# Aleksander Rečnik

# Minerals of the Mercury Ore Deposit Idria



## Minerals of the Mercury Ore Deposit Idria

Funding: Public Research Agency of the Republic of Slovenia. Research project No. L1-2232, entitled »Exploration and preservation of Slovenian mineralogical heritage« 2009-2012. The research published in this monograph was done in a project collaboration with the Mercury mine Idria during 2004-2012.

Slovenian Book Agency. Co-financing of Scientific monographs in 2012, under the Decision No. 6130-2/2012/02.

Project group: Dr. Aleksander Rečnik (project leader), Dr. Uroš Herlec (geologist); Partners from the Mercury mine Idria: Bojan Režun and Martina Peljhan.

> The materials published in this book were contributed by: Municipal Museum Idria, Mercury Mine Idria, Faculty of Natural Sciences in Ljubljana, Geological Museum of Jagiellonian University in Krakow, Natural History Museum of Slovenia and Natural History Museum in Vienna.

The displayed specimens are from private and institutional collections.

**Translation**: Blaž Miklavič and Dr. Nina Daneu **Review**: Prof. Dr. Jože Čar and Prof. Dr. Breda Mirtič **Proofreading**: Dr. Paul McGuiness

Illustration: Marija Nabernik

Aleksander Rečnik

# Minerals of the Mercury Ore Deposit Idria



Aleksander Rečnik Department for Nanostructured Materials Jožef Stefan Institute Ljubljana, Slovenia

ISBN 978-3-642-31631-9 DOI 10.1007978-3-642-31632-6 (eBook) Springer Heidelberg New York Dordrecht London

Library of Congress Control Number: 2012954611

#### © Springer-Verlag Berlin Heidelberg 2013

This work is subject to copyright. All rights are reserved by the Publisher, whether the whole or part of the material is concerned, specifically the rights of translation, reprinting, reuse of illustrations, recitation, broadcasting, reproduction on microfilms or in any other physical way, and transmission or information storage and retrieval, electronic adaptation, computer software, or by similar or dissimilar methodology now known or hereafter developed. Exempted from this legal reservation are brief excerpts in connection with reviews or scholarly analysis or material supplied specifically for the purpose of being entered and executed on a computer system, for exclusive use by the purchaser of the work. Duplication of this publication or parts thereof is permitted only under the provisions of the Copyright Law of the Publisher's location, in its current version, and permission for use must always be obtained from Springer. Permissions for use may be obtained through RightsLink at the Copyright Law.

The use of general descriptive names, registered names, trademarks, service marks, etc. in this publication does not imply, even in the absence of a specific statement, that such names are exempt from the relevant protective laws and regulations and therefore free for general use.

While the advice and information in this book are believed to be true and accurate at the date of publication, neither the authors nor the editors nor the publisher can accept any legal responsibility for any errors or omissions that may be made. The publisher makes no warranty, express or implied, with respect to the material contained herein.

Printed on acid-free paper

Springer is part of Springer Science+Business Media (www.springer.com)

### CONTENTS

Introduction	3
The History of Mining	4
Geology and Formation of the Ore Deposit	22
Mercury Ores	26
Minerals of the Idria Ore Deposit	33
Native Mercury	35
Hydrocarbons and Idrialine	36
Pyrite and Other Sulfide Minerals	40
On the Idria Cinnabar	44
Twinning of Cinnabar	56
Mineralogical Expedition	64
Metacinnabar and Calcite	72
DOLOMITE AND QUARTZ	82
Silicate Minerals	88
Baryte and Celestine	90
Minerals of the Oxidation Zone	94
Geological and Technical Heritage of Idria	101
References	109





Illustration of twinned cinnabar crystals from Grübler ore body. Tempera on paper – Marija Nabernik © 2010

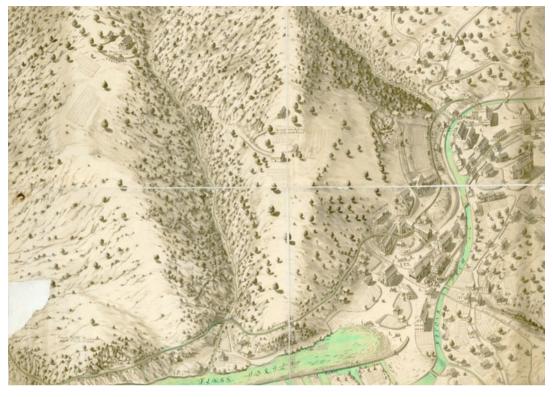


Morning view of the Idrijca valley. Photographed from Ledine in autumn 2004 – Photo: A. Rečnik

#### INTRODUCTION

Slovenia boasts the world's second-largest mercury deposit, located under the historical town of Idria. The most important ore mineral was cinnabar and only to a minor degree native mercury. The ore field extends along the Idria Fault zone over a relatively small area of 0.6 km<sup>2</sup>. In a 500-years long mining history, more than 700 km of tunnels and seven shafts have been dug to access the ore bodies and transport the ore to the surface. Deep drilling revealed that the ore extends to 450 m below the surface. With 15 levels, a depth of 382 m was reached with the deepest tunnel plunging 36 m below sea level. The Idria ore deposit has a very complex tectonic structure. Ore mineralization occurred in two consecutive phases in the Middle Triassic. In this process, all the rocks from Carboniferous to Triassic were mineralized. Due to intense tectonic activity in the Tertiary, the mineralized rock sequence was brought in an inverse position with Carboniferous rocks sitting on top of the younger beds. By far the richest are the interstratified ore bodies, which are mainly of synsedimentary origin, while some were formed by metasomatic replacement of the soluble layers in Triassic limestones. Mineralogically the most interesting were poorly mineralized discordant ore bodies, occurring in tectonically shattered zones along the steep faults that served as conduits for ore solutions. In these zones, fissures with up to 50-cm large cavities covered with crystals of dolomite, guartz, calcite, baryte, pyrite, cinnabar and other accessory minerals were encountered during mining. For mineralization of the ore deposit was the presence of hydrocarbons in the bedrock was crucial. In the process of pyrolisis, polycyclic hydrocarbons formed and the sulfur needed for cinnabar formation was released. Hydrocarbons influenced the crystallization and they occur in form of bitumen alongside the ore minerals throughout the deposit. Until today, 25 minerals were identified in the Idria deposit. For two of them, siderotil and idrialine, Idria is their type locality. Ruby red crystals of cinnabar from Idria are found in all major mineralogical collections and museums around the world.

A. Rečnik, Minerals of the Mercury Ore Deposit Idria, DOI 10.1007/978-3-642-31632-6, © Springer-Verlag Berlin Heidelberg 2013





View of Idria in the direction of Nikova creek in a mid of the eighteenth century, Joseph Mrak (1744). Austrian State Archives, Vienna

#### THE HISTORY OF MINING

According to legend, the mercury in Idria was discovered in 1490 by a woodenware maker when soaking a tub in a spring near the present-day church of the Holy Trinity. Overnight, a heavy silvery liquid accumulated in the tub. The man took his find to the bishop's town of Loka and showed it to a goldsmith, who quickly realized what it was. The news about the invaluable discovery spread quickly and the valley was soon flooded with miners from Friuli, Carinthia, and Tyrol, who began searching, digging, and washing the mercury-bearing rocks. A mining town emerged in the previously uninhabited valley. The origin of the name Idria is unknown and dates back to the pre-mining era. A similarity with the old Greek name for a water jug (Hydria) or mercury (Hydrargyros) appears to be coincidental.

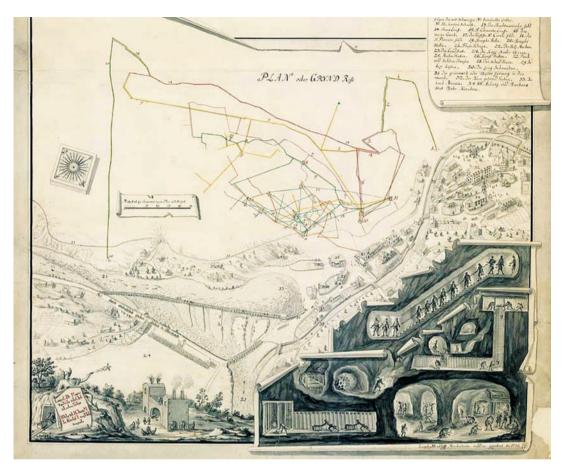
The cover of the municipal chronology of Cividale del Friuli in 1493, reporting on the arrival of Tyrolean miners to Idria. The original is kept in the Archaeological museum in Cividale (Italy)



Prospecting for ore veins in streams and underground mining in the Middle Ages after Agricola (1556)

The oldest records of the early mining history in Idria are kept in the Cividale archives (MOHORIČ 1960). In these early beginnings the discoveries of ore were purely fortuitous, but based on their observations the prospectors gained valuable experiences that helped the future generations of miners. The knowledge about the ore-bearing rocks and their occurrence was rapidly improving. At first, the mining was limited to following the surface outcrops of mercury-rich slaty claystone, which turned into underground mining. Soon after, the first mining company was founded by Venetians, and in 1493 the first mining rights were granted to miners. The ore near the primary outcrop was soon mined out, but while digging, they encountered large deposits of mercury-rich cinnabar ore. Drifts were dug to follow the inclined ore bodies, while deeper parts of the deposit were accessed through vertical shafts. Following the rich ore vein, the still accessible Anthony's shaft under Smuk's hill was built in 1500. When excavating a shaft in the present-day town square, they hit upon the richest cinnabar bed in the history of mining, which enabled flourishment of the town. This fortunate event happened

