnosis analysis constitutes the qualitative vulnerability matrix that allow visualize and identify the relationships found for the environmental conditions and the conservation degree of the Historical Centers.

The vulnerability index (VI%) for each monument was determined by an "in situ" study, where the frequency and weathering degree of the deterioration patterns was taken into account.

In this study, the index is evaluated for the predominant lithotype by the equation (1):

$$VI(\%) = \frac{Vx}{\sum_{f=3} vdp} \times 100 \tag{1}$$

where: VI is the Vulnerability Index, Vx is the evaluation of the damage and vdp is the worst scenario, that is, the maximum value of the weathering forms that could be found in these environmental conditions.

The appearance of weathering forms is set between 1 and 3: 1 means that it is difficult to detect this weathering form, 2 implies that the weathering form is identified easily and 3 is applied if the pathology occurs at a high rate. On the other hand, the weathering degree is classified in five relative classes, according to the scale used by Fitzner (2007). Weathering forms Frequency and damage value are combined in order to obtain a numerical value of the intensity of weathering forms in each monument.

Finally, the vulnerability index (VI%) is classified by vulnerability degree using classes described by Galán et al. (2006).

The hazards have been classified in three categories following ICR methodology (Baldi, 1991): Static-structural hazards: seismic factors, landslides, floods, underground water and geotechnical factors, Environmental-air hazards: wind, rain, river erosion, pollution, temperatures cycles and dew point and Anthropogenic factors: fires, accessibility to the monument, tourist pressure and demographic changes.

Each hazard has a frequency and intensity that varies according to the environmental conditions in the different areas of the city. The frequencies and intensities of hazards in the historical cities are set up using a relativity scale with five levels. These assessments are developed from the local, regional and national institutions data (AEMET, IGME, Consejería de Medio Ambiente de la Junta de Andalucia, Town-Hall of Estepa and Carmona, ...).

The influence of each hazard has been weighted to overlap the factors in the hazard maps and finally in the risk map.Weighted factors were obtained using the Delphi protocol and consulting a multidisciplinary group of seven experts: archaeologists, geologists, chemists, architects, engineers and environmentalists.

3 CASE STUDY

Carmona was an Iberian town that was Romanized and nowadays maintains the Roman urban plan. The two defensive gates of Seville and Córdoba date from that period. Afterwards, Carmona had a relevant role during Muslim domination that ended in 1247. During the reign of King Pedro “the Cruel”, Carmona reached a high level in the country region. In this period, the “Alcázar” was developed near the path to Marchena.

For this work the studied area of Carmona covers around 2,5 km^2 and nineteen monuments have been taken into account, as shown in Figure 2.

Estepa is also located in Seville province (South Spain). The original town was standing on an elevated area called Hill of San Cristobal. Formerly, it was a Roman town (Ostippo) and a Muslim town (Istabba), which had an important border role. The “Alcazaba” and the wall of Estepa have their origins in the Islamic period, although they have had subsequent modifications.

For this work the studied area of Estepa covers circa 2,5 km^2 and seventeen monuments have been taken into account, as shown in Figure 2.

4 RESULTS AND DISCUSSION

The most frequent pathologies are the presence of vegetation, staining, black crusts, deposits, flakings, fissures, alveolization, missing parts and erosion in the case of Estepa (Fig. 1). These nine weathering forms are found in more than 80% of the monuments studied while other pathologies less observed in this city are scratches, blistering, deformation and fractures.

Carmona monuments present biological colonization, staining, black crusts, deposits, erosion and missing parts. This weatehrering forms appear in more than 60% of the buildings.

The results of the vulnerability index of the 36 monuments studied are showed in Figure 2.

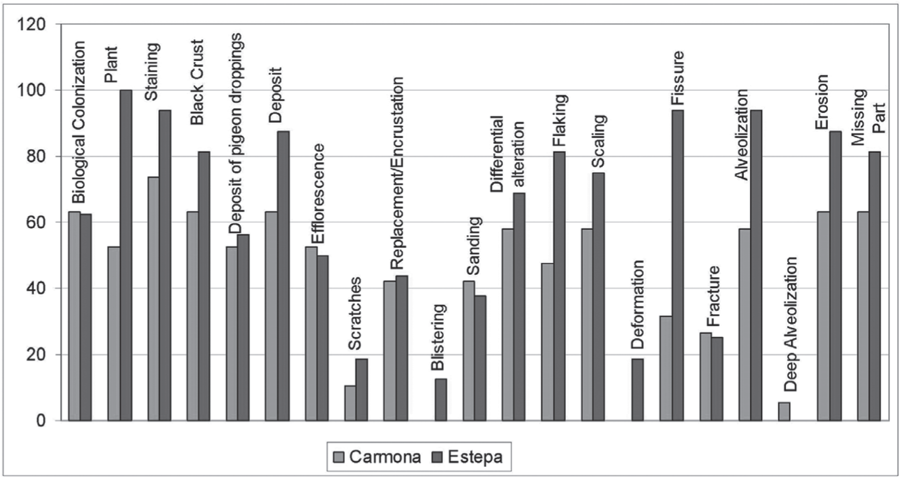

Figure 1. Weathering forms found in the monuments of Carmona and Estepa (Spain).

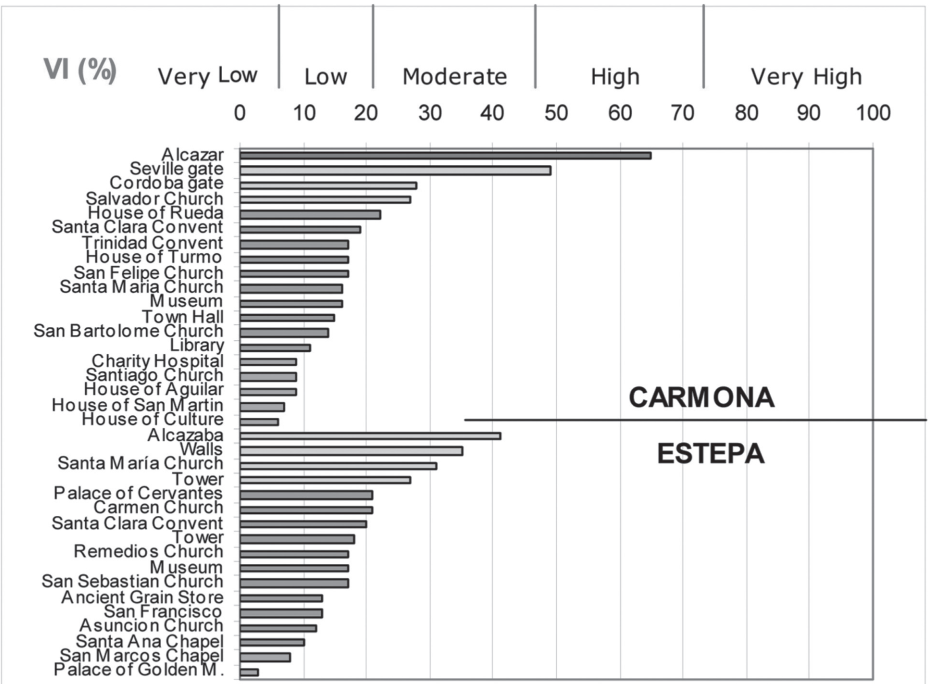

Figure 2. Vulnerability degrees of the studied monuments.

Seven monuments exhibit a very low degree of vulnerability, twenty one have low vulnerability and seven of them present moderate vulnerability. The "Alcazar" of Carmona has the highest vulnerability index (65%) which implies critical conditions. The vulnerability index comparisons reflect that the "Alcazar" of Carmona should be restored the first, following by the Gate of Seville (Carmona) and the "Alcazaba" of Estepa. This methodology allows to identify, evaluate and prioritize the restoration budgets of a city.

The Vulnerability Identification Matrix of the monuments of the two cities is mainly due to the impacts associated to erosion, pollutants, interventions and vandalism. Meanwhile, some weathering forms in Carmona and Estepa highlight stability influence, and in the case of Estepa temperature changes. Moreover, the most common stone in both cities are calcarenites and limestones, that are very vulnerable to the effect of traffic in Historical Centers.

The highest value of the risk in the cities of Estepa and Carmona are dominated by the hazards due to static-structural hazards (landslides). The presence of clay minerals around the edge of the hill is the cause of this static-structural risk.

The "Alcazar" is located in the area with highest risk of landslide in Carmona. The risk of landslide is added to its high vulnerabilty index (65%). The Walls, the Tower and the "Alcazaba" of Estepa are also under static-structural hazards of landslide. For this reason, the conservation degree of the "Alcazaba" and the Walls, which is moderate, also could worse the conditions of conservation. The monuments under this risk must improve the conservation degree and employ measurements of stability.

The environmental hazard maps are dominated by the traffic and enhanced by the calcareous stones employed in most of the building. The weathering hazards in Estepa are dominated by the change of temperature, that could generate the occurrence of scaling.

Urban rules minimise the risks of anthropegenic hazards, but must be evaluated in different scales.

5 CONCLUSIONS

The monuments of Carmona and Estepa are in good conservation conditions, except "Alcazar", "Alcazaba", and Gates of Sevilla and Cordoba that have high or moderate vulnerability indexes. The static-structural hazards are the highest risks in those cities, due to the landslide. The monuments under this hazards in worse conservation degree must monitore their stability and undergone a preventive conservation plans.

The Vulnerability matrix methodology is an economic and effective tool to evaluate the conservation degree of a monument and to prioritize future interventions. This methodology overlapped with risk analysis is a very useful tool to identify, evaluate and prioritize the restoration budgets of a city and to forecast the preventive conservation.

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The MHS system as an active tool for the preventive conservation of Cultural Heritage

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ABSTRACT: The MHS project (Monitoring Heritage System) is designed as a monitoring system adapted to historical and artistic heritage that has been implemented and tested since 2005 by the Heritage Conservation department of the Santa María la Real Foundation– Center of Romanesque Studies (FSMLR). The system has been developed to measure, record, evaluate and control various crucial and influential parameters in the conservation of heritage monuments in order to ensure sustainable management and optimal maintenance of the building as well as all the elements housed within. To date, the project has become a system of reference in the cultural sector, a powerful tool to efficiently control the status of historic preservation in real time, thanks to an innovative system of sensors that transmit data wirelessly. This leads to intelligent management and dynamic results.

1 THE NEED FOR THE MHS SYSTEM

It is clear that there is a continuous need for preservation and maintenance of historical heritage. However, the huge amount of heritage is overwhelming and has gone beyond the capabilities of traditional management, which normally goes into action once significant deterioration is detected. Such “curative” types of interventions are very costly and unfortunately, it may be too late to reverse the damage already done.

It is imperative, therefore, to change this action model and to have the ability to anticipate the deterioration, to have the information needed to assess the status of each building, painting or sculpture at any given moment, and to do so sustainably. The operational viability to meet this need is subject inexorably to process automation and the application of new technologies.

The MHS system is a direct consequence of the practical need to develop functional equipment that monitors the status of heritage conservation in real time, is adapted to specific needs, is easy to install and maintain, is invisible to the eye of any visitor and at the same time is economical and efficient. Furthermore, the infrastructure required to implement the system allows a number of other features to be managed remotely from a single control center: energy consumption, environmental and structural parameters, dissemination (lighting scenes, video projection, audio guide, etc.), visitor control (automatic opening doors) or safety. To manage these elements, an identical configuration of equipment in all scenarios is required.

2 DESCRIPTION OF THE MHS SYSTEM

The MHS system has been developed as a tool to control, environmental, structural, and security parameters in movable and immovable goods. It has two objectives: to implement a methodology of preventive conservation in heritage monuments and also to generate a system and an infrastructure that permits sustainable and integral management.

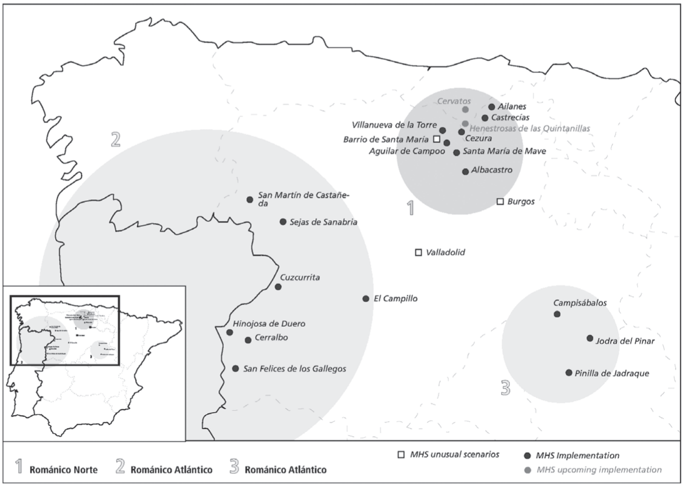

Figure 1. Location of MHS implementations in Spain.

Currently, the MHS system is installed in 21 heritage monuments in Spain (Fig. 1). In all the cases, the system has been implemented according to what was published in the VII International AR & PA Congress (Chiriac et al. 2010), following the different stages:

– Previous investigation
– Installation and activation
– Research and parameter control
– Maintenance.

2.1 *Equipment*

The system consists of both hardware, which includes the necessary equipment for measurement, reception, transmission and data storage, as well as computer applications or a software package that provides the user interface (Fig. 2). The configuration is set with the following components:

– A "*smart" control center* that processes all the information received from all the heritage buildings under the supervision of a specialist. It will consist of:

  a. *Server*. It receives data from central nodes in each historic building.
  b. *Database*. It stores the historical data.

– An *infrastructure of sensors* in each historic building will collect real-time measurements of parameters with different physical, chemical, mechanical, and security frequencies as well as the amount of usage. These sensors are connected to *local nodes* which periodically transmit the data to the respective central node using ZigBee technology. A *central node* in each historic building will collect all the information received by the wireless sensor infrastructure. In turn, the central nodes are connected through the available infrastructure with the "smart" control center.
– A *platform for the collection and storage of data* from the sensors manages all the matters relating to the sensors, their status, reception of the measurements originating from the sensors, sending "commands" or orders to the actuators or sensors, the storage and indexing of measurements in appropriate databases, and the implementation of reporting mechanisms for applications that are assigned to specific events or sensors.
– A set of *user interfaces* allows the possibility to access and configure the various components and obtain the information reported by the system.