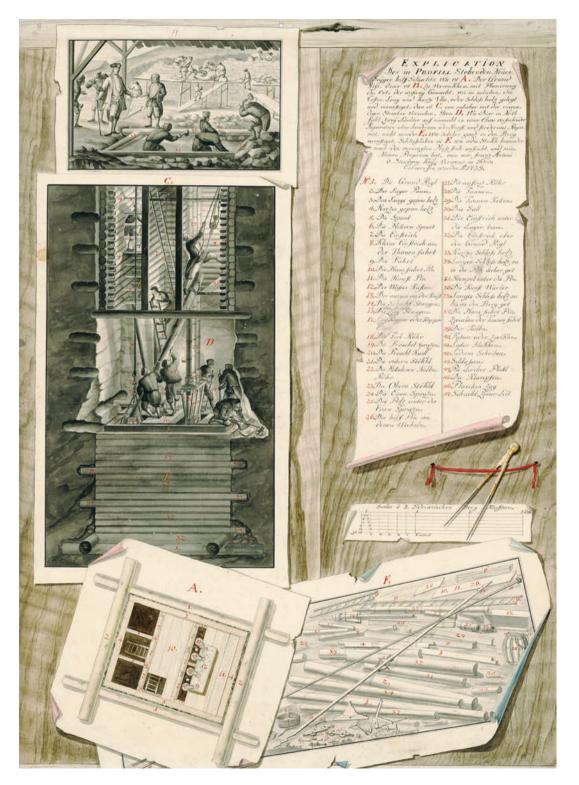
on June 22 in 1508, on the St. Achatius day. In gratitude, the shaft was named after this saint, and the day of discovery remained a major miners' holiday in Idria. The extraction of mercury was conducted in the following way, depending on the processed ore type. Slaty bedrock, rich in native mercury, was first crushed and then washed through the sieves to collect mercury drops. To some extent this procedure was efficient when dealing with the native mercury-containing slaty claystones, but it was not applicable for cinnabar-bearing ores. To extract mercury from the bedrock and cinnabar ores they introduced ore roasting in adapted charcoal kilns (AGRICOLA 1556) and later on iron retorts suited for a more efficient mercury condensation. In the first half of the sixteenth century the water power was used. For the transportation of wooden logs used for supporting the tunnels and shafts in the mine they exploited the Idrijca river. To prevent flooding they constructed powerful water wheels to pump the pit water. In a catastrophic earthquake in 1511 a part of the mountain on the northwestern side of Idria collapsed into the river and blocked its flow. The town was devastated and

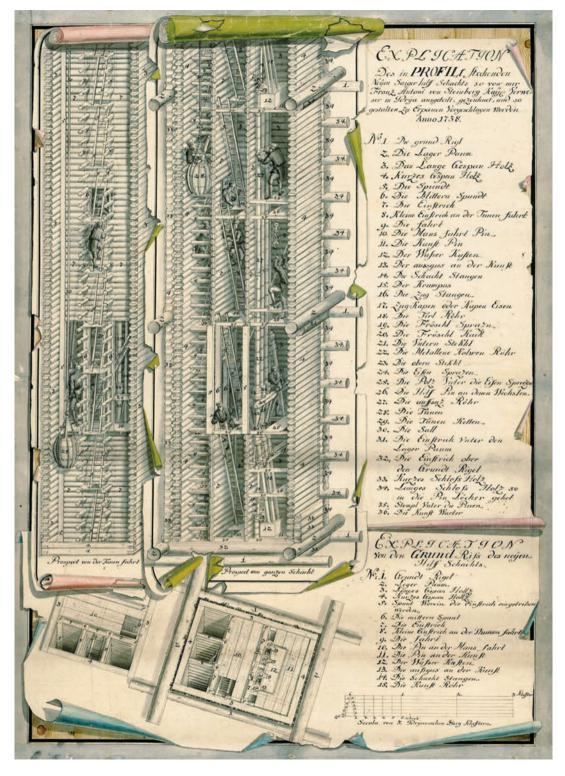


The town of Idria and ground plan of the mine with underground workings, Joseph Mrak (1770). Archive of the Republic of Slovenia

most of the underground objects were flooded. It took 7 years to rebuild the town and the mine. During reconstruction they started to dig the Katarina shaft, which followed a new ore vein in the area of today's main square. The richest ore at that time was mined on the so-called Knez's stope (Fürstenbau), which greatly helped the mine to recover and become profitable. To protect stocks of mercury and store cereal supplies from the frequent incursions of robbers, the owners decided to build a mighty fortress. For this purpose Gewerkenegg castle was built between 1522 and 1532, and served Idria until the present day (MOHORIČ 1960). In the first half of the sixteenth century many different companies were running the mine. As they were mainly interested in profit, they did not invest in prospective works and the mine infrastructure. With nationalization in 1575, the Idria mine came under the management of the Austrian court. By the end of the sixteenth century miners reached depth of 170 m, which was the European record at the time. Throughout its history, the mercury mine in Idria provided an important revenue to the monarchy. The annual production of mercury was nearly 100 tons, which presented an important share of the world's market. With the improving mining and ore processing techniques Idria became renowned as the most advanced mine in the Habsburg Empire. In spite of the fact that the production of mercury in Almadén

(opposite page and overleaf) At its peak, Idria attracted worldrenowned engineers and scientists. The famous cartographer, mining engineer and Karst explorer Franz Anton Steinberg produced the most accurate illustrations of mine shafts of that time. Shown is the construction of Theresia shaft in 1738. The original illustrations are kept in the Austrian State Archives in Vienna



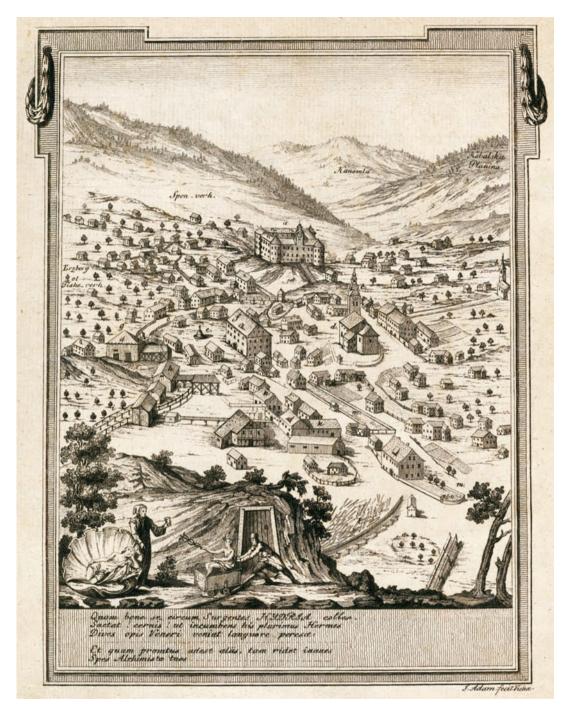




Due to the high content of mercury cinnabar-rich sedimentary ores were highly appreciated by the miners. Photograph shows liver-ore from Skonca beds with cinnabar impregnation and tiny crystals of cinnabar. The specimen with its original label is from the eighteenth century mineral collection of Balthasar Hacquet. Size 8 x 8 cm. Mineralogical collection of the Geological Museum of Jagiellonian University in Krakow – Photo: A. Rečnik



was about three times higher than in Idria, the demand for mercury due to emerging new gold prospects in the Spanish colonies in the Central and South America was so large, that its price reached the historical high. The conditions in the Idria mine were first described by W. POPE (1665), who reported that there were two types of ore excavated in the mine; the hard red ore and the softer one with visible droplets of native mercury. He also found small golden fragments that did not contain any gold. In the beginning of the eighteenth century the British entered the market with large amounts of mercury from China and India (MOHORIČ 1960). In order to stay competitive on the world's market the Idria mines had to considerably increase ore production and optimize the ore processing technology. The Achatius shaft was abandoned and a new Theresia shaft was excavated to reach deeper ore bodies. It cut through several rich ore bodies and soon extended down to today's IX<sup>th</sup> level at a depth of 226 m. The very complex geologic structure of the deposit forced the geologists to study the stratigraphy of the ore-bearing rocks. By the end of the eighteenth century the annual production of mercury exceeded 600 tons. In 1790 a collosal 13.6-m water wheel "kamšt" was built to pump the pit water from the Joseph shaft (later renamed to Delo shaft). The water wheel was used for 160 years and is preserved until the present day. Joseph's shaft connected all 15 levels of the mine to a depth of 382 m below the surface. In 1763 the Habsburg empress Maria Theresa established a school of mineralogy, metallurgy, and chemistry in Idria and



Panoramic view of the old mining town of Idria in the second half of the eighteenth century. At the far end of the town lies the magnificent Gewerkenegg castle, which was built in the sixteenth century to defend the cereal stocks and mercury from predatory incursions. On the right side of the castle is the church of the Holy Trinity, built in the immediate vicinity of the first finds of mercury ore. In the foreground are the Theresia and Barbara shafts. Illustrated from east side of the town. Source: Balthasar Hacquet, Oryctographia Carniolica (1781)