Following recent developments in the MHS system, the central node is comprised of a coordinator node, an industrial computer and a GSM device for sending data. The local nodes have

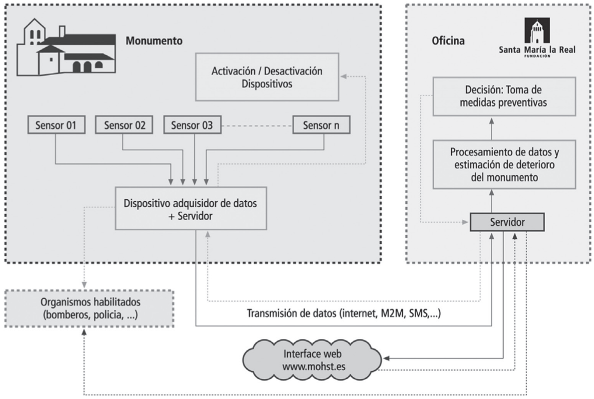

Figure 2. MHS operating generic scheme for a single building.

been designed and optimized by the FSMLR basing its development on the use of a minimum circuit optimized for specific needs, without unnecessary ancillaries such as USB, LEDs, interface elements, expansion or input/output, yielding a device with the following features:

– ATMEGA 1281V with 8 MHz frequency with external or internal ceramic antenna
– AT86RF212 Transceiver
– Radio Frequency 900 MHz
– JTAG connector for external programming
– Communication with I2C sensors
– Digital inputs and outputs for actuators
– Power Source with industrial batteries –3.6 V
– ABS Protection box with ventilation for sensors
– Digital sensors like SHT25 from the Sensirion brand

The local nodes collect the information from the sensors and transmit to the coordinator node directly or via an intermediate node configured as a router connected to the electrical grid. The data received by the coordinator is interpreted by a software application, which stores them in a BBDD or text file and sends it to the control center via the Internet, M2M or SMS. The goal of the Control Center is to process information either automatically or by means of a software tool based on preset protocols or by customizing it using a specialist to recognize and analyze the information.

For most rural buildings the cheapest variant is the M2M but this method is not feasible in areas with poor GSM coverage. In these cases, the communication via SMS is the most suitable. An example of this particular circumstance takes place in some of the churches involved in the Atlantic Romanesque Plan. Although they are located in Spanish territory, they are close to Portugal and get more of an intense signal from the neighboring country, making communication with the national phone lines inoperative. Similarly nationwide telephone companies vary depending on geographic location, this not only effects data transmission but it would also be extremely costly to contract several different telephone companies.

2.2 *The MHS system as a diagnostic tool*

Currently, data received in the Control Center is analyzed by technical specialists for each scenario individually. Incrementally, there is a plan to develop a tool to process the information automatically, estimate the damage that the assets may have under certain short term and long term conditions, trigger automation to stabilize parameters or recommend specific corrective actions. Thus, the objective is to develop software based on the implementation of mathematical algorithms developed by Statistical Process Control (SPC) and Pattern Recognition in collaboration with the University of Valladolid and the University of Salamanca.

In relation to the study and analysis of environmental parameters, we are currently collaborating with the University of Madrid in order to use the data collected by the humidity and temperature sensors of the MHS system as a diagnostic tool for moisture in historic buildings. The data provided by the monitoring must be framed within a diagnostic protocol to be meaningful (García-Morales et al. 2012), and that there are one or more underlying questions behind monitoring. The monitoring itself is not a diagnostic tool. Therefore, in the implementation of the MHS system hygrothermal inspection is being used, developed in said diagnostic protocol to provide the necessary background information to reach the prediagnosis, which may require monitoring of the heritage building.

2.3 *The MHS system as a comprehensive heritage management tool*

The MHS project goes beyond just being a mere heritage monitoring system focused on preventive conservation. We believe that the technical structure proposed in the MHS system can be a powerful, effective, and comprehensive heritage management tool.

The functionality of the system depends on operating centrally around three fields of action for effective and efficient management of the assets: *knowledge*, *conservation* and *use* (López 2012). The useful information collected by the system, along with other processes, substantially facilitates decision making by technicians and institutions with horizontal economic control.

By customizing the equipment needed for each section or activity and integrating the corresponding software module, a tool can be coordinated to adapt to the needs of each manager. Six different and complementary modules relative to critical sections are proposed to meet the needs that can converge in the current management activities in the field of heritage: cataloging, conservation, safety, resource efficiency, distribution and visit control. The conservation module considers the bulk of the complex section of preventive conservation, specific maintenance actions and recommendations on actions needed in restoration.

The FSMLR gives the end user access to data via the website www.mohst.es or via custom software installed in the client´s computer.

3 CONCLUSIONS

MHS is a quality and secure monitoring system that provides understanding of the monitored building as well as the data needed to establish the optimal times to execute conservation action before the damage is irreparable.

To this we must add that monitoring should be framed in a diagnostic protocol to obtain data that serves to achieve an accurate diagnosis. Additionally, for the MHS system to be complete, the involvement of specialists in different disciplines (architects, pathologists, historians, engineers etc.) is critical. These specialists should participate in the various stages of system implementation.

The FSMLR has verified and implemented the MHS system successfully in a large number of heritage scenarios. Today we can state that the MHS system has become a reference in the sector of heritage in Spain.

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Science and Technology for the Conservation of Cultural Heritage –
Rogerio-Candelera, Lazzari & Cano (eds)

Significance and social value of Cultural Heritage: Analyzing the fractures of Heritage

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ABSTRACT: Heritage is a metacultural process in the sense that artifacts, buildings, landscapes, festivals or any other heritage element are not by themselves heritage unless there is social value attached to them. From this point of view, heritage is a peculiar type of cultural product because it implies a metacultural reflection about culture itself. Heritage implies "adding value to culture." It is a value-laden concept with no neutral ground of connotation. Therefore, heritage-related projects need to incorporate critical research on the instrumentalizations of heritage policies and the conflicts that arise. This contribution analyzes some of the factors that are part of heritage-making processes -or heritagization processes- and concentrate on the fractures that can be observed in heritage research and practice. A first type of divide is linked to the distance between those who understand heritage as socially constructed and those who continue having the perspective that heritage are things. Other fractures are related to the distance among the various social actors involved in heritagization processes, particularly the distance between managers of heritage, policy makers, and local population.

1 HERITAGE AS A SOCIO-CULTURAL CONSTRUCTION

In a conference dedicated to the conservation of heritage, where many presenters are from areas as diverse as biology, ecology, chemistry, art history, architecture, geography and archaeology, among others, it is important to include some reflections on the significance and social value of cultural heritage. During the first days of this conference, very detailed research on particular conservation problems has been brought up to the front: from monitoring environmental conditions, to the mechanisms of deterioration of built heritage. However, the social practices of valorization of any heritage entity, which are an essential part of its conservation, are frequently silenced.

This contribution analyzes some of the factors that are part of heritage-making processes -or heritagization processes- and concentrate on the fractures that can be observed in heritage research and practice. A first type of divide is linked to the distance between those who understand heritage as socially constructed and those who continue having the perspective that heritage are things, a position named "substantialism" by Davallon (2010). Other fractures are related to the distance among the various social actors involved in heritagization processes, particularly the distance between managers of heritage -and policy makers- and local population.

While in anthropology and other social sciences it is not questioned that heritage is socially constructed, other professionals and managers of heritage defend the intrinsic quality or value of heritage. French anthropologist Jean Davallon differentiates among three positions in relation to this issue: substantialism, that seeks to define what "true" heritage is independently of their social context; extreme relativism, that acknowledges heritage as a social construction and, according to Davallon (2010: 43) "ignores the features of the object"; and moderate relativism or the anthropological viewpoint, that defends the idea that "in a given society, where the category of heritage exists -which is obviously not the case in all societies-, it [heritage] is an institutional fact and thereby the recognition of an object as heritage is a social construct" (Davallon 2010: 43). The problem with Davallon's division of positions is that she does not mention who can be considered "extreme relativists", and some of the most extremists positions in that regard, for instance, archaeologist and museologist Laurajane Smith also recognize the objects themselves. I propose to look at this contradiction in heritage practice in terms of "substantialism" and "anthropological perspective".

From an anthropological perspective, the fact that cultural heritage is a metacultural production is not questioned. Heritage is a metacultural process in the sense that artifacts, buildings, landscapes, festivals or any other heritage element are not by themselves heritage unless there is social value attached to them. From this point of view, heritage is a peculiar type of cultural product because it implies a metacultural reflection about culture itself (Kirshenblatt-Gimblett 2004, Novelo 2005, Smith 2006). The term "metacultural" can be better understood with an example from literature. Metaliterature is a piece of writing about writing. If we apply it to heritage, it can be said that heritage is not just culture; it necessarily implies "adding value to culture." It is a value-laden concept with no neutral ground of connotation. Therefore, heritage-related projects need to incorporate critical research on the instrumentalizations of heritage policies and the conflicts that arise. Among historians and archaeologists, Laurajane Smith has been influential since the publication in 2006 of her book, *Uses of Heritage*. According to Smith, heritage is always intangible because it necessarily implies a valorization process, "'heritage' is not a 'thing', it is not a 'site', building or other material object. While these things are often important, they are not in themselves heritage. Rather, heritage is what goes on at these sites, and while this does not mean that a sense of physical place is important for these activities or plays some role in them, the physical place or 'site' is not the full story of what heritage may be" (Smith 2006: 44). Smith's main contribution is the concept of "Authorized Heritage Discourse" (AHD). She applies critical discourse analysis to understand what heritage "does" and not only how it is used.

Any heritage process participates of two interrelated forces or "logics" that constitute two sides of the same coin; although some times, one of them can dominate. On the one hand, heritage is characterized by its symbolic power; it is linked to identity processes and plays a fundamental role in the politics of identity, belonging and exclusion. On the other hand, heritage is a powerful economic resource, linked mainly to tourism and the so-called "culture industries."

Both logics can be seen in various definitions of heritage. For instance, Mexican anthropologist Victoria Novelo defines heritage as "Something that somebody or some people considers to be worthy of being valued, preserved, catalogued, exhibited, restored, admired (etc.); and others share that election (freely of by various mechanisms of imposition) so that an identification process takes places and that something is considered ours" (Novelo 2005: 86). This definition takes the focus out of the "thing" to include the value construction. The two logics are implicit: the logic of the market in the "considers to be worthy" and the logic of the politics of identity in the part where she mentions that "something is considered ours." In anthropology, history, and archaeology, heritage is also commonly defined in reference to the past in the present, see, for instance Barbara Kirshenblatt-Gimblett's definition of heritage as "a mode of cultural production in the present which has recourse to the past" (Kirshenblatt-Gimblett 1995: 369), or Felipe Criado-Boado's "the footprint of memory and oblivion" (Criado-Boado 2001: 40).

2 FROM HERITAGE TO HERITAGIZATION

Paraphrasing Davallon, anyone looking at the notion of heritage today will notice the relative instability of such a notion as it designates realities which are largely contradictory, "this is the reason why the quest for the right definition of this notion has been replaced by the study of the concept of heritagization" (Davallon 2010: 39).

Heritagization refers to the processes by which heritage is constructed. This concept has been widely used among scholars in the south of Europe in contrast with the invisibilization of this term in English. The terms *patrimonialización* in Spanish, or *patrimonialisation* in French, have been employed since the mid-1990s and its use was well established in the decade of 2000. In Spain, see for instance Ariño Villarroya (2002), García (2007), Pereiro (1999), and Prats (2005), and in France, Faure (1998), Amougou (2004), Davallon (2006), and Drouin (2006, cited after Roigé & Frigolé 2010).

In the Anglo-speaking world, heritagization was first used by Kevin Walsh in 1992, as a pejorative way to refer to "the reduction of real places to tourist space (…) that contribute to the destruction of actual places" (Walsh 1992: 4); focusing on the idea of the destruction of culture produced by tourism, in line with the idea of selling "culture by the pound" that Greenwood developed in 1970s (Greenwood 1977). This pejorative connotation marked the use of the term in English until very recently. For instance in a couple of articles that Carmen Ortiz and Sánchez-Carretero wrote for *Ethnologia Europaea* and for a book published in Sage, the word "heritagization" was rejected by both editors because it was not a common term in English (Sánchez-Carretero & Ortiz 2008, 2011). However, in the last few years, the term "heritagization" is being employed in English with the same meaning as the equivalent terms in French, Portuguese or Spanish, referring to the processes by which heritage is constructed: Bendix (2009), Flesler & Pérez Melgosa (2010), Lung-chih & Min-chin (2012), Margry & Sánchez-Carretero (2011), Margry (2011), are some examples of the use of heritagization in English. Nevertheless, these articles rarely cite prior works on the topic from non-Anglo traditions; producing an invisibilization, in the Anglo-speaking academic world, of works on "heritagization" conducted in the South of Europe.

The term in English is now well-established, due, in part, to the role of Canadian scholarship. For instance, the Encyclopedia of French Cultural Heritage in North America funded by the Canadian Heritage Department, the Quebec Government and Laval University, describe their project using the word "heritagization" as a synonym of heritage building processes: "the Encyclopedia's editorial approach focuses on the heritage building processes (heritagization), whether through institutional, community-oriented or individual initiatives. Therefore writers are called to shed light on the cultural, social and political currents (movements and trends), as well as the contexts that lead to the building up of a heritage asset (heritagization)" (http://www.ameriquefrancaise.org/en/authors-instructions.html, accessed October 2, 2012). In addition, a Network of Researchers on Heritagizations was recently created to serve as a network of "critical researchers on heritagizations of different countries and languages" (http://respatrimoni.wordpress.com, accessed October 2, 2012). Even though the term "heritagization" with this meaning has only been recently incorporated in English, the concept has been used since the decade of 1990. For instance, Kirshenbaltt-Gimblett (1995, 1998), Hufford (1994) or Abrahams (1994) stress the idea of heritage as a metacultural production and a social construction.

Leaving aside Walsh's pejorative use of the term heritagization, most of the definitions of heritagization have common elements, for instance the emphasis on the process aspects and its social construction. Roigé & Figolé (2010: 12) define it as "those processes of cultural production by which cultural or natural elements are selected and reworked for new social uses"; Margry (2011: 336) as "the process by which cultural phenomena or cultural objects, old and modern, are labeled 'cultural heritage' by the involved actors and, as a consequence, get new meanings and undergo transformative changes and become an instrumentalization of the past for the future"; and Davallon (2006: 95, cited after Roigé & Frigolé 2010: 11) as "the act by which a norm, a canon inherited from the past, is contested, subverted, submerged by a new categorization constructed from the present".

3 THE DIVEDES BETWEEN HERITAGE POLICIES AND LOCAL CONCEPTIONS OF HERITAGE

To explore the divides between heritage policies and local conceptions of heritage, I will focus on a research project developed at the Institute of Heritage Sciences (Incipit) that analyzes the heritagization processes along the Camino to Finisterre (INCITE09606181PR).

One of the objectives of this project is to compare heritage policies at the regional and municipal level with the ideas that other local actors have in relation to what their heritage is (Ballesteros-Arias & Sánchez-Carretero 2011). A first conclusion of this analysis is the fracture that exists between those levels. In relation to this gap, I will concentrate on two aspects. First, the municipality constructs a sophisticated discourse on heritage. For instance, in Dumbría -one of the municipalities that the Camino de Finisterre crosses- out of the three main lines of action of the municipality, two of them are related to heritage: one deals with the conservation and promotion of the Camino and the other with natural heritage. This use of heritage contrasts with the lack of a term to name it at the local level. Our informants at some of the towns with pilgrims hostels (Olveiroa, at the municipality of Dumbría; Vilaserío, at the municipality of Negreira and Fisterra, municipality of de Fisterra), have a clear idea of what is most valuable and belong to all of them. At the same time, they do not use the term heritage. The absence of this term -which does not imply an absence of the concept- contrasts with the overwhelming use of the word "heritage" by local politicians.

The second aspect is related to the concept of heritage. While politicians and heritage managers have a limited concept of what heritage is, some of our informants from the local populations include a broader variety of possibilities. The former have an idea of heritage as objects and buildings, which includes churches, crosses and grain containers (*hórreos*). The latter, offer a wider variety of examples, adding also cultural practices, such as festivals, religious celebrations, or the local way to raise funding to organize community activities; and also other elements of heritage, which are more difficult to catalogue, such as "continuing working the land," "the rural landscape," or "our local water supplies" (recording GR041).

In this section, I will analyze the limitations of the concept of heritage used by those actors that are part of "the heritage regime" and the naturalization processes that are taking place. By "the heritage regime" I refer to the institutions in charge of heritage policy-making; and by "naturalization of an idea" I refer to the assumption that this idea is taken from granted as if it were the "natural" way. In this case, the naturalization that I will explore is the idea that developing heritage industries are exclusively related to the development of tourism. Tourism and heritage are commonly associated; and the tourism industry is an essential part to understand how heritagization processes work. Anthropologist Llorenç Prats studies the links between heritage and tourism in an article entitled "Heritage + Tourism = Development?" (Prats 2003). However, the sign "+", as it will be explored below, is being substitute by "=" with the naturalization process of assuming that tourism is the only productive sector affected by heritage.

To develop my argument about the naturalization of the links between the tertiary sector and heritage, I will concentrate on the idea that heritage can be "continuing working the land," which was expressed by our informants. This idea is indeed anchored in the nostalgia for a past that no longer exists (Abrahams 1994: 79, Jameson 1989) but also in the demand to develop the primary sector, as the main income in these municipalities continues being the primary sector (Río Barja 2009). For our informants, working the land is one of their most precious heritage goods and they are reclaiming to keep that possibility; not as musealized traditional knowledge, but as a productive source of income. Leaving aside if this is possible, I want to stress the lack of naturalization of the link between heritage and tourism industry for the local populations. On the contrary, representatives of municipal and regional political bodies had a naturalized or unquestioned assumption that any possible economic benefit related to heritage is linked to the tertiary sector.

In this case, the naturalization of the link between heritage as a resource and the tourist sector takes place among the institutional social actors. A plausible hypothesis that needs to be confirmed in future research is that the heritage regime and its institutionalization implies a limitation in the possibilities; for instance, the possibility for heritage to become an economic resource to develop the primary sector. Other social actors who are not involved in the Authorized Heritage Discourse maintain open other possibilities, as it has been explored in the previous example. With this idea, I do not intend to criticize the link between tourism and heritage, but to question that it is the only way in which heritage can become a resource.

4 CONCLUDING REMARKS

Among anthropologists as well as many historians and archaeologists, the social construction of heritage is the departure point; however, this starting point is not always shared by other disciplines, policy-makers and professionals working in the field of heritage, for whom conservation and activation of heritage as objects is their main objective. In fact, those who understand heritage as objects -or the so-called "substantialist position"- tend to control the Authorized Heritage Discourse. From this point of view, it is important to include the anthropological perspective in heritage formation programs and facilitate communication channels among the various disciplines dedicated to heritage, managers of heritage projects, and policy-makers. In addition, civil society needs to be integrated in any heritagization process, not only as passive receivers, but as the fundamental axis at the center of heritage policies. These are precisely the objectives of the recently created Association of Critical Heritage Studies, as it is explained in their manifesto/provocation: "heritage studies needs to be rebuilt from the ground up, which requires the 'ruthless criticism of everything existing'. Heritage is, as much as anything, a political act and we need to ask serious questions about the power relations that 'heritage' has all too often been invoked to sustain. Nationalism, imperialism, colonialism, cultural elitism, Western triumphalism, social exclusion based on class and ethnicity, and the fetishising of expert knowledge have all exerted strong influences on how heritage is used, defined and managed. We argue that a truly critical heritage studies will ask many uncomfortable questions of traditional ways of thinking about and doing heritage, and that the interests of the marginalised and excluded will be brought to the forefront when posing these questions" (anu.academia.edu/AssociaitonofCriticalHeritageStudiesCriticalHeritageStudies/About, accessed June 2, 2012).

Working on heritage needs to be a participatory endeavor. It implies co-building processes among various agents and not only among heritage specialists. Communities are asking to be part of these processes not only as passive public but as co-creators of heritagization processes. It needs to be a public heritage, in the sense that "the public" is formed by those who risk something in a decision and, therefore, need to be heard and be part of the decision making process (Funtowicz et al. 2000). The difficult questions remain how to determine who are these social agents; and who speaks on behalf of whom.

I mentioned various fractures, divides and gap. One more fracture –or challenge– in heritage studies consists precisely in the separation among disciplines which requires to establish bridges using a radical transdiciplinarity approach, and also to construct bridges among the academia and those actually working on heritage (in museums, NGOs, community centers, or policy-makers, for instance). It is time to move beyond the criticism of these gaps, to conduct research on the divides themselves, and to know more about how the heritage regime instrumentalizes those divides.

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*Science and Technology for the Conservation of Cultural Heritage –
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CSI: Sittingbourne: Conservation science investigations in a town center shopping mall

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ABSTRACT: This paper discusses the public response to and participation in Anglo-Saxon CSI: Sittingbourne -an investigative conservation lab working on finds from a 6th to 8th century Anglo-Saxon cemetery site in Sittingbourne, Kent. It is a unique community led heritage conservation project. It allows public access to the conservation techniques involved in treating objects from an archaeological dig. The project opened in late 2009 and has had more than 6,000 volunteer hours contributed to it and nearly 20,000 visitors. Conservation volunteers have been trained to work under supervision and discuss the conservation project with visitors.

1 INTRODUCTION

CSI: Sittingbourne (Conservation Science Investigations) is a grass roots community archaeological conservation project, located in a shopping mall in South East England. It was founded in 2009 as a partnership between a local conservator, an archaeological organisation (Canterbury Archaeological Trust) and a voluntary local museum (Sittingbourne Heritage Museum), with the support of local businesses, and the wider community. The project allows public access to the conservation techniques involved in treating objects from an archaeological dig' invites public engagement, interpretation and inquiry (Ternirsien 2009; www.anglosaxoncsi.wordpress.com). Much of the success of the CSI: Sittingbourne project has derived from the input of recent conservation graduates, interns and students who have helped the senior conservator with the supervision of the volunteers and production of presentation materials in the exhibition space and beyond. The intrigue of the objects being worked on, craftsmanship of the conservation professionals, locality of the archaeological find, and accessibility of the project represent other strengths.

2 ACADEMIC CONSIDERATIONS

Several of the CSI volunteers have participated as an adjunct to their academic courses (in conservation, heritage, history and forensic studies). One student focused her dissertation on the public's perception of conservation both before and after the opening of the project. (Mitchell 2010). Her study identified a shift in public perceptions and opinions after the exhibition began.

For example, before opening, when a random selection of the public were asked to rank the level of importance of heritage to different groups: tourism ranked higher than communities and academics, for the residents surveyed. When questioned after they visited the CSI exhibition, communities clearly outscored academics and tourism.

Some of the comments gathered by Mitchell include: "...Hopefully this project will remind people what and who lead us to where we are now. Shame so much of the past is lost to 'progress'..."; "Incredibly interesting, and a gift that something so extraordinary is present in our locality. I would love to learn more and will keep visiting."; and "So important for us to know our history!! Excellent dedicated work being done here" .

Many more comments from exhibition and on-line visitors can be viewed on a video from the opening (http://www.youtube.com/watch?v = 4Px_NHKTG38&feature = youtu.be, and www.anglosaxoncsi.wordpress.com/, 2012). Current attention in heritage towards engaging audiences on a deeper, more personal, level challenges pre-existing notions of professional authority. It is a mutually beneficial arrangement, in that volunteers come from a variety of backgrounds and make fresh contributions to the project, while sharing their learning and new understanding of heritage materials with exhibition visitors and friends and family.

This work can be seen as helping to 'bind communities and other social and cultural groups through the creation of shared experiences, values and memories, all of which work to help cement or create social networks and ties' (Smith & Waterton 2009). The CSI: Sittingbourne project has developed a vehemently proud body of volunteers (see volunteers' declarations of the 'pride we feel in our work' on the project's website) who are involved in unlocking the stories of the past, deepening their understanding of their particular physical and social locality.

It is clear that making heritage conservation accessible and/or participatory has a beneficial effect on social cohesion. Developing professional transparency and honesty within heritage projects and institutions seems increasingly important to embedding their value within the community they serve. Boyle & Harris (2009) identify this need, stating that 'one choice that so many want in their public services—a continuing and respectful relationship with a supportive professional—is less and less on offer'. If community heritage projects such as CSI: Sittingbourne do not place themselves in a position to offer this, they expose themselves to the dangers of resting in a consumer focused field.

2.1 *Conservation narratives, social cohesion and meanings making*

A second dissertation (Price 2012) explored the significance of narratives within the work of CSI: Sittingbourne. This included looking at the work of the project's Artist in Residence (Robert Bloomfield) and at a record sheet used between volunteers and investigative conservator. Within this study, it became apparent that narrative is embedded within the investigative conservator's craft as well as in volunteer's activities. Danto (1985) suggests the act of creating a narrative from an end point (as can be found in investigative conservation) can be regarded as a means by which to gain authority over materiality and our perception of time. The 'back story' so to speak, it not a predetermined entity, as it awaits the personal reflection of the individual, together with the conservator's skills, to enable it to unfold.

When the conservator opens themselves up in dialog with the public, they are uniquely placed to 'tell stories' which help individuals make meaning of, and find connections with, others in their community -past & present; 'Memory, autobiography and stories go hand in hand with artifacts and tools to tell histories not only of craft but also of the people in whose life these 'things' were embedded' (Rowley 1997). The process can be tracked through many elements of the community archaeology project. Price's study argues that the record sheet contains a narrative with many strands, invoking the investigative conservator's efforts to peel back time, through conserving objects and documenting discoveries made about them in order to conceptually reconstruct them.

Perhaps the CSI exhibition and volunteers with their acts of creating and sharing narratives can also be seen as belonging to a broader field of literature concerning performance. Many regard the processes within heritage as inherently discursive (Smith 2011, Bagnall 2003, Kidd 2010, Jones 2010), occupying 'a number of liminal spaces' (Kidd 2010) and allowing for intellectual exchanges that enable participants (visitors and volunteers) a deeper and more personal understanding of an object, event or concept. Alongside this is the simplicity of tangible experiences with objects from the past. As Dudley points out, sensory experiences with material objects present the 'potential for value and significance in their own right' (2010).

3 ART AND CONSERVATION SCIENCE

The CSI project has had valuable input from a volunteer resident artist, Rob Bloomfield. His works include interpretive drawings, reportage, promotional materials (Fig. 1) and original compositions based on conservation processes and scientific examination of the surfaces of objects using a digital microscope (Keyence 2000) and a SEM (Hitachi, TM3000).

By creating images that infer narratives of discovery or the 'chase' for knowledge, using digital 'micro-textures', Bloomfield is encouraging viewers to feel an 'aura of mystery and magic' (Rowley 1997) in the work of the investigative conservator (Fig. 2). The excitement of this 'magic' is increased further by the prospect of members of the community becoming more closely involved in the project.

Figure 1. Artist Rob Bloomfield's poster for CSI: Sittingbourne, 2012.

Figure 2. Rob Bloomfield interpretations of the investigative conservation processes involving airabraision.

4 CONCLUSION

The CSI: Sittingbourne project is an example of how to create an environment based on science, technology and cultural heritage in which the visitor feels they can contribute and in which professionals can offer their personal responses as well as those born from academic or professional training. The aforementioned treatment of objects within narratives implies an inherent value within the act of interpreting objects and processes in this way. Rowley (1997) considers the place that everyday objects have within narratives, suggesting that they play a significant role in individuals' and communities' construction of identity.