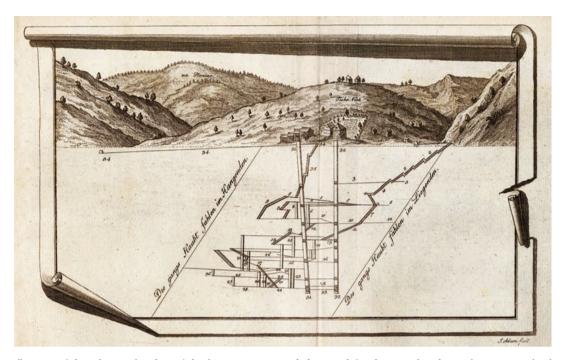


Illustration of the underground workings of the Idria mercury mine with the main shafts Theresia and Barbara and connecting inclined shafts and tunnels reaching down to the then deepest Karl's ore field. Source: Balthasar Hacquet, Oryctographia Carniolica (1781)

appointed the Tyrolean naturalist and an official physician of the Idria mine GIOVANNI A. SCOPOLI (1723-1788) as the principal. With its rapid technological development, Idria became an important scientific center of the time in Europe, hosting several world-renowned researchers and engineers. In the eighteenth century the most accurate cartography of the mine and the surroundings of Idria was done by Scopoli's assistant JOSEPH MRAK (1744) and a Swedish mineralogist JOHANN J. FERBER (1774). Hand-in-hand with mining a knowledge of mineralogy was emerging. One of the founders of mineralogy in Idria was Scopoli's contemporary BALTHASAR HACQUET (1739-1815), an esteemed polyhistor of Bretonian origin. In his monograph "Oryctographia Carniolica" (1781) he dedicated more than 100 pages to the mining, geology, and mineralogy of the Idria mine, accurately verifying all the previous findings and often complementing them with his own observations. A good example of his scientific mindset was his investigation of the

In Oryctographia Carniolica (1781) Balthasar Hacquet describes more than 50 different mercury and cinnabar ores with other accessory minerals. In Vol. II he described form-rich cinnabar crystals, which did not exceed the size of wheat grains (4–5 mm) 50) Cinnabaris pura folida cryfallis 14cdris irregularibus pellucidis, non prismaticis pyramide trapezoide inclinata fuper minera hydrargyri ponderofa. Delisle Tab. VII. Fig. 9.

Die Zinnoberfrystalten haben 14 Flächen ohne Prisma. Dahingegen jebe Ppramibe sieben unregelmäßige Flächen hat. Ueberhaupt find biefe Krostallen noch ziemlich durchsichtig, wonn sie nicht mit einer feinen Bitriolerbe gefärbt sind. Sie fißen auf einem reichen Queefslibererg, welches mit bem Eisenocher, ben der Bitriol finterläßt, übergogen ist.

51) Cinnabaris pura folida cryftallis diaphanis pyramidatis trigonis fuper breecia impura. Berlin. Befcháftig. No. 39. l. c. Tab. III. Fig. 1 et 7.

Diefe fehr fchonen balb gang balb halbburchfichtigen Zinnoberfreystallen machen meiftens eine breyectigte Caule, find von ber Größe eines Nedentorns, und fichen auf einem ungefalten Zinnober, welcher mit gebiegem Duecffilber gemilcht ift. Zuf einer enwas großen Stufe findet man nicht allein bie angeführten brevertigen Gaulen, fondern auch viele andre verchieben gebildere, nämlich folche, wo die Ppramide abgestumpft oder auch vielfeitig ift. Ueberhaupt find alle dieje freystallifirten Zinnoberarten von einem fehr fchönen Aufehen, beinabers wenn in einem Schlag in bet Beube eine gange Band bamit bebecht ift, fo ift bas der fchönfte Anblich, ben man nur unter der Erbe erporten fann.

Alle oben angeführte Zinnober, und Mercurialerze find bald mehr, bald weniger zu volltommenem Zinnober gebildet. Die lefteren Erze find mehr ein Mohr ober Archivops mineralis als Zinnober, indeffen fam man auf naffem Beg, boch nicht nach wieglebicher Urt, aus allen hydrianer Erzen einen Zinnober erhaten; es ift alfo leicht zu erachten; daß, aus allen hydrianer Erze burch das bald ichmächtere, bald ftartere Bitriolwaffer aufgelöft werden, fich die fchweren Theile, nämlich das vererzte Dueckfilber, durch ihre naturliche anziehende Kraft vereinigen muffen, und die leichten oder erdigen Theile in der Höfe bleichen, und das also in alten Begenden der Bruden, wo es Maffer giebt oder einmal gegeben hat, fehr leicht und gewißt die Kroftallen entstehen können; wie benn die Erfahrung ichon-

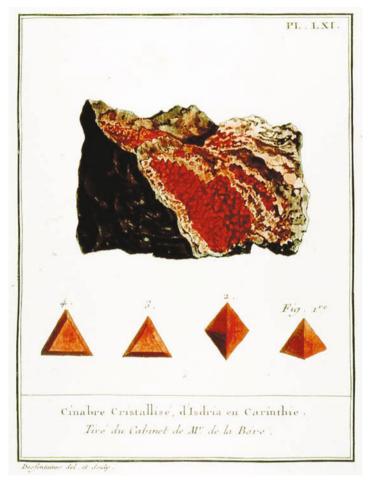


Illustration of the mining town Idria with the main shafts and tunnels engraved on a piece of steel-ore from the second half of the eighteenth century. The upper part of the drawing shows the Roman god Mercury, a link between the earth and heaven, watching over the town. According to the motif and the style of the engraving it can be concluded that it was most probably made by the former mining engineer Joseph Mrak around 1776. The specimen measures 16 cm across and is part of the Hacquet's mineralogical collection in the Geological Museum of Jagiellonian University in Krakow – Photo: W. Obcowski

Illustration by Swebach Desfontaines shows a 12 cm specimen of cinnabar from the Idria mine. The specimen is from the ex Bóve's mineral collection from 1791. Similar specimens are found in the Museum of Natural History in Vienna. Source of reproduction: the Mineralogical Record Museum of Art – Photo: W. Wilson

records to which VALVASOR (1689) had referred to when dating the discovery of mercury back to 1407. He located the original source in the Tolmin archives, but did not believe it, as there were no other records confirming that date. The great value of Hacquet's work is the accurate description of the types of ores and minerals mined in the Idria mine during his time. He described various forms of calcite, quartz, pyrite, gypsum, vitriols, mountain leather, and bitumen and paid special attention to the classification of the mercury ores. Among these he identified over 50 different forms of cinnabar, from amorphous to crystalline. He described spherical aggregates of black cinnabar, which were determined to be metacinnabar some 100 years later. After his descriptions of several centimeters long crystals of gypsum, scalenohedral calcite, translucent doubly terminated quartz crystals covered by cinnabar, and sharp octahedral pyrite crystals, one can just imagine the mineral wealth they were discovering at that time. In the 12 years of his life in Idria he established a rich collection of ores and minerals, now kept at the Geological Museum of the Jagiellonian University in Krakow, where he was employed during 1805–1809. His collection contained 3,352 specimens, of which about 1,400 are preserved. In addition to cinnabars from Idria, he also collected other minerals from Carniolan localities.



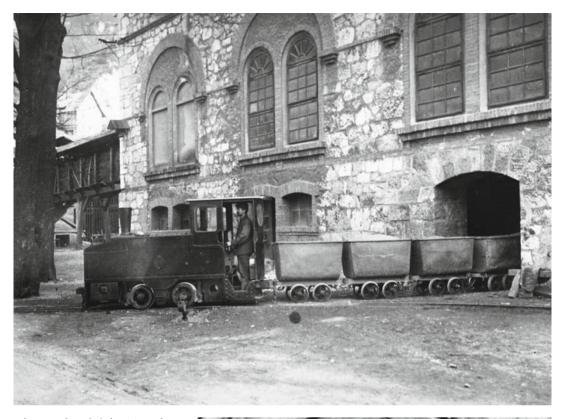
In Hacquet's time, minerals from Idria were also described by the Austrian mineralogist WOLFGANG MUCHA (1780). At the end of the eighteenth century cinnabars from Idria became widespread in European mineralogical collections. A good example is the illustration of cinnabar crystals by SWEBACH DESFONTAINES (1749–1793). In the second half of the nineteenth century, extensive mine workings paved the way for booming geological research. An important milestone in this field was contributed by the Slovenian geologist V. LIPOLD (1874) with the first geological map of Idria and the surroundings. His work presents a foundation of the modern geology of the Idria deposit. Based on his work, KOSSMAT (1899; 1911) further classified the pertinent lithological sequence. At the turn of the twentieth century several Austrian geologists studied the formation of the Idria mercury deposit. KROPAČ (1912) made very accurate maps of the underground workings, which were used for mining until 1957. During this period we find the most comprehensive studies of the mineral paragenesis of the Idria deposit. SCHRAUF (1891) analtyzed metacinnabar and determined a new mineral siderotil along with other vitriols. Not long after that JANDA (1892) isolated yellow-green crystals of the organic mineral idrialine, which he named after Idria. It occurs in tabular crystals in clumps of polycyclic hydrocarbons that accompany ore minerals in crystal-lined vugs.