Professionals and volunteers at CSI: Sittingbourne project blend their diverse knowledge and experiences within the project to achieve a more communal and intimate relationship with the objects, their historical and material nature and the scientific and technological processes they undergo. Carthy (2003) argues that 'we do a disservice to the archaeological record when, or if, we lose touch with ... our unique and privileged position to discover the material past and make it meaningful in the present'. It is perhaps not just the archaeological record that we 'do a disservice to' (ibid) in making this mistake, but all of the processes that take place within archaeology and investigative conservation. Should we endeavor to open the processes up to all of those involved, no matter how incidentally, we approach a far more meaningful, and therefore more valuable, end result.

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Neomudéjar Architecture in Seville: Urban and social background, interventions in the Patio House (1880–1930)

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ABSTRACT: Since the second half of the19th century, as a solution for the needs of the wealthy bourgeois society for a clean, attractive and comfortable town, Spanish cities were forced to grow outside the city walls, thus creating extensions. Industrialization in turn caused a massive influx of immigrants from rural areas who demanded affordable housing. However, speculation had excessively driven up land prices of the extensions. In Seville, however, the city grew mostly inward, there were new alignments, interior plots were built and the urban grid was filled. Nevertheless, this phenomenon was not observed before the second decade of the 20th century when the population undertook a major quantum leap. The population increase was due to the soaring of rural immigration to the city, as well as to the preparation for the Latin American Exhibition of 1929, which required additional labor.

1 INTRODUCTION

This paper aims to analyze the sources of inspiration neomudéjar Sevillian style, particularly in the speeches that were made in the late nineteenth and early twentieth century courtyard houses in the city. In Europe in the mid nineteenth century arises a predilection for the Islamic world, for its art and architecture, a trend that eventually ends up materializing and expressed through the design of buildings, gardens and Mediterranean homes, giving in a stylistic phenomenon that some authors have become known as "Moorish" and others like orientalism or neomudéjar. In the case of Seville, one of the styles that gained greater prominence in the physiognomy of the city was the Moorish Revival style inspired by Arabic forms, the so called neomudéjar style that was not fully inspired in the original Islamic culture, but in its local Andalusia soil, exploiting also the boom taking place in the craftsmanship and traditional skills, all under customer requirements, generally bourgeois, which wanted an unique building in style but executed with limited financial means.

The urban regeneration process also affected existing patio houses, in which the renewal was done from within, where the key was the courtyard while the façade had still little representative value. Soon thereafter, coinciding with the urban transformations that occurred in the city and the beginning of construction of dwelling houses, mostly rentals, the existence of the court had an unique function: ventilating rooms. Design of the interior courtyards of the great Sevillian palace house would come to the exterior façades resulting in the emergence of a significant amount of façades inspired by moorish style that still remains in the city, currently known as sevillian neomudéjar style. The temporal scope considered in this study for the development of neomudéjar style in Seville, ranges from 1880 to 1930, and is determined by two facts that may be the beginning and end, respectively, of the overall trend of designing and implementing in Seville buildings for domestic architecture or industrial under neomudéjar taste. The start date coincides with the original design of the Pavilion built by Juan Talavera and Vega between 1880 and 1890 in the gardens of San Telmo to D. Antonio de Orleans and Ms. Maria Luisa Fernanda de Borbón, popularly known as the "Pavilion Costurero de la Reina", located on the Paseo de las Delicias. The date marks the end of the closing of the American Exhibition in Seville in 1929, which closed its doors in 1930.

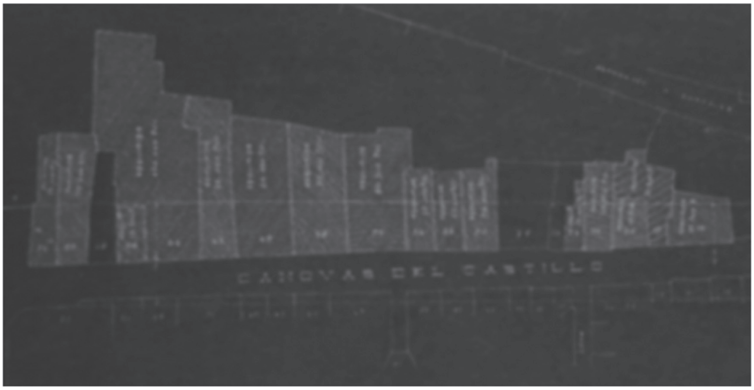

Figure 1. New alignment Av. Constitución (1910) Original project. Aníbal González.

2 SOURCES OF INSPIRATION

The main models or sources of inspiration for the sevillian neomudéjar style are the Almohad Giralda Tower and the original mudéjar style, specially the palaces of Pilatos and Dueñas, as Alberto Villar Movellán defined as "neomudéjar plateresco", visible especially in the plasterwork in their yards. Moreover, it is quite important also as a reference for all architects of the neomudéjar in Seville, the constant and visible presence of the Almohad Giralda Tower in the city and the Alcázar Palace, specially certain areas like the "Patio del Yeso" and the "Patio de las Muñecas".

References and sources of inspiration of the Sevillian Neomudéjar style could be structured into two groups.

2.1 *Religious buildings*

Even today Seville is a city with a strong presence of mudéjar architectural monuments, such as the churches of Omnium Sanctorum, San Andres, San Pedro, Santa Marina, San Gil, Santa Catalina, San Marcos, San Julian and Santa Lucia, where many of these influences can be seen both as moorish and gothic (presbyteries with the gothic vaults and aisles with wooden ceilings and arches inspired Muslim). Gradually, while they were Islamized, traces of arches that originally were settled on square pillars are substituted by pointed horseshoe arches (Almohad tradition). According to historian D. Angulo (1932), all these monuments "are relatively late dated, and certainly could be considered as the most original creations of religious mudéjar architecture style in Seville", which is evidenced by the popular feel of this architectural style in Andalusia.

2.2 *Civil buildings*

The most representative civil and mudéjar building in Seville is the Alcázar of Seville, considered by F. Chueca the most important Spanish Moorish palace which, despite being a part of it a Christian monument, designed under the reign of D. Pedro the Cruel, and is executed following the artistic criteria Hispanic Muslims.

Within the group of buildings which constitute the enclosure of the Palace, stands out as important Almohad vestige the so called "Patio del Yeso" with large arches and plasterwork Granada type and its adjoining "Hall of Justice", a large room where the light is filtered through the gypsum lattice arches.

As mudéjar itself, we highlight the main courtyard of the Palace, or "Patio de las Doncellas" and the first floor of the "Patio de las muñecas", being, however, the floor restorations result of nineteenth century.

They are also references to the Sevillian neomudéjar architectural style in the Dueñas Palace, Pilatos House, Olea Seville House located on Guzmán el Bueno Street, the

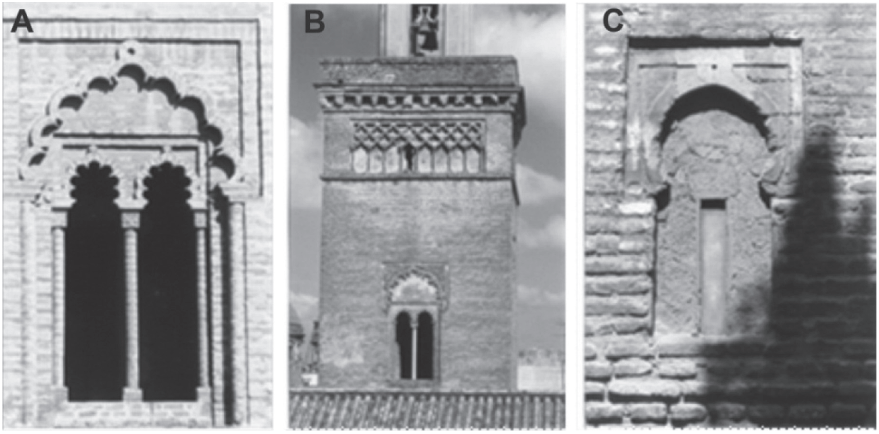

Figure 2. Mullioned lobed arches. Mudéjar Churches of S. Pedro (a) and S. Marcos (b, c).

Figure 3. (a) Facade of Palace of Rey D. Pedro. (b) Picture of Real Alcázar of Seville, by Louis de Clercq, Years 1859–60, Kowasa Gallery, London.

Moorish courtyard Plateresque of Pinelo Palace and the Salinas House, located on Mateos Gago Street.

3 INTERVENTIONS IN THE PATIO HOUSE

Under these sources of inspiration, courtyard houses and palaces there you can find nowadays reforms s late nineteenth or early twentieths, usually in their large courtyards, reforms implemented under Arab reminiscent artistic criteria (arches horseshoe, plasterwork, etc.). As examples of courtyards of houses Palacios reformed under this style, stands the house of the Marquesa de Lebrija, Seville street located in the Cradle, Decorative reform backyard of the Counts of Ybarra, located on the street that bears his same name and for the beautiful backyard of Placentines street, 1, and the house of Count de Aguiar, among others.

In 1901, the Countess of Lebrija commissioned the architect José López Sáez the reform of her house located in Cuna Street using Roman remains of the ruins of Italica. He builds up the main stair and the yard neomudéjar plateresco. At the same time, Mr. Juan Bautista Calvi and Rives begins a beautiful reform of his courtyard house located in Placentines street, made from a variety of steel arches and Moorish-inspired décor profuse, witnessing the industrial revolution by the use of new materials, as in this case the steel.

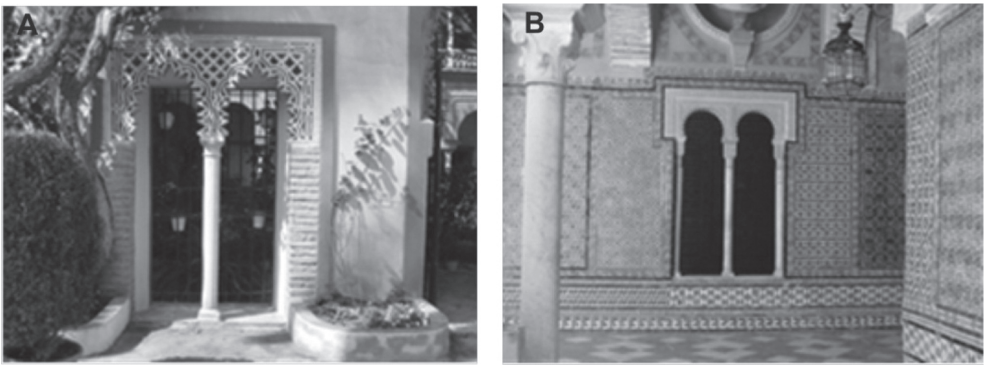

Figure 4. (a) Poly-lobed arches, Dueñas Palace. (b) Plaster arches, Pilatos House.

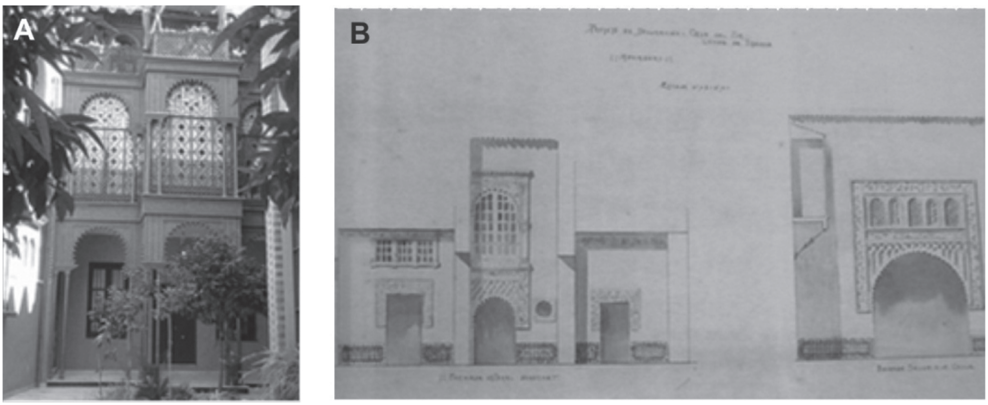

Figure 5. (a) Reform of the House of Mr. J. Bautista Calvi Rives, Placentines Street, 1. Patio. (b) Project House Reform of Count de Ybarra, Anibal Gonzalez (1921).

It is noteworthy the Reform Project that the architect Aníbal González performs at Counts of Ibarra Palace House, which recreates the profuse production of plaster covering the arches and plinths and friezes, following the alhambrista style. Many of the buildings that are built in the style neomudéjar in Seville since the end of XIX until the beginning of XX, have been definitively incorporated into the urban layout of the historic center of Seville, as those projected by Aníbal González, José Muñoz, José Espiau and Sáez and Lopez, among others, but others failed to stay on time and now are refurbished or missing. We can say to conclude that, although neomudéjar Sevillian architecture has a low incidence quantitative (occurs in no more than fifty buildings spread throughout the city), it has a high qualitative impact, since it is in the "image of Seville", and it is nowadays the architectural style that represents the city.

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Iron Age goldwork as Cultural Heritage: Building strategies for its research, conservation and social valuation in NW Spain

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ABSTRACT: In this paper we present some theoretical and methodological proposals for the research, conservation and social valuation of NW Iberian Iron Age goldwork. Though this jewelry is among the most outstanding in Western Europe, our knowledge of it and its social appreciation have been hindered by various factors. We suggest that the best way of changing the current situation is to integrate Iron Age goldwork into a cultural heritage value chain that links its social appreciation to the work of research and conservation. This requires a strongly interdisciplinary approach, which is summarized here and illustrated principally through two examples studied within the framework of a research project in progress.

1 INTRODUCTION

Goldwork is one of the most outstanding material manifestations of protohistory in the northwestern Iberian Peninsula (the so-called Castro culture). The abundance of local gold-bearing sources is one of the factors that explain why large numbers of gold items of a high technical quality and great beauty are found. We currently know of more than one hundred torcs and around half that number of earrings, as well as less numerous diadems/belts, bracelets, pendants and hair rings. Most of these pieces are preserved in the region's museums and in national museums in Madrid and Lisbon, although some are in foreign institutions such as the Ashmolean or the British Museums. However, only two museums have published catalogues of their Castro culture gold pieces, the Lugo Museum (Balseiro 1994) and the National Archaeological Museum in Madrid (García-Vuelta 2007).

There are three ways of looking at Castro culture gold as archaeological pieces and these needs to be analysed. Basically they can be summarised as follows: a) *technical*: raw materials, manufacturing processes, use, wear, and conservation/handling in museums; b) *economic*: social production relations, use value, exchange value, and distribution; and c) *social*: consumption, symbolic meanings, ideological manipulation, ritualisation, appropriation, etc. This triple view is valid for the period of their historic use, but can also be extrapolated to their current use. In summary, the goldwork of the Castro culture is plurisemantic and diachronically changing.

The understanding and social assessment of these three dimensions has been limited by various factors. Among them we can mention the hackneyed subject of its apparent "decontextualisation", as finds are often made by chance during farm work, as well as the burden of a tradition of investigation and conservation that considers the gold items as untouchable "works of art". As a result, the recent patrimonial history of Castro Culture goldwork is generally invariable and monotonous, with its exhibition being limited to museum display cases and with little generation of social value. The aesthetic value has been the dominant factor in the exhibition of Castro culture goldwork. This is a heritage that is displayed for its contemplation and enjoyment. Its value is that of beauty and its enjoyment lies in the subliminal suggestions awoken in the onlooker by that contemplative action. It is, therefore, an "easy" heritage to exhibit, as it requires no explanation and is easy to manipulate. An example of this would be the "treasure rooms" found in certain museums, in which gold from all periods and places are accumulated, because together they are more impressive.

However, it is worth pointing out that in recent years advances have been made in our knowledge of Castro culture goldwork. Finds made during archaeological excavations, mainly earrings, provide us with chronological information, although for the time being this is not conclusive (Parcero-Oubiña et al. 2009, Villa 2004). Nevertheless, the technological study of torcs—the item on which most research has been concentrated—together with their morphotypological observation, have allowed specific features to be proposed for the goldwork from each phase. A good example of this is Armbruster & Perea's proposal (2000: 112) for torcs with double scotia terminals. According to this hypothesis, the First Iron Age would have been characterised by the use of solid structural elements, lost wax cast and casting-on to join two structural elements. Second Iron Age features would have been joining the pieces by soldering, hollow terminals and ornamental techniques such as filigree and granulation. The pieces from the Second Iron Age required a greater investment of social work, the technology was more complex and they often contained more metal, all of which is in keeping with the social evolution of the Castro culture and the increase in inequalities towards the end of the first millennium BC (Armada & Grau, in press). Finally, a group of bronzes studied in recent years shows representations of torcs, probably used as offerings, in a context of animal sacrifices (Armada & García-Vuelta 2006). This reinforces their polysemous nature and leads us to question the unambiguous interpretation of torcs as an individually owned masculine adornment.

These advances in research allow the construction of new discourses on the subject of northwestern Iberian Peninsula goldwork and its social role. We are going to describe some of the theoretical and methodological proposals that have guided these approaches. We also present some examples from our recent research and offer brief proposals that favour the social evaluation of Castro culture goldwork.

2 THEORETICAL AND METHODOLOGICAL PROPOSALS

A fundamental aspect of our hypothesis lies in combating the hackneyed subject of the "decontextualisation" of this goldwork. Some years ago, one of us proposed that "the context of the torcs is precisely the *absence of context*" (Armbruster & Perea 2000). In other words, the relatively frequent finds of torcs near settlements, with no associated archaeological structures, is in itself a significant contextual pattern and allows them to be interpreted as *archaeological deposits*. At the same time, experience has shown us that in most cases it is possible to "recontextualise" the finds; in other words, to recover the relevant contextual information by applying a suitable methodology. This methodology should entail a review of the unpublished documentation (correspondence between scholars of the period, museum records, etc.) and information in the newspaper, the recovery of oral information and a visit to the area of the find.

Normally, a search of this kind offers not only information about the archaeological context and conditions of a find, but also about its subsequent vicissitudes: its passage through private collections, the dispersal of ensembles, alterations to the material, entry into museum collections, etc. This leads us to a second important premise: our reconstruction of the "biography" of an object does not only cover its protohistoric stage, but also everything that has happened between its deposition and the present day. All the chronological stages in the "biography" of an object are relevant. In the past few years the biographical focus of material culture has undergone considerable development in the human and social sciences, assuming that "things both have and shape social lives" and that "an object's life story can affect how people interact with it" (Stahl 2010: 155). On the other hand, we believe that explaining an object from a biographical similitude has great potential to make it comprehensible and to encourage its social valuation. For the public, stories about the discovery and contemporary vicissitudes of objects are often as or even more interesting than the archaeological information.

Archaeometry is a basic tool for reconstructing the biography of a find (Perea 2010, Armbruster 2011), as it can cover from when it was made (the techniques, working processes and tools used), its period of use (use marks, wear, repairs, etc.), the processes it underwent between being deposited and subsequently rediscovered (chemical changes, deterioration, etc.), and the events subsequent to its find. Perea (2010) has divided this archaeometric working process into two basic phases, one topographic and the other analytic. The basic tool of the former is the scanning electron microscope and the main objective of the latter is the characterisation of the alloys using techniques such as energy dispersive X-ray spectrometry (EDX), X-Ray Fluorescence (XRF) or particle induced X-ray emission (PIXE). In addition to these techniques, which are currently widely used by investigators, in our research we have applied procedures that are less common in the study of protohistoric goldwork, such as radiocarbon AMS dating of the organic remains conserved in some of the finds and the characterisation of their interior fillings.

The most appropriate theoretical model for favouring to the social valuation of the research is, in our opinion, that proposed by Criado and known as the cultural heritage value chain, a model which considers that "heritage elements are configured by acts of identification, documentation, signification, valorization, conservation, diffusion and reception, and establishes that good working practices in relation to the research and management of these elements must include all of these dimensions" (Criado-Boado et al. 2008: 6).

3 TWO EXAMPLES

We would like to refer to two finds that are being studied in our current research project, as they exemplify the application of these theoretical and methodological proposals.

The Recouso treasure (Fig. 1, left) was found by chance at the beginning of the 1920s by farmers at a *castro* (hillfort) in San Martiño de Marzoa (Oroso, A Coruña), near Santiago de Compostela. It is composed of 16 decorated earrings, some of them with associated hanging elements (ornamented *terminals*, rings and *"loop in loop"* chains). It also comprises several fragments of these elements, as well as four ingots made of a gold-silver alloy. The treasure remained in private hands for several years until it arrived to the Museo das Peregrinacións (Pilgrimage Museum) in 2002 (García-Vuelta & Armada 2011). More than seventy years after its discovery, it is now being systematically studied for the first time as part of our project. The first steps in our investigation consisted of reconstructing the history of the find and its vicissitudes and carrying out a topographical study of all the elements using a binocular magnifying glass, documenting the whole process with macro photography. This initial study showed a technological variability among pieces that are typologically the same -a feature already pointed out by Armbruster & Perea (2000) for torcs-, as well as other new data including interior fillings in the earrings, heavy surface wear, a possible unfinished earring and a smelting mass that had trapped multiple charcoal remains. This led us to a second study phase, archaeometric in nature, in which we are using scanning electron microscopy (SEM), X-Ray Fluorescence and EDX analysis, radiocarbon AMS dating of the identified charcoal remains, and the characterisation of interior fillings using pyrolysis. To date the Recouso treasure is the collection of Castro culture goldwork to which the largest number of archaeometric techniques has been applied.

The second example is the Calvos de Randín treasure (Fig. 1, right). It is composed of 17 plano-convex gold-silver alloy ingots that were discovered by chance by workers building a country road (Lorenzo 1970). The information we have been able to recover indicates that the ingots were found inside a pottery vessel with a lid, and allows us to hypothesise that the site of the find is a hillfort. In addition, the 16 ingots currently in the Ourense Museum have

Figure 1. The Recouso (left) and Calvos de Randín (right) treasures.

been subjected to X-Ray Fluorescence analysis and the charcoal remains detected in one of them have provided the first direct radiocarbon dating for Castro culture goldwork.

4 CONCLUSIONS

The study of the Recouso and Calvos de Randín treasures offers a major body of information for renewing the discourse on Castro culture goldwork. It is evident that the data obtained are not only relevant in research terms, but that they also allow us to *explain new things* to a public interested in cultural heritage. That will obviously require an effort on the part of the researcher in making the archaeometric data understandable and in promoting the socialisation of the knowledge generated. The resources available to help in achieving this objective are now much more numerous than they were just a few years ago.

The objects that make up these two ensembles no longer have to be exhibited merely for their aesthetic value, but can become items of cultural heritage capable of generating new discourses on past and present societies. Cultural heritage is no longer limited to the object; it now includes all the technological knowledge associated with its manufacture, as well as the successive concepts and evaluations it has generated throughout its biography.

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Las Médulas: The social appraisal of a cultural landscape

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ABSTRACT: Scientific dissemination, a way of promoting the social appraisal of cultural landscapes from a very early age, is a constant reality in the activity carried out by the Las Médulas Foundation. It has always paid special attention to the grade-school environment, seeking to improve heritage and scientific education among teachers, students and families. Thus, through the paradigmatic example set by Las Médulas, a complete educational and didactic program has been implemented, including all the initiatives and activities which have fostered the communication between Heritage and Society.

1 INTRODUCTION

Las Médulas (León) is known as the largest opencast mine in the Roman Empire. Surrounding it, a territory has been transformed by the human communities that inhabited it since Antiquity. The profound changes, historical and social processes, which took place there, have turned it into a cultural landscape.

Its relevance as a valuable part of our heritage has been brought to light through the diachronic study of its territory as a historical document (Orejas 2001), carried out since 1988 by the "Social Structure and Territory-Landscape Archaeology" (SST-LA) research group of the Spanish National Research Council, CSIC (Sánchez-Palencia et al. 2000a). This exceptionality has been the motivation for the inclusion of Las Médulas into the UNESCO World Heritage List in 1997. In this sense, more recently, the Council of Europe established common criteria for the adequate protection, planning and management of a cultural landscape through the European Landscape Convention (Ruiz del Árbol 2006), ratified by Spain in 2007. In 2010, Las Médulas has been declared a Cultural Space by the regional government of Castilla y León, a new protection figure which correctly integrates landscapes into cultural heritage protection strategies.

All these issues evidence the need to endow landscapes with a social dimension which can facilitate the transmission of the scientific knowledge obtained through on-site research. In the case of Las Médulas, it was Science which began to promote the landscape by valorising it (Sánchez-Palencia et al. 2000b, Sánchez-Palencia & Fernández-Posse 2001).

This social dimension of landscape has been central to the activity of the Las Médulas Foundation, since it began to collaborate with the SST-LA research group. This perspective integrates the landscape reality into the appraisal of heritage, thereby conferring it with a significance based on the dissemination of territorially-based scientific knowledge (Serra & Fernández 2005).

This complex task goes far beyond mere communication, or the dissemination of scientific conclusions. It requires a bidirectional rapport between Heritage, Science and Society through specific initiatives which can empower the inherent value of Las Médulas, thus promoting its understanding and appraisal as a cultural landscape.

Figure 1. Panoramic photography of Las Médulas cultural landscape.

In this dissemination environment, it is important to remember the issues enumerated by Sonia García (2007). The transversal nature of landscapes confers an educational and didactic potential which has been well used since then. Education is the main tool to transfer knowledge and an understanding of landscapes as heritage, as a step towards their protection.

This integrated perspective on territory comes from Landscape Archaeology, which uses the landscape as the basis of generating knowledge. The different values which come together in the landscape allow us to approach different areas of Science from a Humanities and Social Sciences perspective. In this way, we can build a significant knowledge with a transdisciplinary base, the landscape becoming the learning environment (Martínez 2008, Hernández 2010).

These pedagogical considerations, as well as those related with the didactics of heritage (Hernández 2002, Serrat 2005), have led to the creation of a specific methodology: the didactic of cultural landscapes (Martínez 2008, 2010a), which defines the work strategy currently carried out by the Las Médulas Foundation.

This work has led to the creation of a complete educational and didactic programme on the cultural landscape of Las Médulas. Its main goal is to empower the transference of knowledge concerning it, and thus improve the social, scientific and heritage appraisal as a cultural landscape. This programme has been progressively implemented since 2007 through different dissemination projects funded by the Spanish Science and Technology Foundation (FECYT) and the Ministry of Culture (MEC), projects in which the research group SST-LA has participated actively through advising and technical-scientific supervision.

The group of activities and initiatives which partake in it have a clearly curricular-oriented nature, specifically designed to promote the participation and interaction of the users: professors, students and families.

2 FORMAL EDUCATION

In this aspect different working tools oriented towards teachers and students have been used, always destined to enhancing heritage education in the classroom.

2.1 *Teacher training*

In this learning process, training teachers is paramount, since they are the necessary interlocutors in the dialogue which must be established between heritage and children, and the ones who must correctly transfer knowledge regarding landscape and its research. Their professional role has been supported through different seminars, conferences and training courses.

These training activities have been carried out in collaboration with the education administrations, specially the *Centros de Formación e Innovación Educativa* ("Centres for Educational Training and Innovation", CFIEs).

These courses have a wholly interdisciplinary nature, with the participation of researchers, professionals and disseminators of different disciplines. Among them, we can highlight the Botanical Garden of Madrid, and the "CSIC in School programme", both of the CSIC.

In them, the scientific activity carried out from Landscape Archaeology and integrated territorial studies have played a part, as well as the value of cultural landscapes in general -and Las Médulas in particular- as an education tool for children to use in learning different concepts and values related to Science and Heritage.

2.2 *Educational resources*

In parallel to the work carried out with teachers, a set of educational resources has been designed for the students, always with a teacher's guide attached, in which the transference of scientific and heritage knowledge, regarding Las Médulas, in an educational environment is central. These resources are innovative because of their use of cultural landscapes, and the use of Information and Communication Technologies (ICT).