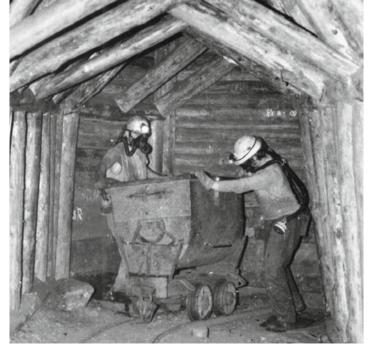
(above) Joseph's shaft with timber storage. After World War II the shaft was renamed as Delo. Here was the main access to the deepest levels of the mine, and also to the mineralogically interesting Grübler Fault zone. Today, the mine is geomechanically stabilized. The water level is presently at the  $IX^{th}$  level, and it will gradually rise to the VII<sup>th</sup> level. (left) An old ore separation (Bašerija) with wagons of ore prepared for smelting around 1900. Photo archive of the Municipal Museum of Idria – Photo: M. Papež

Due to mainly interstratified nature of the ore bodies, the cross-stope mining method with backfilling was developed for ore excavation. Mining preparations started at the lower main level and from here first, up to 2 m high stope, over the whole width of the ore field was excavated in the horizontal direction. On the active level, the excavation of several parallel, up to 2.5 m wide stopes, was carried out from the main gallery, until the active level was completely mined out. For a long time the work was done manually with a hammer and chisel, loading with a hoe and for transportation, wooden carts, the so-called coffins, were used. All the ore was sorted



(above) At the end of the nineteenth century the mine was electrified and locomotives were introduced for the transportation of the ore. Photograph shows removal of slag from the smeltery. Photographs are from the archive of the Municipal Museum of Idria

(right) Small wooden carts formerly used for the transportation of ore were replaced by larger iron carts with a load capacity of ~0.7 m<sup>3</sup>. Through the whole history of mining the tunnels were carefully timbered. For their protection the miners wore filter masks that prevented the inhalation of mercury. Photographed around 1974 at the 15<sup>th</sup> stope of the mining field Ziljska – Photo: J. Čar



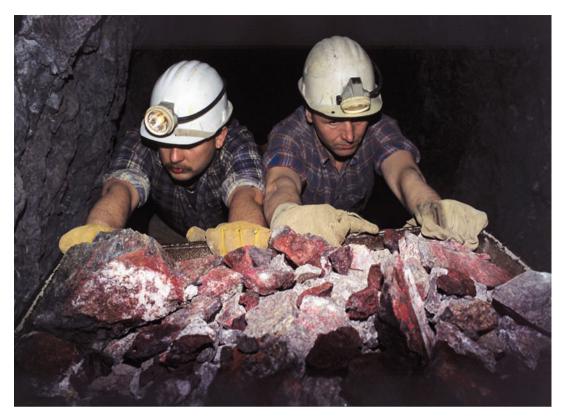




(above) In the postwar period the mine was modernized. The work was assisted by powerful water-drilling machines and instead of old oil lamps the miners wore helmets with rechargeable lamps. Compressed air installations were accessible in every part of the mine so that pneumatic hammers could be used for work even in the most remote mining fields

Photographs on these two pages (and p. 22) are from the Archives of the Mercury Mine Museum Idria – Photo: B. Kladnik

on the spot and transported to the surface, while the gangue was used to backfill the mined area of the active level. To completely fill the stope and prevent caving in, the gangue for backfilling had to be brought into the mine also from the surface. When the stope was excavated, they moved to a higher stope and in this way up to the upper main level or till the overburden of the ore body. Depending on the nature of the ore body, the distance between the levels in Idria mine was 15–30 m, so that between two main levels 7–12 stopes were excavated. Using the cross-stope mining method it was easy to adapt to the ore body shape and to selectively



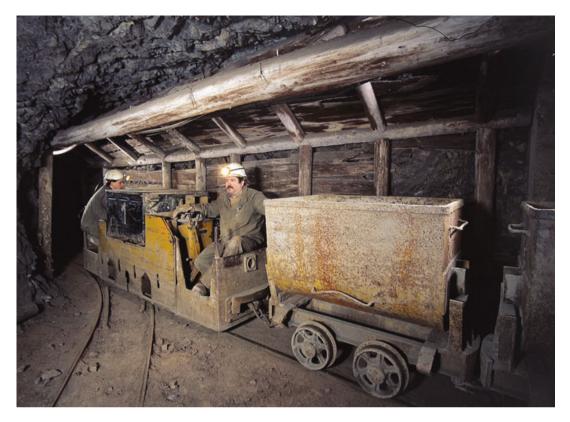
(above) Before its closure in 1995 the mine produced only poor ore, mainly from shattered mineralized faults in Scythian dolomites (Grübler ore body), which contained open veins and pockets with cinnabar crystals and were as such very interesting from the mineralogical point of view. Similar ore is seen on a cart pushed by miners; photographed around 1990

#### (the opposite side below)

Work on a chute. The extracted ore was collected in chutes on the main transportation levels, where it was loaded to carts and transported to the vertical shafts and from there to the surface by a cable elevator

A group of miners reflecting their daily experiences on the III<sup>rd</sup> level, Delo shaft







Electric train used for transportation of ore to the shafts, where it was loaded on elevators and lifted to the surface. After shutdown, this became a part of the technical heritage – Photo: B. Kladnik

Before the mine's closure the tunnels were backfilled and reinforced with concrete in order to prevent caving of the mine. Shown is an abandoned gallery on the IV<sup>th</sup> level, Delo shaft. During the shutdown works all systems were operational until 2009. Photographed around 1988 – Photo: R. Podobnik

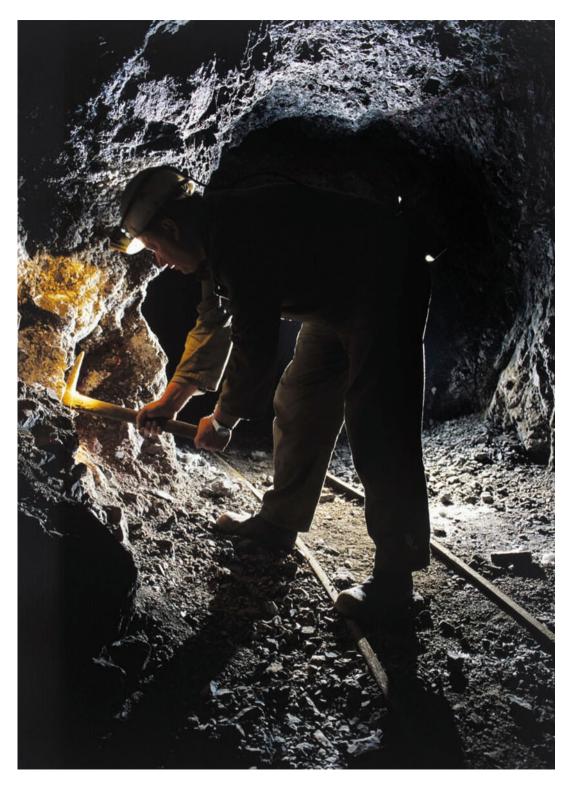
extract the ore. The mining method, except for minor improvements, remained practically unchanged for more than 300 years until the mine's shutdown. The described method was perfectly efficient in stable dolomite rock, whereas for the soft slaty rocks an underhand cut-and-fill mining method was introduced in the late 1970s (BAJŽELJ 1984). With this method, the ore was mined from the top to the bottom. The losses of native mercury were reduced and by cementing the backfill, the mine's stability was increased. Moreover, this technique allowed access to the ore-bearing gangue in the older parts of the mine.



Flooding the mine in 2008. Shaft Inzagi at XI<sup>th</sup> level. Archive of the Mercury Mine Museum, Idria – Photo: B. Režun

Soon after the tunnels were abandoned the wooden pillars could not sustain giant lateral pressures and began to break. Constant humidity assisted the growth of fragile epsomite stalactites. These processes were also present when the mine was active, but at that time the timbers were regularly replaced and the tunnels were ventilated to prevent caving in. Shown is an abandoned tunnel in the tectonically shattered Langobardian conglomerate at IV<sup>th</sup> level of the blind shaft Zergoller – Photo: R. Podobnik





The dawn of the twentieth century was marked by the electrification of the mine. In 1913 the mine produced 820 tons of mercury, an amount that has never been exceeded. During the First World War compressed-air drilling was introduced. Detailed studies of the ore-deposit formation began after the Second World War, when market demands for mercury rapidly increased. Using modern mechanization they were able to excavate up to 8 km of tunnels and 9 km of drill holes per year. In this way, in the 1970s all parts of the Idria deposit were connected by tunnels, except for the deepest ones (ČAR 2010). After more than 500 years of uninterrupted operation, at the end of the 1990' the mine was shut down, mainly for environmental reasons related to mercury pollution. The loss of mercury during the active period is estimated to 40,000 tons. In the past, the slag being dumped on the banks of the river Idrijca still contained a lot of mercury, which represents a constant source of contamination of the Adriatic Sea (ŽIBRET and GOSAR 2005).