The resources' multimedia contents have been designed for different educational phases in compulsory schooling ages (Martínez 2008), non-compulsory High School (Martínez 2010a), and bilingual education (Martínez 2010b).

In this way, different knowledge domains and basic competencies are established in each resource, with a directed research which fosters learning through discovery: students build their own knowledge.

3 NON-FORMAL EDUCATION

Beyond the classroom, much effort has been placed in developing a wide educational activity in non-formal education. On the one hand, there is the design of didactic activities oriented towards grade-school children: experimental workshops, educational itineraries. On the other hand, there are the resources designed for family use.

3.1 *Didactic activities*

Their implementation, based on a recreational motivation, has two main objectives. On the one hand, to actively involve participants in the construction of their own understanding of the cultural landscape of Las Médulas through direct manipulation and experience. On the other hand, to empower values and positive attitudes towards heritage and the scientific activity carried out in it.

Experimental archaeology plays a significant role in the methodology used in didactic activities. This sub-discipline plays an important didactic role (Santacana 2008), which allows people to approach concepts which, if not, it would not be assimilated due to the necessary high degree of abstraction. In other words, no significant learning would take place, which is a priority for us.

It allows us to deal with aspects related with pre-Roman *Castro* and Roman societies, such as their lifestyles, material culture, etc. It also enables students to come in contact with the scientific activity carried out in Las Médulas, and the methodology used (excavating using an archaeological method, stratigraphic interpretation, use and interpretation of aerial photography, etc.).

Meanwhile, educational itineraries have focused on bringing down the usual view of Las Médulas: just a gold mine. Thus, their routes focus on different aspects of the heritage (both Human and natural), which confer it with the cultural landscape value, and the historical and social processes which took place in it (García et al. 2007). These contents also enable the users to be submerged in the imprint of Human action in the environment, thereby fomenting attitudes of appraisal and respect to heritage.

3.2 *Family resources*

Apart from schools, families also play a fundamental role in the education of children. In Las Médulas, families amount to a high proportion of visitors. Because of this, a collection of resources and activities has been prepared, aimed at helping all the members of the family to understand the heritage value of the area through different actions (Martínez 2010c). In this way we also stress the importance of heritage education in minors in all aspects of their daily life.

In conclusion, the educational and didactic programme of Las Médulas has proven its validity in using cultural landscapes as an educational resource. The implementation process has also highlighted other benefits:

- They confer heritage with significance.
- They empower the interaction between Science and Heritage.
- They facilitate the understanding of scientific activity.
- They generate significant amounts of intuitive knowledge.
- They reinforce the knowledge acquired in the classroom.
- They awake the interest and motivation of students.

Given all this, we are convinced of the need to continue, and expand, this line of work, in order to create new tools which allow us to deepen the communication channels which have been opened between landscape and society.

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Documenting the architectonic heritage: The best way of preserving it

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ABSTRACT: Restoration of historical buildings often takes place without knowledge exchange between architects and geologists. Architectonic heritage should be preserved under the same regime within which it was originally conceived, using the same natural stone for its construction, which most of the times consisted on local material sourced from nearby quarries. However, the non existence of documentation of historical quarries or a precise description of the natural stones used in many historical buildings often leads to the inappropriate action, both detrimental to the building itself and the cultural heritage of a region. National and international networks should join efforts to cover the lack of information.

1 INTRODUCTION

Architectural heritage is generally built in natural stone sourced from nearby quarries. We can say that for over 10.000 years our ancestors selected suitable building stone, where the strength of the stone was not of paramount importance. Moreover in most modern buildings, although built with natural stone, the outer stone wall is, in most cases, only cladding consisting of thin sheets of stone fixed to the concrete of the building with corrosion resistant metal fittings. If load building properties are required, the majority of building stones have compressive strengths at least as great as bricks or concrete. Evenso, capillarity absorption is very different from one type of stone to other, and this characteristic is important because today the surroundings of the historical buildings experience very different conditions including acid rain and atmospheric contamination.

A clear example is shown in historical buildings using sandstone in their base course. In historic times, the streets were paved with pebbles compacted in earth. All the subterranean water draining underneath the cities could evaporate or exit in some way through the permeable material. But most historical city centers today are paved with granite or similar material. The subterranean waters cannot exit easily and they escape using the porosity of the sandstones, thus resulting in deterioration of these rocks. It is easy to see how buildings that utilised granite (or other non porous material) have been preserved until the present, while buildings that used the porous sandstones or other local natural stone that at the time seemed appropriate, are quickly deteriorating.

A general practice in restoration is to clean, repair or even replace the damaged part of the buildings with similar rocks. However, the restoration work is not always done properly, either because the repair is poorly executed, causing further damage, or because the natural stone used for the replacement is poorly selected. The only means to deal professionally with replacement work is to determine the original stone and use it as replacement in order to avoid contrasts in the building, or if the stone has proved to be unsuitable under present conditions, to choose a suitable alernative replacement following the appropriate technical assessment. This is important especially when dealing with historical towns or monuments that have been recognized as world heritage by UNESCO.

Several projects at international level have attempted to deal with documentation about ornamental stones. Until now none have been succesful over time or with results. This is why national and international networks have now been created to document all data on historical natural stone and historical quarries. Creation of databases seems to be a good tool to use in any case (Hyslop et al. 2010). CONSTRUROCK is a Spanish network involving research teams from universities, research and development institutions and natural stone related companies. Its aim is to catalogue all natural stone and quarries in Spain, focussing on both new and historical buildings. Another one is the Global Heritage Stone project,a project of a Task Group of the International Union of Geological Sciences (IUGS) whose aim is to introduce a new formal international designation for natural stone materials that have achieved widespread use as well as recognition in human culture. It also aims to formalize specific characteristics of a dimension stone in an internationally accepted context.

As a consequence of these projects, some specific and up-to-date databases will be created and maintained so we, as experts, can offer advice on the important issue of restoration of the architectural heritage based on a real situation.

2 THE NETWORKS

2.1 *CONSTRUROCK*

In 2004, following the Spanish Geological congress that took place in Zaragoza (Spain), researchers from that university and from the Spanish Geological Survey discussed the lack of joined information on geological and architectonic characterization related to the architectonic heritage. They got to the conclusion that a national database was needed to be widely offered to researchers, architects and other actors interested in the matter.

2.1.1 *Some firsts*

The early success of the original network led to subsequent expansion: in 2011 the network was thus set up with a national objective, but with international perspectives. At present, a total of ten institutions from ten Spanish regions are linked to CONSTRUROCK (Baltuille et al. 2012).

CONSTRUROCK is seeking:

- To list and facilitate protection for the historical quarries that were used in the construction of the Spanish Architectonic Heritage;
- To encourage and promote the importance of Natural Stone in the construction context, both for new building and heritage conservation and restoration;
- To develop, publicize and maintain the CONSTRUROCK database;
- To lead research projects and participate in others related to Architectonic Heritage and new construction.

These objectives have a common final goal: to identify, for the purpose of protection, those quarries involved in the construction of the Spanish Architectonic heritage. A catalogue of the major quarries their identification and protection status will permit the quarrying of heritage stone resources for restoration if needed.

CONSTRUROCK will be a network at the service of professionals related to natural stone and the architectonic heritage.

2.1.2 *Current state of CONSTRUROCK*

The database is structured in four large independent themes, each of them subdivided in fields:

- Quarry site (with 54 fields)
- Geochemical and petrographic analysis (45 fields)
- Physical and Mechanical testing (45 fields)
- Heritage buildings (42 fields)

At present, the database has 3.629 files, and is been maintained by the Spanish Geological Survey (IGME). It is almost ready to be adapted for on-line management by each participating member.

2.1.3 *For the future*

- CONSTRUROCK should maintain, develop and manage the database both at national and international level.
- The network will have to participate and/or be responsible for natural stone projects related to architectonic and historical heritage as well as new buildings, seeking for national and international funding to:
  - Characterize natural stone that is employed in architectonic heritage and new building;
  - Undertake in depth petrological research of the rocks to comprehend, prevent and treat pathologies affecting them;
  - Research and locate rock bodies to be quarried for replacement in heritage restoration.
- Locate, study and catalogue the historical quarries that were used in historical building construction.
- Collaborate with the authorities in the design and development of protection for historic quarries.
- Promote the importance of natural stone in all the constructive contexts, both for restoration and for new building.
- Facilitate the Spanish Geological Survey as a National Reference Centre for Natural Stone and its application in architectonic heritage and new building, as well as the recognition of all its members in each Spanish community.

2.2 *Heritage Stone Task Group*

The Heritage Stone Working Group was initiated in Oslo in 2008 during a meeting of the IAEG C-10 (Cooper 2010). By September 2012, 154 people from 40 countries were involved.

The First Circular was issued in May 2009 with subsequent circulars in September 2010, June 2011 and March 2012. These are available at www.globalheritagestone.org. The first draft of "Terms of Reference" were circulated in 2009 with approval of final draft by the IUGS Council at the 34th International Geological Congress that took place in Brisbane (Australia) in 2012.

During 2011 a positive dialogue was begun with UNESCO World Heritage, the International Council on Monuments and Sites (ICOMOS), the International Council for the Study of Restoration and Preservation of Cultural property (ICCROM).

The Heritage Stone Task Group (HSTG) was formally established as a Task Group within IUGS in addition to association with IAEG C-10 with approval and initial funding at the IUGS Executive Committee in San Sebastian, Spain in February 2012.

2.2.1 *Some firsts*

The HSTG is the largest international grouping of dimension stone geologists that has been created.

In addition, with the GHSR, it has established the first ever international geological (as opposed to technical/mechanical) standard associated with dimension stone.

It has also resulted in the first IUGS involvement in dimension stone.

2.2.2 *Current state of the HSTG*

Several projects and links with other groups and networks have been achieved. At present, the Task Group has completed a draft citation for Portland Stone in the United Kingdom, has draft citations in preparation for Welsh Slate (United Kingdom), Podpeč Limestone (Slovenia) and is carrying out research on the Piedra Pajarilla (Martinamor granite), Salamanca sandstone and Villamayor sandstone, all three from Salamanca, Spain (Pereira & Cooper *in press*).

At the moment, the HSTG is linked to various national groups and networks: the English Stone Forum, the CONSTRUROCK network (in Spain) and is looking forward linking interest with many others.

2.2.3 *For the future*

This Task Group looks forward to expand its register of correspondents, to solicit draft citations for GHSR status and maintain a standing list of these. It also aims to facilitate essential research papers discussing these citations, to consult national or regional authorities and correspondents with respect to draft citations, and to approve draft GHSR citations thus formally establishing the GHSR designation. Finally there is a need to maintain a publicly accessible register of approved GHSR designations, to expand the liaison with international, national and regional organisations and to establish a regular system of technical meetings. Long term benefits include the provision of a mechanism for legally defining a stone type, for example in a similar manner to existing EU legal provisions that protects food and wine varieties from specific regions.

3 CONCLUSIONS

Several projects aimed at documenting natural stone for construction have been attempted in the past with no ongoing support. Our purpose is to make available all information on natural stone used for restoration and new constructions by the creation and diffusion of national and international networks. CONSTRUROCK and the Heritage Stone Task Group have been established to bring together a large number of interested participants. Promoting ongoing involvement through information updates, contributions to international meetings and papers in journals will help to maintain the documentation role of the networks and ensure a prosperous future, thus avoiding the fate of earlier trials.

Documenting architectonic heritage is a very important contemporary issue, because of the challenges involved with maintenance and restoration. This is especially important in the case of protected buildings and those that were inscribed on the list of World Heritage by UNESCO. Those responsible for the conservation and management of World Heritage properties have the complex task of anticipating and dealing with these challenges, most often in an environment of limited financial and organizational capacity (UNESCO 2008). We will try to contribute by working on the consolidation of the presented networks.

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Quantitative research underpins heritage management: Preserving ferrous metals

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ABSTRACT: Conservation has traditionally focused on preventing change to objects. In many instances this is technically and financially unrealistic. The recognition is growing that controlling change is more realistic and central to the role of conservation. To predictively control and manage change requires quantitative data on decay rate and the nature of change occurring. The type of data and its link to the heritage value of objects is discussed and evidenced using an AHRC/EPSRC funded Science and Heritage research project investigating the rate of corrosion of archaeological iron. This type of research can transform management of heritage preservation into an evidence-based predictive activity and improve benefit cost benefit assessment.

1 INTRODUCTION

Museums worldwide are faced with the same problem; inadequate funds to care for collections. To manage collections effectively museum professionals must know what level of preservation their money can buy. The goal of a preservation strategy and the decision making process that will justify it must be clear and evidence-based, as prediction is at the centre of managing heritage. This requires data derived from an in-depth understanding of decay mechanisms and quantitative measurement of their progress, as a function of the intrinsic and extrinsic variables that drive it. Without quantified data, all treatment design must remain empirical, reliant on guesswork and good ideas. Quantitative measurement of change will also identify how best to prevent or control it, as well as offer data for predicting future rates of decay. This supports cost benefit calculations and prioritization of resources within heritage management. This paper focuses on the nature of the material science evidence required to manage heritage preservation and comments on the role it can play as a predictive management tool.

2 PREDICTIVE MANAGEMENT AND RATE DATA

Since conservation has traditionally focused on preventing change to objects, its research has centred on determining when decay stops and what prevents it occurring as opposed to how fast objects decay and what change this produces. This is a function of the mindset that conservation is about prevention rather than control; prevention requires no knowledge of the rate of decay or change in a material. It must be accepted that, more often than not, to prevent decay is a luxury, while controlling its rate is realistic and deliverable as a function of resources. Rate data is almost entirely absent from conservation literature and yet it is the foundation of treatment design and assessment of its success, as well as monitoring ongoing object decay.