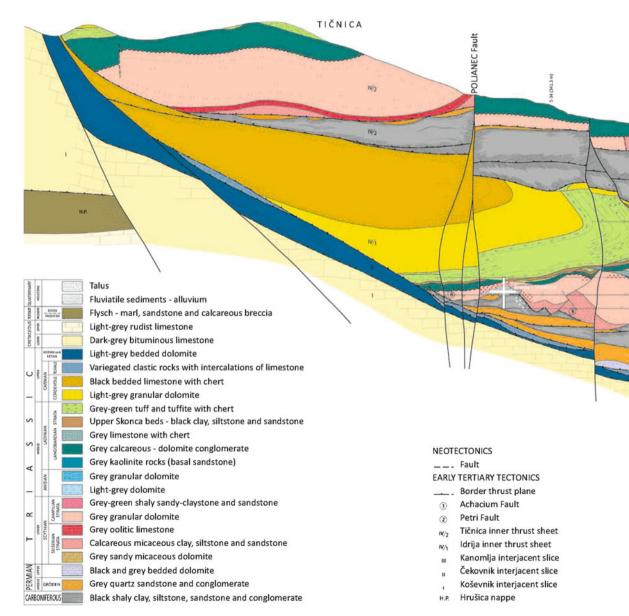
During the shutdown process, started in 1992, the pumping of water from the lowest levels was stopped. Today, the water level is slightly above the IX<sup>th</sup> level. If there will be no significant deformation processes, the water table will be raised to the VII<sup>th</sup> level, which still prevents contamination of the groundwater. Presently, the mine is maintained and kept accessible for visitors down to the III<sup>rd</sup> level. From the 300-600 m wide exploitation field, stretching 1,500 m in NW-SE direction, in total 3 million cubic meters of ore and gangue were excavated (BER-CE 1958). Out of the 158 ore bodies documented in this mining field, 141 were mineralized with cinnabar and in the rest, native mercury prevailed. From 12 million tons of ore, 147,000 tons of Hg was extracted, representing 13 % of the world's total production (ČAR 2010). Following Spanish Almadén, the Idria mine was the second-largest mercury deposit in the world. According to the final estimations, the Idria mercury ore deposit still contains more than 6 % of the known global reserves.



A view into a mysterious underground world of the Idria mine, open to the visitors of the Anthony's passage – Photo: R. Zabukovec

#### GEOLOGY AND FORMATION OF THE ORE DEPOSIT

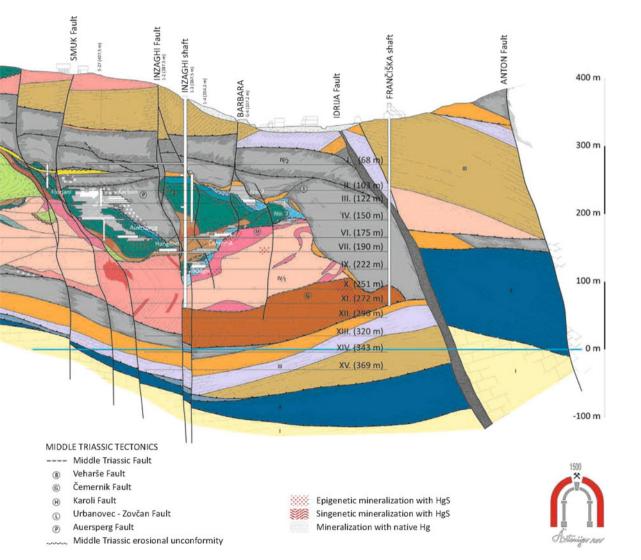
The surroundings of the Idria ore deposit is composed of four SW-verging nappes, with the mercury mineralization being emplaced in the lower part of the Trnovo nappe, in the Idria inner-thrust sheet. The geologic structure of the Idria-Cerkno mountain range was described by ČAR (2010). The mercury ore occurs in the Upper Carboniferous slaty claystones with lenses of quartz sandstone, Gröden sandstones, in Upper Permian and Lower Triassic (predominantly Scythian) dolomites, slaty siltstones and oolitic limestone, in Anisian dolomites, Ladinian dolomitic conglomerate, and younger Ladinian Skonca beds consisting of shallow-water sedimentary and pyroclastic rocks deposited during the volcanic phase. The tectonic transformation of the ore deposit began during the mineralization (PLACER and ČAR 1977; PLACER 1982), whereas the Idria Fault has been active until the present day.



The formation of Idria ore deposit is closely related to the development of the Idria Fault (PLACER and ČAR 1977). In the Middle Triassic the northern verge of the African Plate began to disintegrate. Alongside one of the arms of the continental rift crossing the central part of the present-day Slovenia, formed a few tens of kilometers wide Slovenian tectonic Trough. Consequently, a parallel Idria Fault started to form on the south, measuring about a

few kilometers in width and several tens of kilometers in length. During the Idria tectonic phase in Middle and Upper Anisian, stress releases in the Earth's crust caused the formation of deep faults. These served as conduits for mercury vapor degassing from ultrabasic rocks in the upper mantle. On their way to the surface the temperature and pressure dropped and the vapors started to condensate and accumulate in the fissures of tectonically shattered

Geological cross-section of the Idria ore deposit in E-W direction with depths of the mining levels and some shafts and mining fields. Mercury Mine Idria by J. Čar and coworkers (1967–1993)





A drop of native mercury in the Carboniferous slate in Anthony tunnel – Photo: R. Zabukovec

rocks along the faults. Transposition of the rocks caused the formation of new fractures and changed the flow paths of the ascending vapors. Mercury-rich solutions initially filled the fractures in sandstones and siltstones of the lowest part of sedimentary rock strata. In Carboniferous siltstones the mercury appears in its native form. Because of its silvery appearance the miners called this rock a silver slate. Minor amounts of mercury are found in cracks of the marcasite-pyrite concretions. Only a small part of mercury is bound to cinnabar in these layers, indicating a lack of sulfur in the Carboniferous strata. As a consequence of the intense tectonic activity associated with the Idria Trough formation in the Middle Triassic, extensive volcanism and a related sulfur release was triggered. It is believed that in this process a large fraction of mercurv reacted with sulfur to form cinnabar (MLAKAR and DROVENIK 1971). The volcanism was followed by a weak hydrothermal phase bringing other sulfide minerals into the fault system. Isotopic analyses showed that only a minor part of the sulfur is of magmatic or basement rock origin, while the vast majority of the sulfur is of sedimentary origin (PALINKAŠ et al. 2004). One of the possible sources of sulfur were gypsum and anhydrite lenses present in Upper Permian dolomites, which is supported by rich cinnabar mineralization right above these beds. Another carrier of sulfur were probably hydrocarbons, present in variable quantities throughout the Triassic sedimentary sequence (LAVRIC et al. 2003). The most intense mineralization processes took place in the Ladinian with two consecutive inflows of ore fluids, while minor recrystallization events also happened at the later stages (see Grübler). The primary ore deposit formed ~36 km northeast of the present-day location in the Jelovica area (MLAKAR 1959; PLACER 1973). A tectonic transformation of the deposit occurred during Oligocene-Miocene thrusting along the Idria Fault zone. Paleozoic, Triassic and Cretaceous rocks were folded and overthrust onto younger Cretaceous and Eocene rocks. As a result, the ore beds were brought to a subvertical and even to an inverse position. Due to the Alpine orogeny in Miocene, the whole deposit was overthrust to the present-day position in the upper limb of the fold of an



Cinnabar impregnation in Lower Scythian dolomite at the XI<sup>th</sup> level. Such ore was called basperh – Photo: J. Peternelj

overturned syncline, whereby one-third of the deposit was cut and lagged behind in depth under the thrusts (ČAR 2010). During the Upper Tertiary and to a lesser extent in the Quaternary, a small part of the ore deposit was cut off by the Idria Fault and shifted 2.5 km towards the south-east (MLAKAR and DROVENIK 1971). The catastrophic earthquake in 1511, occurred on this fault. In the Idria mercury deposit a simultaneous metasomatic, epigenetic-vein, and syngenetic sedimentary-exhalative mineralization is documented. The ore formed in two Ladinian phases (MLAKAR and DROVENIK 1971; DROVENIK and PLENIČAR 1980; DROVENIK et al. 1990). In the first phase, the oldest layers, i.e. Upper Paleozoic, Scythian and Anisian beds, was mineralized, whereas the second phase coincides with the emergence of ore fluids and the formation of Skonca beds (LIPOLD 1874) and Upper Ladinian pyroclastic beds. Cinnabar of the first phase impregnated the rock by mineralizing the pores and fractures along the fault zones forming brecciated and vein-type ores. In the sedimentary sequence corrosive ore fluids preferentially dissolved calcite, which was then metasomatically substituted by cinnabar during mineralization. Following this process, rich ore bodies formed by replacement of oolitic limestone layers interbedded in the less permeable Lower Triassic slaty claystone. The second phase of mineralization is characterized by an increased regional geothermal gradient resulting from the regional volcanic activity in the immediate vicinity of the ore deposit. A new fault system was formed. The mineralization of the older ore-bearing rocks was reactivated (KOSSMAT 1911). Epigenetic ore formed by crystallization of cinnabar in the new open fissures along the faults. In the same process, metasomatic ore bodies were formed by replacement of more soluble lenses of gypsum, anhydrite and calcite. The replacement was especially efficient along the limestone beds lying under impermeable claystone layers. Following new pathways large amounts Hg-rich solutions were released in a basin with depositing sediments in the rapidly submerging Idrian tectonic Trough. The emerging solutions reacted with free sulfur to form microcrystalline sedimentary cinnabar ores, explained in the next chapter.