Accepting the need for data on rate change begs the question, "What to measure and how to measure it if the data is to be suited to predicting decay within heritage contexts?" The direct measure of material loss in elemental or chemical terms may be of limited value when compared to physical change measured as heritage value, but could be the direct driver of this change in many instances. Deciding what to measure relates to how the measure degrades the heritage value of the object, which is not necessarily an arithmetic progression of material loss. If material loss is to be the measure, its relationship to value must be determined. Heritage value needs to be defined and scaled, but it will differ according to factors like object context, heritage function, physical make up, visual interpretation and initial condition. This makes it difficult both to derive and solve a heritage value equation. Whatever decisions are made relating to heritage value one thing is clear; to measure it requires a full understanding of decay mechanisms and quantitative measurement of their progress, which is then related to loss in heritage value by a construct and a scale of what constitutes heritage value.

3 IRON AND CORROSION CONTROL

For metals it is relatively easy to prevent corrosion by removing oxygen from the ambient environment, but this is clearly both costly and largely impractical. More realistic options are required such as desiccation, removal of electrolytes from objects and the use of protective coatings. To develop these preservation options corrosion mechanisms must be understood and their rate evaluated in typical heritage environments (Neff et al. 2007). It is recognized in corrosion science that understanding corrosion is the precursor to controlling it and conservation must adopt this approach if it is to offer successful predictive conservation methods. Unfortunately, the demand for immediate preservation solutions can produce uninformed outcomes. Methods of control and treatment are often implemented before research into corrosion mechanisms and their reaction rate is sufficiently complete, which is followed by failure and disillusion from lack of success. With an emphasis on controlled change rather than costly, unachievable or unrealistic prevention, determining corrosion rate becomes essential for predictive corrosion control. Adopting this rationale accepts that objects have a finite life, which is not revolutionary, but rather a logical state of affairs; nothing lasts forever. This is a positive move for conservation, as it frees it from the label of 'failure to prevent' to one of 'successfully extending lifespan'. For this reason it is essential to have rate data for worst and best case scenarios for comparative purposes and calculation. This parallels conservation with corrosion science, where measuring corrosion rates experimentally supports the prediction for the service life of a metal.

4 CORROSION RATE OF ARCHAEOLOGICAL IRON: AHRC/EPSRC SCIENCE AND HERITAGE RESEARCH PROJECT

An illustration of how the concepts and values advocated and discussed here can begin to be investigated and be translated into conservation practice is illustrated by an AHRC/EPSRC Science and Heritage project studying corrosion of archaeological iron. Cardiff University is beginning the task of quantifying the corrosion rate of archaeological iron and translating this into change in the heritage value of objects. This is teamed with exploring methods for using this data to scale a corrosion rate sensor that is undergoing development at Manchester University.

Studying corrosion rate of heritage metals is highly challenging because of ethical constructs that relate to the condition of objects. Thus archaeological iron must retain its corrosion layers as they contain detail of original shape and technology (Neff et al. 2005). Since it is stored and displayed dry, experimentally measuring corrosion rate using immersed methods does not offer a realistic representation of how archaeological iron objects will corrode in typical storage conditions of perhaps 20% to 50% RH. Fortunately in normal atmospheric conditions, weight gain can record, but not distinguish between, oxidation and hydration (Watkinson & Lewis 2005), while oxygen consumption records conversion of iron to iron oxide (Matthiesen 2007).

The experimental set up used measures the oxygen consumption of individual archaeological iron nails to determine oxidation rate of iron and hence corrosion rate of each nail as a function of ambient humidity, object size and chloride content. Each object is placed in a reaction vessel with an airtight lid and the interior is controlled to a specific relative humidity by pre-conditioned silica gel to determine the reaction of individual objects in differing humidity. The oxygen consumption is determined by remotely detecting oxygen concentration via quenching of fluorescence in a sensor spot sealed in each jar. All tests are run at 20°C for comparability and reproducibility. Controls containing nitrogen gas recorded minor leakage from the reaction vessels over 400 days to provide error calculations and limits of detection. Overall the method was reproducible, with good accuracy and precision. Corrosion rate can be represented either as the slope of the oxygen consumption line (rate factor), which can be related to the object weight to allow for sample individuality, or the weight of iron lost can be calculated. Ideally, relating surface area of iron to corrosion rate is preferred, but is impractical due to overlying corrosion layers. Around 200 individual measurements of objects are being carried out for statistical validity and determination of average corrosion rates. Some objects are tested at a single relative humidity for several months, while others are tested at several humidity values to record change in corrosion rate as a function of humidity (Fig. 1).

The quantitative measure of oxidation is being transformed into impact on physical structure by recording images of the objects and delivering criteria anchored assessment of change. This will be translated to change in heritage value as a function of the role of archaeological iron objects via a damage scale, which can be used to predict real time object longevity. Thus the experimentally determined corrosion rate of the metal is related to heritage value. The loss of iron is a readily calculable value, but it is not a direct measure of corrosion in heritage terms. Finally, the nails used in the tests will be digested to determine their chloride content, which addresses another corrosion variable; the impact of electrolyte concentration. Digestion investigates this empirically, as knowledge of the form of chloride is unknown and some of it may not be available to act as electrolyte, being bound up in βFeOOH (Watkinson & Lewis 2005). Location of chloride within an object is also unknown, but investigation using Prompt Gamma Activation analysis at the Budapest Neutron Centre has begun to address the problem of chloride location non-destructively. These unknowns illustrate the complexity of identifying relationships between multiple uncontrolled variables to develop cause and effect interpretations and relevant rate data. Overall, this study will begin to relate oxidation of chloride infested archaeological iron to reduction of its heritage value, offering a management tool for decisions on longevity of archaeological iron as a function of its environment. Full data from this project is being published elsewhere.

Having quantified rate of corrosion as a function of these selected intrinsic and extrinsic variables, it would be useful to be able to measure the impact of the environment on objects.

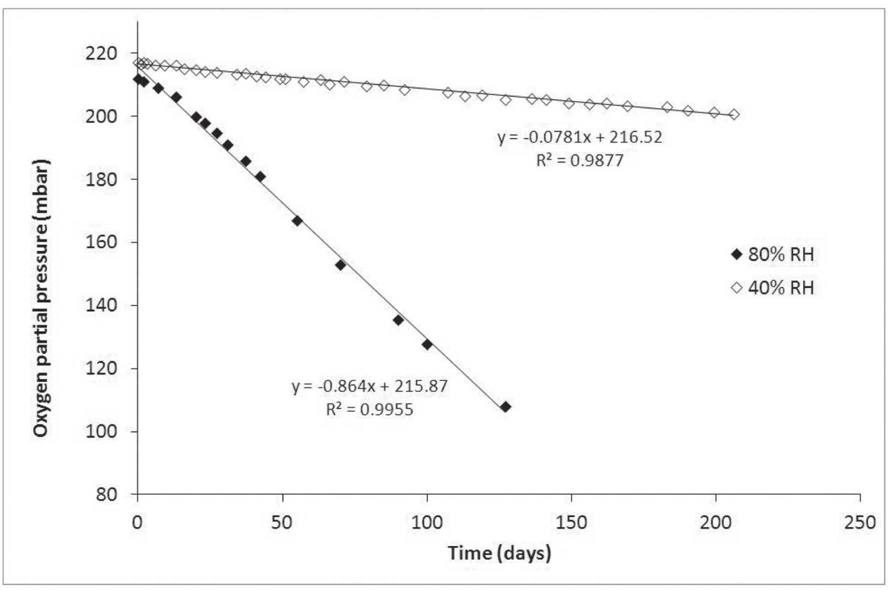

Figure 1. Corrosion rate of Roman nail from Caerleon at 80% and 40% relative humidity.

This is readily achieved with static relative humidity values, but not so easily when the values are fluctuating, as there is a need for a cumulative rate factor to be calculated and converted into heritage value loss. Collaboration with Manchester University and Professor Stuart Lyon is addressing this problem. Development of an Electrical Resistance Corrosion Monitor that corrodes by the same routes as chloride-infested iron is underway. This builds on previous work in this area (Kapatou & Lyon 2008). The ERCM sensor consists of an iron foil attached to a non conducting base plate. The iron is pre-corroded using chloride to deliver a Fe/Cl corrosion model that corrodes by the same post-excavation $\beta FeOOH/FeCl_2$ corrosion mechanism as archaeological iron (Turgoose 1983, Watkinson & Lewis 2005). This cumulatively records corrosion rate as a function of RH by comparing the lowering of resistance of the foil through loss of metal to a non corroding standard. The challenge is to produce reproducible sensors. The data from the iron corrosion rate tests in Cardiff can be used to scale these sensors so they offer data on how real archaeological objects would have corroded in the given environment. This provides a remote sensing tool for corrosion of chloride infested iron that is linked to change in heritage value, as well as loss of iron. The potential impact of environments on archaeological iron can be determined by this method.

5 CONCLUSION

Faced with limited resources to preserve heritage conservation can only normally afford to control decay rather than prevent it. By targeting its research towards understanding mechanisms of change in materials, quantitatively measuring their rate of reaction in differing environments and linking this to heritage value, evidence to support predictive management of heritage is produced. This offers conservation a stronger and more valued role in heritage preservation. Studies such as the AHRC/EPSRC project highlighted here could be initiated in other fields of conservation to increase its management power and standing within the sector.

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New protocols for built heritage protection in the Basque Country: Towards an automatic analysis tool for built heritage

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ABSTRACT: This paper presents the past and current research work carried out in the development of an ICT tool to automate the analysis of built heritage. The aim of this tool is to help in and speed up the application of the new protection protocols (in development) in practice. This paper presents this tool and its two distinguished parts: the analysis component and the decision making component. The decision making component applies the criteria established in the protocol.

The analysis component aims to automate the analysis process through the use of data in different formats to obtain the information necessary for the decision making component. The analysis component is the centre of current research. This paper shall finish with an analysis of the possible impact and consequences of such a tool for the protection of built heritage in the Basque Country.

1 CONTEXT: STRATEGIC PLAN FOR THE INTEGRATED MANAGEMENT OF ARCHITECTURAL HERITAGE

The main objective of the Strategic Plan (SP) is to set out the guidelines for the Cultural Heritage Department of the Basque Government in coming years by redesigning and updating the management of Immovable Cultural Heritage (ICH) in the Basque Country. The Roadmap, planned to run between 2011 and 2013, establishes a feedback system divided into four work packages.

The first two—analysis of the current ICH management situation in the Basque Country and benchmarking the best international practices for their possible extrapolation to the Basque situation have now ended (2011), allowing the establishment of the starting points to address subsequent challenges.

The third work package—especially important—is being implemented at present and deals with the design of conceptual tools required to manage ICH, based on three aspects: a) Updating cataloguing tools; b) Defining new standard assessment criteria; c) Defining new protection standards and protocols.

The fourth work package—also important—was raised to respond to one of the major shortcomings detected in the initial analysis of the process: the state of collapse generated by an obsolete and extremely slow rating and protection system. With a view to reversing the situation, the creation of an expert management system aimed at supporting and protecting the inventory was proposed. The main objective would be to automate ICH assessment and protection protocols with the subsequent objectification and streamlining of the process.

This raised an important research challenge, since there are not many experiences that have probed the basic requirements (basic functional analysis) of an automatic sorting system applied to Architectural heritage. This text will succinctly explain the current state of a project that must take shape over the next fifteen months.

2 ICT TOOL

2.1 *Tool design*

The ICT tool for the automation of the protection protocols will have to fulfil some requirements in order to be validated and gain the trust of its users.

2.1.1 *Learning and updating*

The analysis component will be required to learn from experience and be able to update itself automatically in a periodic fashion, re-training itself taking into account new cases added to the database, through the use of machine learning algorithms (Mitchell 1997). To this end, the system must provide the mechanisms necessary to allow an expert user to store raw data together with feedback on the results of the analysis in the database.

2.1.2 *Similar case retrieval*

The tool must include a mechanism for the retrieval of similar cases that have been evaluated in the past and are stored in the database. It will be necessary to define a metric that will allow to measure the "similarity" between two cases.

2.1.3 *Explanation*

The tool will produce a report outlying the results of the analysis and how these lead to the corresponding protection.

2.2 *Components*

The ICT tool has four main components (Fig. 1) as described next.

2.2.1 *Inputs*

Different features are taken into account for the evaluation of built heritage. These features, quite often, are evaluated through visual inspection and, thus, in these cases using digital images as the input data seems like the logical path to take. In other cases, we might find the necessary information in texts, for example historical documentation of the different, most important interventions carried out on the building. Then, a digitised version of the text will serve as the input data. As well as digital images and text, digitised building plans and drawings, laser scanner 3D point clouds, photogrametry, ... might also serve as input data.

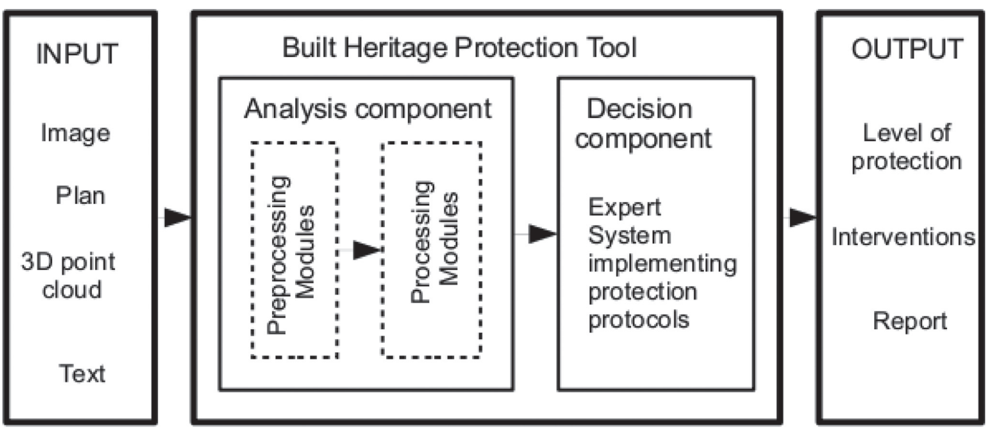

Figure 1. ICT tool design.