Sedimentary ore from the Skonca beds with laminated cinnabar layers in black Langobardian shale. Skonca beds were named by Lipold (1874) after the creek Skaunca (today Skavnica), where he found outcropping shales, which contain a rich syngenetic mineralization with cinnabar in the ore deposit not far from the creek. 11 x 8 cm. Find J. Čar. Collection of the Municipal Museum of Idria – Photo: A. Zelenc

#### MERCURY ORES

The mercury ores in Idria were named empirically after their appearance and mercury content. These names were preserved through the centuries of mining. A detailed classification of Idria ores was given by SCOPOLI (1761) and HACQUET (1781), who described dozens of varieties, mainly related to sedimentary ore types. Here we introduce only the most common ones. Sedimentary-exhalative ore bodies are emplaced in the upmost part of the mineralized strata. They formed by the exhalation of brines into shallow marine swamps in form of thermal springs. In a reaction with sulfide ions released under reducing sedimentary conditions chemical precipitation of cinnabar-opal slurry took place. It was deposited alternatively with colloform pyrite in the layers of clastic material. Unconsolidated cinnabaropal slurry was transported by the turbid flows, forming various layered ores (MLAKAR and DROVENIK 1971). In sedimentary ores, the ore minerals serve as a binder of clastic material and form continuous monomineralic layers. Mercury exhalation in the Langobardian period was accompanied by an intense volcanic activity, which contributed a large fraction of clastic material into the sedimentation basin. This is indicated by the variable impregnation of tuff layers with ore minerals depending on its porosity. In the process of precipitation of ore minerals in swampy sedimentation basin massive, fine-grained, and to a large extent also laminated sedimentary ores of the so-called Skonca beds were formed. Such type of ore was found in up to 1 m thick beds having up to several hundred square meters large surface areas. This was the largest concentration of mercury found in the history of Idria and gave the mine a



(above) Mercury oozed into a sedimentation basin through thermal submarine springs, where under reducing conditions it reacted with the available sulfide ions and formed a cinnabar-opal silt. Under similar geochemical conditions, iron sulfides were produced. Cinnabar and pyrite alternately precipitated with clastic material on the basin floor. Turbid silt with ore laminas was transposed by underwater currents, which is shown by the folded laminar texture of sedimentary ores. 10 x 7 cm specimen is from the Skonca beds, mining field Kropač. Geological collection of the Municipal Museum of Idria – Photo: A. Zelenc

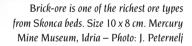
(right) Langobardian slate interleaved with layers of fine crystalline syngenetic pyrite. Mining field Ziljska 1/14 specimen (1970). View 4 cm. Collection of the Municipal Museum of Idria – Photo: A. Zelenc





Liver-ore with characteristic tectonic glide surfaces. Size 15 x 9 cm. Natural History Museum, Vienna – Photo: A. Rečnik

decisive impetus at the beginning of mining. The Skonca beds are located in the uppermost horizons of the ore deposit. They are bound to the bituminous Langobardian siltstones and sandstones. The ore bodies extended through the whole thickness of this stratum having lengths from a few tens to hundred meters. The majority of the sinsedimentary ore bodies was located above the IV<sup>th</sup> level, except in the area of Inzaghi shaft, where they extended all the way down to the IX<sup>th</sup> level. Compared to other lithological units, the ores from Skonca were the most diverse. The richest of all ores was steel-ore. occurring in concordant beds and lenses in Skonca layers. It formed by differentiation of the colloidal silt, where cinnabar and bituminous matter were concentrated. Indicative of this process are the remnants of bacteria mineralized with pyrite and rarely with cinnabar. The ore is fine crystalline to colloform. It contains up to 79 % of Hg. The fracture shows a steely-gray luster with a faint reddish undertone. Its metallic luster is specially pronounced on polished surfaces (see p. 15). Cinnabar, precipitated in bituminous swampy mud formed a clayey dark red liver-ore. It contains significant amounts of uranium bound to hydrocarbons, which is to a lesser extent present in all bituminous clastic rocks from the Skonca beds. During the exploration of uranium deposits in former Yugoslavia the first samples of concentrated uranium oxide, the so-called yellowcake, were produced in Idria (DROVENIK et al. 1980). Liver-ore is mineralized bituminous slaty claystone or radiolarite, which contains up to 65 % of Hg. In tectonic processes the mudstone beds were deformed and fractured, which induced characteristic tectonic glide faces with liveryred luster. On the fractured surfaces it is black with red patches of cinnabar impregnations. The majority of cinnabar though, is concentrated in chalcedony grains and radiolarie. Older fractures in liver-ore are impregnated with quartz, pyrite, cinnabar or bitumen, whereas younger fissures contain native mercury. In liver-ore beds, the amount of cinnabar gradually depletes into black bituminous claystone without cinnabar. On crystallization of cinnabar-opal slurry, brick-ore is formed. It is characterized by a high content of mineralized chalcedony grains and a low amount of bitumen. This composition gives the ore a typical brick-red appearance. Its boundaries with the host rock are sharp. Another ore typical for the Skonca beds is the coral-ore, which is



Coral-ore with fossilized brachiopods and cinnabar impregnation. 9 x 8 cm. Find and collection G. Velikonja – Photo: A. Rečnik



Mineralized dolomitic conglomerate. Collection of the Mercury Mine Museum, Idria – Photo: J. Peternelj



Karoli-ore. Size 9 cm. Mercury Mine Museum, Idria – Photo: J. Peternelj



Langobardian dolomitic conglomerate is composed of poorly sorted white and grey dolomite clasts mineralized with cinnabar, pyrite and bituminous matter filling fissures and pores of the tectonically shattered rock. The specimen of brecciated cinnabar ore originates from the Skonca beds. Size 15 x 10 cm. Geological collection of the Municipal Museum in Idria – Photo: A. Zelenc

characterized by the presence of brachiopods from the Discina family. This ore was first described by SCOPO-LI (1761). Although no corals are present, the name remained until today. It occurs in bituminous sandstone of the upper Skonca layers. The coral-ore contains up to 40 % of Hg, which is present in the form of cinnabar impregnations in the sandstone cement. Cinnabar is often accompanied by marcasite and pyrite, which can reach up to 40 % of the binder. In the second half of the nineteenth century, the *coral-ore* became economically interesting because of the phosphates and fluorine in the shells of brachiopods (JAHN 1870). They could be the source of fluorine for the formation of fluorite, occurring in the Skonca beds (SCHROEKINGER 1877). It forms to 0.5 mm thick purple fillings of fissures lined by dolomite, calcite and cinnabar crystals (VOSS 1895). Fluorite from Idria was further mentioned by BERCE (1958), MLAKAR

and DROVENIK (1971) and later by VIDRIH et al. (1995) and HERLEC et al. (2006). A true specialty of Idria is the socalled karoli-ore, named after the Karoli ore body. It was found in a block of Anisian and Langobardian conglomerate, trapped in Upper Carboniferous claystone. The ore is dominated by pyrite, representing 50-90 % of the composition (MLAKAR and DROVENIK 1971). It comprises fragments of pyrite concretions cemented by cinnabar. Karoli-ore formed by the accumulation of pyrite concretions eroded from the Carboniferous claystones in the slopes of the rapidly opening Idria tectonic trench. The pores were later cemented with cinnabar from the inflowing mercury-rich brines. The mercury-poor ore is called *bašperh*. It contains less than 1 % of Hg and can be of different origins. Cordevole is the youngest mineralized stratum in Idria. Hg anomalies were measured at several localities near Idria (PLACER and ČAR 1977).



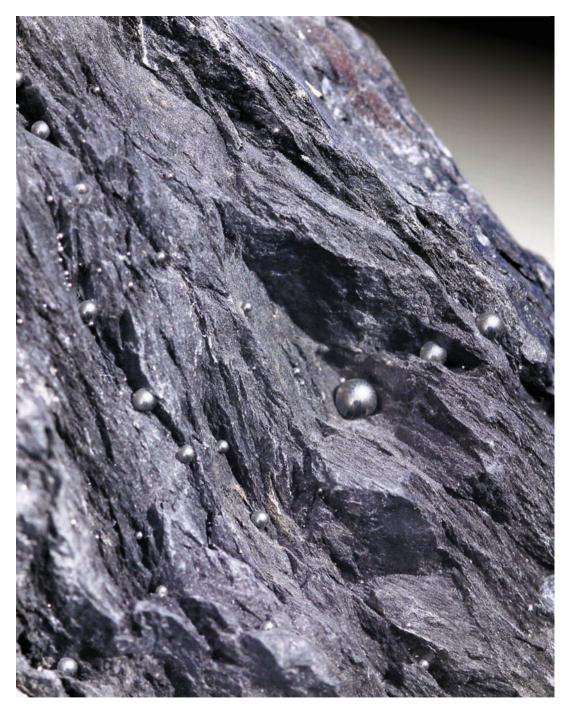
Alchemistic symbol of the link between earth and heaven (Mercury) made of iron floating on native mercury. Mercury is the only metal that is liquid under normal conditions. Despite the fact that mercury is a liquid, its density is higher than most of the metals, including lead. One liter of this magic liquid metal weighs an impressive 13.6 kg. It was known already in antiquity. Its name comes from the Greek word Hydrargyros, which means liquid silver. At -39 °C it crystallizes in a trigonal form – Photo: J. Peternelj



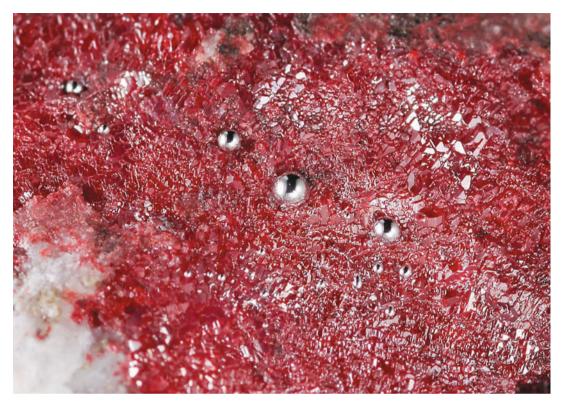
Cinnabar is the main ore mineral in Idria. It occurs as a massive ore or in the form of face-rich crystals with adamantine to submetallic luster. At elevated temperatures mercuric sulfide forms two polymorphic modifications, cubic metacinnabar and hexagonal hypercinnabar. Metacinnabar is well known in Idria, whereas hypercinnabar has not yet been determined in this ore deposit. Photograph shows ruby-red crystals of cinnabar on dolomite. Detail 12 mm. Collection of the Faculty of Natural Sciences in Ljubljana – Photo: A. Rečnik

## MINERALS OF THE IDRIA ORE DEPOSIT

Idria is considered a monomineralic ore deposit, since most of the ore bodies contained only cinnabar, whereas native mercury occurs only sporadically. Trace elements are found in low quantities. In addition to cinnabar, other primary minerals, such as marcasite, pyrite, sphalerite, dolomite, quartz, metacinnabar, calcite, fluorite, baryte, celestine, kaolinite and paligorskite are found, whereas among the secondary minerals vitriols like epsomite, melanterite, halotrichite, siderotil, szomolnokite, and also gypsum, limonite and vivianite are present. Specific to Idria deposit are two organic minerals pyrobitumen and idrialine. The interest in mineralogy had its peak in the nineteenth century. In Idria, siderotil (SCHRAUF 1891) and idrialine (JANDA 1892) were determined as new minerals, while mineral paragenesis was studied by several renowned mineralogists (VILLEFOSSE 1819; ZEPHAROWICH 1893; VOSS 1895). This was followed by a sharp decline in mineralogical studies in the twentieth century and only in the very recent period we see a new outburst of popular scientific articles and monographs (BANCROFT et al. 1991; VIRDIH et al. 1995; VIDRIH and MIKUŽ 1995; HERLEC et al. 2006; REČNIK et al. 2010 and 2011).



Native mercury in Carboniferous slate from the mining field Karbon on the III<sup>rd</sup> level. In Idria, mercury was originally discovered in the same type of host rocks, which are constituting the overlying beds of the ore deposit. In the slate mercury is dispersed in the form of micro-scopic droplets that condensate into larger drops on the exposed outcrops. Because of their specific weight they quickly slip and disappear in the ground. Overall specimen size 15 cm, detail 6 cm. Collection of the Municipal Museum in Idria – Photo: A. Rečnik



Fissure in oolitic limestone richly mineralized with cinnabar, calcite and native mercury. The fissure was originally filled with crystalline calcite. After intrusion of hydrothermal solutions calcite was metasomatically replaced by cinnabar to some extent. This was followed by a further extension of the fissure with the empty space being filled by dilute, oxygen-rich solutions. On freshly opened surfaces cinnabar recrystallized by forming many small facets in identical orientation to the primary cinnabar grain, while some cinnabar was reduced to native mercury. The droplets of mercury on a 6 cm specimen measure up to 1 mm. Collection V. Pavčič – Photo: A. Rečnik

## NATIVE MERCURY

The origin of mercury lies deep below the Earth's crust. It is released during degassing processes in the Upper Mantle. Following deep faults, its vapors rise towards the Earth's surface where they concentrate in less permeable strata (i.e. claystones) in the form of elemental mercury. Besides radon, mercury is an important marker of tectonic activity. It has been shown that just before earthquakes, increased concentrations of mercury are measured in thermal springs (POPIT 2004). In reducing environment it rapidly reacts with free sulfide ions to form cinnabar, whereas under strongly oxidizing conditions, again mercury is released. It is believed that part of the native mercury in Idria formed by retrograde oxidation of cinnabar (DROVENIK and PLENIČAR 1980), as observed in open fissures of Scythian oolitic limestone. Significant quantities of native mercury in Idria occur in Carboniferous clastites, in mineralized Scythian oolitic limestones and related siltstones, in the Skonca beds and in the lowest part of the Langobardian pyroclastites. In clastic slaty Carboniferous rocks it occurs in form of droplets, pouring from the cracks and interlayers. Within the slaty matrix microscopic droplets of native mercury are finely dispersed, while on the outcrops they condensate to form larger drops, which quickly disappear in the rubble. In this way, large amounts of mercury were lost during excavation and ore transport. Because of the presence of silvery droplets, the rock was called a silvery slate by the miners. Native mercury can still be seen in its natural environment in an outcrop of Carboniferous siltstone in Anthony's shaft.

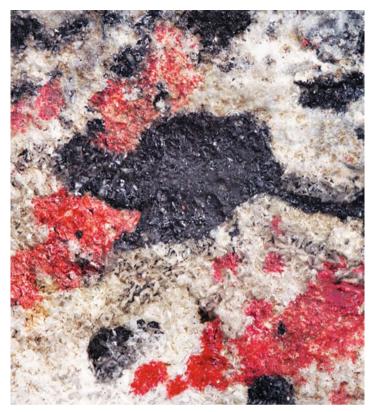


A specimen of Anisian dolomite with black and red spots of bitumen and colloform cinnabar from the famous Hacquet's collection of ores and minerals. The specimens size is 10 x 6 cm. Geological Museum of the Jagiellonian University in Krakow – Photo: A. Rečnik

#### HYDROCARBONS AND IDRIALINE

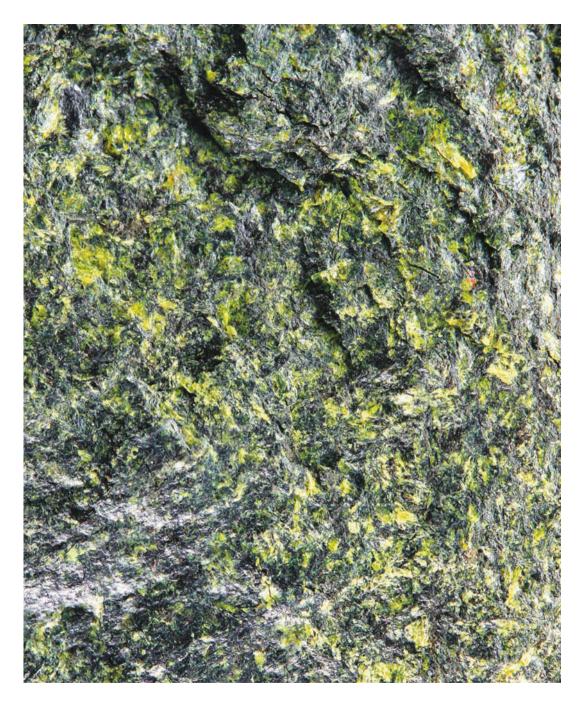
In addition to native mercury, the ore brines also carried small amounts of zinc, copper, manganese, barium, strontium and fluorine, but no sulfur (BERCE 1958). The question is, therefore, where did the sulfur come from in sufficient amounts to form such large quantities of cinnabar? Let us first consider what are the possible sources of sulfur, which occur abundantly in the ore deposit. One of the most widespread carriers of sulfur are definitely hydrocarbons, which are a constituent part of the rocks in a vast Triassic strata and played an important role in the mineralization processes. Just recently, scientists started to pay the necessary attention to the role of hydrocarbons (SPANNENBERG et al. 1999; LAVRIČ et al. 2003). They formed during diagenesis of sedimentary rocks through the pyrolisis of the organic matter, present in these rocks, at the temperature of the oil window (REČNIK 2007). Simple hydrocarbons from the host rock, migrate towards open fractures, where they are mixed with hot hydrothermal solutions. At higher temperatures, they are transformed into higher hydrocarbons, such as pyrobitumen and idrialine. During mixing of non-polar hydrocarbons and polar ore brines colloidal solutions are formed. On cooling, they form a mixture of colloform HgS with pyrobitumen (DROVE-NIK et al. 1990), or bituminous-cinnabaric gel (MLA-KAR and DROVENIK 1971). Vugs filled with glassy anthracite-black pyrobitumen clumps can still be seen on the IIIrd level of Delo shaft. Pyrobitumen has a typical conchoidal fracture and a deep-red shine at higher contents of colloform cinnabar. On slow cooling of colloidal solutions, the differentiation of hydrocarbons occurred, and fractionated crystallization of idrialine took place. Pyrobitumen as well as idrialine may contain significant amounts of oxygen and sulfur, and (right) A detail of the specimen shown on the opposite side. Spots of bitumen (black) and cinnabar (red) on the surface of recrystallized Anisian dolostone suggest that they were simultaneously precipitated from the solutions, while their spatial separation implies their immiscibility on excretion. This interesting specimen belonged to Balthasar Hacquet, a distinguished eighteenth century scientist, who noted this unusual play of minerals and found it so fascinating that he decided to keep it in his collection. Jagiellonian University in Krakow – Photo: A. Rečnik