2.2.2 *Analysis component*

The analysis component aims to automate the analysis process through the use of data in different formats. Different technologies will have to be used in the development of this component: image processing (Gonzalez & Woods 2008) to extract information from digital images, natural language processing (Jurafsky & Martin 2009) to process text, point cloud processing (Rusu et al. 2012) technologies for laser scanner data, ... Previous experiences in the use of these technologies within the context of cultural heritage exist. Image processing techniques have been used to recover hidden writing in the Archimedes palimpsest (Tonazzini et al. 2004). Natural language processing techniques have been used to capture the mental model of a gothic cathedral that architecture historians have (Hollingsworth et al. 2011). Point cloud processing has been used to automatically computer 3D lines (Rodríguez et al. 2008) for geometric documentation of heritage.

The different algorithms used will need to be trained using training data, i.e. representative example data used to let the algorithm adjust its parameters. The information revealed by the analysis component is the information fed into the decision making component. The analysis component is the centre of current research.

2.2.2.1 Databases

The training data is kept in a database. As the tool is used, new cases processed by the tool can be added to the database after they have been revised by an expert. The algorithms can then be re-trained periodically with more data and this should imply an increase in their accuracy.

2.2.3 *Decision component*

The decision making component applies the criteria established in the protocol and is implemented as a rule-based expert system (Ignizio 1991). This is straightforward as the protocol establishes unequivocally what protection to give a building given the results of the analysis.

2.2.4 *Output*

The output of the ICT tool is the level of protection to give the building under consideration and the specific interventions to carry out upon it. The tool will also provide a detailed report of the results of the analysis and an explanation of how these results led to those conclusions under the protocol.

3 CURRENT RESEARCH

Current research is focused on the analysis component. As most of the analysis is carried out through visual inspection, we took this as the starting point for the development by performing image processing of digital photographs of the elements of interest. The visual inspection is quite appropriate for automation with image processing and machine learning as, in most cases, we want to detect and classify features that can be characterised geometrically.

3.1 *Objective*

Our objective is to develop a system that assists and speeds up the process of analysing built heritage and applying the new protocols. Therefore, not only do we seek to develop robust algorithms that will perform this analysis automatically, but we also seek to rely on a data capturing system that is easy, fast and inexpensive. The use of sophisticated data capturing equipment that required highly trained specialists and raised the costs would defeat the purpose. Consequently, our first choice as a data capturing system for visual inspection is a standard digital camera.

3.2 *Challenges*

Despite this task being appropriate for automation, it is also very challenging. When computer vision and/or image processing is used for industrial tasks the processing is performed in a very controlled environment. For example, the type of light used and the position of the light source are optimal and stable. The position of the camera and the position of the object of interest with respect to the camera are known. In this analysis, on the contrary, we cannot assume we have a controlled environment. Light, position, and the effect of time and weather are factors that we cannot control. The weather on the data capturing day might have an impact in the image processing as images might have bright and dark areas and shadows. It is not always possible to avoid this using a flash. The position of the camera with respect to the object of interest is not always guaranteed to be the same. In the case of a stonework bridge, for example, it is not always possible to get a front image of the vault. The accessibility for different bridges will be different. Many of the elements that have to be inspected are on the outside of the architectural structure exposed to the elements. This results in discolouring and, thus, we must be careful when using colour in the algorithms. Vegetation growth is another problem as it can cause occlusions.

Wearing out of the stones may also be troublesome if we are relying on feature geometry, what were originally right angles might now be curved.

3.3 *Solutions*

A large database of training data is necessary to train algorithms that are reliable and robust.

We believe the solution is to rely on local changes rather than relying on absolute values. For example, if we want to distinguish timber from other building materials we might try looking at a combination of change in texture and change in colour rather than looking directly at the colour, as this would vary depending on the light, or the texture, it might be that not all timber has the same texture.

4 CONCLUSIONS

The application of the new protection protocols in development has a major consequence: the avoidance of individual, subjective judgement in favour of normalised criteria. Normalisation means the implantation of criteria that are independent of the technician involved with the evaluation of a particular piece of built heritage, the result of the evaluation will be the same independent of the technician assigned to the case. This makes the protection process transparent to the public, eliminates any arbitrariness and is homogeneous across the different cases.

The ICT tool, on the other hand, expedites the application of the new protocols. In the Basque Country, the evaluation of a built heritage piece carried out as part of a protection investigation must be carried out by an expert on the particular type of building being looked at (so, if it is a stonework bridge, the technician assigned to the protection file must be an expert in stonework bridges). This constraint, together with the difficulty and the time-consuming nature of the protection process itself, means that often the protection of built heritage is delayed and endangers the correct conservation of the piece. With this ICT tool, the weight of the analytical evaluation falls on the tool itself and the decision regarding the protection and the interventions to perform is made by the tool by applying the protocols on the information revealed by the analysis. Therefore, the need for an expert to be involved in the protection process is minimised as any technician can be trained to collect the data for the ICT tool. As a result, the expert bottleneck is eliminated and the process is speeded up.

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Review of restoration interventions: Effects on the Roman archaeological site of Merida (Spain)

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ABSTRACT: The exhaustive revision of previous restoration interventions is a key task when considering the real current state of conservation of an archaeological site, especially when planning new intervention project. This involves the study of former projects and reports, when possible, but also scientific analysis of effects derived from those interventions. In the particular case of archaeological sites this is not always an easy task. On one hand because there is a remarkable lack of documentation, and lack of precision on given data, more accentuated when older. On the other, because there is a poor scientific knowledge of the effects of restoration treatments in the mid- and long-term, in aspects such as durability, effectiveness or degradation mechanisms when they have become harmful. The research project presented here is deepening on the study of these effects, focusing primarily on stone material from selected archaeological sites of Merida; mainly the Roman Theatre and the House of Mitreo.

1 INTRODUCTION

Overall reading of the scientific literature related to the study of the effects of restoration treatments shows a panorama really advanced in many fields, such as in architecture, conservation of historical buildings, or painting. Nevertheless researchers in conservation have been slightly concerned about the impact and damage that these treatments have on material exposed in archaeological sites. Those are characterized by particular features in its state of conservation, mainly due to its different exposure to weathering after several centuries and burial period.

Moreover the evaluation of treatments and restoration products has been based largely on laboratory studies, primarily on artificial aging tests. Some others, more limited, have evaluated the durability and efficacy of these treatments after several years after its application (Rossi-Manaresi 1976, 1995, Fassina 1995, Stadtbauler et al. 1996, Haake et al. 2004, Wheeler 2008, Laurenzzi & Simon 2006, Favaro 2007, Hansen et al. 2010).

The archaeological remains of Roman Augusta Emerita (founded in 25 B.C.), has been subject of numerous interventions since the beginning of the excavations in 1910.

From a theoretical point of view studying the development of these interventions it is possible to analyze the evolution of criteria and methodology, associated to the development of rules and international charters. From a pragmatic point of view this research will be focused in analyzing aspects such as durability and efficacy of treatments: suitability of products, influence of the methodology of application, relation between old and new treatments on the same surface or interaction between these products and the archaeological substrate.

2 INTERVENTIONS ON THE ROMAN THEATRE OF MERIDA

From the beginning of archaeological excavations Melida and Macias, archaeologists responsible of the project, had the purpose of conserving on site most of the material and the reconstruction and exhibition of the main structures. Thus, the first project is focused on the Roman Theatre area with the intention of reconstruction and anastylosis work of the Front Stage and Cavea (the stands), as well as the Peristyle and Basilica House. Some main interventions are following listed:

1921–22/1923–25: Reconstruction of the lower colonnade of the Front Stage by architect Aurelio Gomez Millan. Most columns were replaced from the excavated remains; others were created ex novo with marble from quarries of the Estremoz area in Portugal, the same as the original ones.

1948–1969: the architect Menendez-Pidal's work has set the current appearance of some of the most important monuments of the city. The methodology follows a common pattern. These interventions are basically architectural reconstruction, structural consolidation and reintegration of elements (Fig. 1a):

– Architectural reconstruction by using reinforced concrete and cement.
– Structural consolidation of original elements with hidden ties of reinforced concrete, as well as injections of cement slurry.
– Reintegration and recomposition of fragments, mainly marble elements from the Front Stage. Different techniques have been used in this sense: the Perfo© system (an anchoring method that involves the introduction into the hole of a metal capsule filled with synthetic resin), direct adhesion with epoxy resin (Krauto©) or bronze and iron staples.
– Wall paintings and mosaics were extracted in block and consolidated on a new mounting system with cement and an internal iron net.

In 1981 architect Hernandez Gil, executes punctual consolidation works on the Cavea, completed with some facilities for visiting in the nineties.

1996: After some years degradation of materials exposed to weathering was evident-sulfation of marble, biodegradation, moisture problems, soiling, salts, etc. It motivates the implementation of a major restoration project on the Front Stage by the Agora S.L. company.

General treatment:

– General cleaning with an alkaline solution in order to neutralize the acidity of the substrate, due to accumulation of pigeon droppings.
– Repair and fixation of elements with epoxy resin and plaster.
– Removal of former decayed restorations such as iron staples or epoxy resins.
– Treatments on marble elements (Fig. 1b).

Figure 1. a. Structural consolidation and reintegration of elements LOTY Archive (07606), IPCE. b. Treatments on marble elements. Source: Agora S.L.

– After mechanical cleaning, application of urea based fungicides (1.5% concentration) and quaternary ammonium salt for algae removing.
– Demineralized water poultice, occasionally with the addition of ammonium bicarbonate.
– Fragment fixation with stainless steel bars.
– Consolidation with ethyl silicate punctually in deteriorated areas.
– Final protection with hydro-repellent Tegosivin HL 100.

3 EFFECTS OF CONSERVATION INTERVENTIONS

As it has been shown, interventions until the nineties are characteristic of architectural restoration, predominating the use of modern construction materials and methodologies.

The disadvantages in the use of cement and reinforced concrete were visible early after widespread use in reconstruction processes. The different physico-chemical properties between those ones and the traditional materials cause high internal tension and thus severe mechanical damages. This is mainly due to the more rigidity of cement and the great difference in the elasticity of both materials (Almagro Gorbea 1992), which ends cracking and fracturing (Figure 2a). The cement's low permeability to water vapour, used as mounting system for the mosaics and wall paintings between the sixties and eighties, has been seriously damaged as seen in Basilica House (Figure 2b). The replacement of cemented pavement prevents transpiration and thus movement of water from ground to lateral walls. This has motivated a new intervention in order to "restore former restoration", by removing cement reintegration and filling the voids with gravel. In addition, the unstable chemical composition of cement leads to problems due to salt crystallization.

The use of metallic staples, as well as internal iron nets (Figure 2c), cause bursting due to corrosion processes, and rust stains.

The problems arising from the use of synthetic resins on archaeological sites are related to the photo-degradation process due to its exposure to weathering. This involves colour changes, yellowing, and loss of mechanical properties caused by the action of solar radiation (UV) (Melo et al. 1999). This affects specially to epoxy resins used as a fixing system. The fall of fragments of ornamental marble elements from the entablature of the Front stage is one of the most serious problems associated with the latter.

Regarding the evaluation of superficial treatments applied in recent interventions, specific analytical techniques will be used in order to achieve a deep knowledge of the interaction between restoration products and archaeological stone material, as well as aspects such as effectiveness and durability of these treatments, or any damage caused to the stone substrate.

Figure 2. a. Restored column; b. Damages caused by cement pavement in Basilica House; c. Metallic elements.

To assess the presence of any treatment, repair or product that has been either documented in the consulted reports and/or papers, or that can be observed just by looking, the following techniques are planned to be used:

1. *In situ*: portable and non destructive techniques such as Raman, XRF, spectrophotometer, roughness meter, ultrasound velocity, hardness tester, magnetometer, infrared camera, water absorption and humidity recordings of the surface.
2. Sampling: the minimum number and the smallest samples of different building materials will be taken, treated and untreated, unaltered and decayed, to be analyzed in the laboratory.
3. Laboratory analyses: samples will be analyzed by XRD, FTIR, optical and scanning electron microscope (SEM + EDS) and some properties determined as the water-repellence of the treatment by means of the contact angle analyzer. All these analyses will prove the conservation state of both the product/treatment and the substrate.
4. Some treatments will be tested *in situ* and its efficacy and durability measured and monitored by some non-destructive techniques and some other laboratory tests.

4 CONCLUSIONS

The state of conservation of archaeological materials preserved on site depends on many different and changing factors. This significantly influences the effects of restoration actions and makes difficult to predict aspects such as durability or effectiveness of those treatments. However there are still many gaps in our knowledge about the effects of these interventions in the long term.

In many cases, as shown, previous treatments and interventions have become sources of degradation. Moreover, at sites where several interventions have been carried out there could be an overlapping of treatments over the same surface, which can lead to unpredictable and unknown damages.

In these cases analytical studies will be essential in order to determine an appropriate solution, as well as knowing mechanisms of deterioration and the validation, or definitive dismiss, of treatments and products. These analyses would be more realistic and practical if carried out in situ, considering its actual exposure conditions.

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From 2nd to 5th October 2012 an International Congress on Science and Technology for the conservation of Cultural Heritage was held in Santiago de Compostela, Spain, organized by the Universidade of Santiago de Compostela on behalf of TechnoHeritage Network. The congress was attended by some 160 participants from 10 countries, which presented a total of 145 contributions among plenary lectures, oral, and poster communications. The congress was dedicated to eight topics, namely (1) Environmental assessment and monitoring (pollution, climate change, natural events, etc.) of Cultural Heritage; (2) Agents and mechanisms of deterioration of Cultural Heritage (physical, chemical, biological), including deterioration of modern materials used in Contemporary Art and information storage; (3) Development of new instruments, non invasive technologies and innovative solutions for analysis, protection and conservation of Cultural Heritage; (4) New products and materials for conservation and maintenance of Cultural Heritage; (5) Preservation of industrial and rural heritage from the 19th and 20th centuries; (6) Security technologies, Remote sensing and Geographical Information Systems for protection and management of Cultural Heritage; (7) Significance and social value of Cultural Heritage; and (8) Policies for conservation of Cultural Heritage. This volume publishes a total of ninety three contributions which reflect some of the most recent responses to the challenge of cultural assets conservation.

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