. contra argilla phile N.13. Linnoter



Pyrobitumen is formed through the hightemperature pyrolisis of hydrocarbons present in sedimentary rocks. This process was triggered by the penetration of hot hydrotherms through tectonically shattered host rocks. It has a variable composition and does not crystallize for which it is not considered a mineral. Commonly it contains variable amounts of sulfur, oxygen and colloform cinnabar. Photograph shows a small cavity in Scythian dolomite with a group of cinnabar crystals and a mass of black pyrobitumen. On the bottom of the cavity there is an isolated drop of deep red colored pyrobitumen included with cinnabar. Detail 9 mm. X<sup>th</sup> level. Find and collection J. Klemenčič – Photo: A. Rečnik



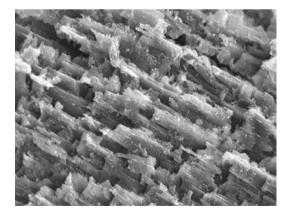


In the late 1970s the miners encountered a small syngenetic orebody with steel-ore in the black siltstone strata of Langobardian beds on the XII<sup>th</sup> level northwest from the Delo shaft. Next to the steel-ore layer there was a thick zone of hydrothermally altered siltstone impregnated with pistachio-green idrialite. Under the microscope we observed corroded crystals of pyrite, cinnabar and iron sulfate szomolnokite. The photographed area is 16 x 20 mm wide. In addition to the prevailing greenish idrialite we can see a few red dots of cinnabar. XII<sup>th</sup>

level, Delo shaft. Find J. Duhovnik. Mineralogical collection of the Faculty of Natural Sciences in Ljubljana – Photo: A. Rečnik



Greenish yellow aggregate of idrialite with lenticular droplets of pyrobitumen and cinnabar on calcite and long prismatic quartz crystals. Similar paragenesis of idrialite is described by Voss (1895). Detail 9 mm.  $XI^{th}$  level. Find and collection G. Velikonja – Photo: A. Rečnik



Idrialine crystals extracted from a larger aggregate of idrialite by chloroform. After dissolving amorphous hydrocarbons crystalline idrialine remains as an insoluble residue. White lamellae in idrialine belong to unknown (Mg,Ca)-sulfate. Width 150  $\mu$ m. VI<sup>th</sup> level, Delo shaft. Find G. Velikonja – SEM Photo: A. Rečnik

sometimes also finely dispersed particles of cinnabar and sulfates. Idrialine has a greenish-yellow to yellowish-brown color and adamantine luster. It occurs in the form of impregnations in porous clastic rocks and in nodular aggregates in the vugs of dolostones. In the early nineteenth century literature, the name idrialite (ZEPHAROWICH 1859) was used to describe a mixture of higher hydrocarbons and JANDA (1892) was the first who isolated orthorhombic crystals of idrialine with the composition C<sub>22</sub>H<sub>14</sub>. Soon VOSS (1895) wrote a detailed description of the yellow-green tabular crystals of pure idrialine occurring in vugs of black dolostone together with dolomite, quartz, calcite, cinnabar and gypsum crystals. In their host rock he observed pyrite crystals. More often idrialine crystals are embedded in clumps of yellow-green idrialite, a mixture of higher non-crystalline hydrocarbons. Using a non-polar solvent, such as chloroform, crystals of idrialine can be readily isolated. It is fairly common in the upper dolomite level and also in the Skonca beds (MLAKAR and DROVENIK 1971).



Pyrite nodule from black Carboniferous slate on IV<sup>th</sup> level, Delo shaft. The nodule is composed of fine crystalline pyrite partly overgrown by up to 2 cm large pyrite crystals. The specimen shows no traces of cinnabar. On the surface there are remnants of glassy quartz crust, which is usually formed at the contact of the nodules with the host rock. Photograph shows front and back side of the same specimen. Specimen size is 6 cm. Find and collection G. Velikonja – Photo: A. Rečnik

# Pyrite and Other Sulfide Minerals

The vast majority of pyrite in Idria ore deposit is of syngenetic origin. It is found in Carboniferous claystones and Langobardian Skonca layers. While most of the pyrite is finely dispersed in these rocks, it can also form up to 25 cm large marcarsite-pyrite concretions covered by well-developed pyrite crystals. Concretions formed in the early diagenesis of the clastic rocks. During their consolidation, sediments contained many plant residues, which used all the available oxygen for their decomposition. In an oxygen-deficient environment, sulfate-reducing bacteria reduce the sulfates present in pore-waters into sulfide ions, which further react with the available ferrous ions to form marcasite and pyrite. Following this mechanism, large amounts of sulfide ions were released into the sedimentation basin during the formation of the Skonca beds where they formed fine-grained cinnabar and pyrite. The high initial acidity promoted precipitation of marcasite, followed by crystallization of pyrite, while due to the depleted concentration of the sulfide ions the acidity gradually decreases (MIKLAVIČet al. 2007). In this process, nodules were formed. Occasionally, macroscopic crystals of pyrite are developed on the surface of the concretions, indicating that the surrounding sediment was not consolidated during their formation. Cementation of syngenetic concretions is often accompanied by the formation of cracks in their interior, where pyrite crystals can grow without restraint. In Idria, hollow concretions with cinnabar crystals and native mercury in their inside were documented (MLAKAR 1959). During the subsequent tectonic activity, the ductile claystones and siltstones were foliated, whereas solid marcasite-pyrite



Pyrite crystallized in Carboniferous and younger Ladinian slates under the conditions of rapid precipitation in a reductive sedimentary environment. Nodules and continuous layers of pyrite were subsequently buried by clastic material. In the process of diagenesis the sediments with the entrapped pyrite layers were lithified. During folding softer claystones were foliated, whereas the embedded hard layers of pyrite cracked perpendicular to the foliation of the host rock. On the inflow of Hg-bearing solutions the voids offered an empty space for condensation of mercury, which partly reacted with free sulfide ions to form cinnabar. On exposure to air melanterite formed as a result of decomposition of iron sulfides. Specimen 8 x 6 cm. Geological collection of the Municipal Museum of Idria – Photo: A. Zelenc

concretions and pyrite beds were fractured and filled with mercury. Some sulfur, released by marcasite decomposition, reacted with mercury to form cinnabar. In addition to cinnabar, other minerals such as quartz, calcite and black organic matter resembling idrialine were found in nodules (MLAKAR and DROVENIK 1971). Beautiful pyrite concretions are found in the Carboniferous beds on the IV<sup>th</sup> level, and in the Skonca beds.

(right) Marcasite-pyrite nodule richly mineralized with cinnabar from Skonca beds. The spiral contour of the nodule suggests that this could have been a fragment of pyritized ammonite. Large pyrite crystals that developed on the surface of the nodule measure up to 7 mm. Municipal Museum of Idria – Photo: A. Rečnik





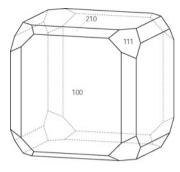
Cubo-octahedral crystals of pyrite modified by pentagondodecahedral faces from tectonically shattered and hydrothermally altered Carboniferous siltstone.  $IV^{th}$  level, Delo shaft. Crystal sizes up to 2 mm. Find and collection G. Velikonja – Photo: A. Rečnik

Form-rich pyrite crystals are found in the tectonically shattered zone of Carboniferous siltstone at the IV<sup>th</sup> level. These beds do not contain any mercury ore. In general, the paragenesis of pyrite with cinnabaris rare (BERCE 1958). Younger hydrothermal pyrite is found in the form

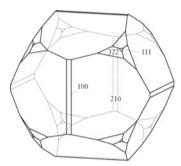


of framboidal aggregates in Scythian dolostones with dolomite, kaolinite, quartz, cinnabar and gypsum. The occurrence of framboidal pyrite indicates the presence of hydrocarbons and precipitation from colloidal solutions. In tectonically shattered zone between the Lower Scythian dolomite and Gröden sandstone, along the Grübler fault, PLACER (1974/75) described a 3–5 cm wide fissure, completely filled with pyrite. Individual pyrite crystals here rarely exceed 2 mm. They display various combinations of pentagon dodecahedron, cube, triakisoctahedron and other accessory forms. The most beautiful examples from this paragenesis are known from mineralized fissures in Lower Scythian dolomite in the Grübler ore body (DROVENIK et al. 1991).

Cluster of framboidal pyrite on dolomite. This form of pyrite is typical for crystallization from colloidal solutions in the presence of hydrocarbons. Ore body Grübler, XIII<sup>th</sup> level. The width of the photograph is 50  $\mu$ m – SEM Photo: A. Rečnik



The morphology of pyrite crystals from the Carboniferous siltstone (above) and Scythian dolomites in Grübler Fault (below)

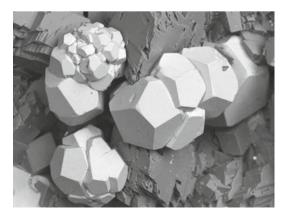




Tiny crystals of pyrite with dolomite, cinnabar and kaolinite from the Grübler Fault zone. Their ground shape is pentagonal dodecahedron. Size of crystals 50–120 μm. Collection of the Faculty of Natural Sciences in Ljubljana – Photo: A. Rečnik

Other sulfide minerals occur sporadically. In the vugs of Lower Scythian dolomites we rarely find sphalerite. During our field explorations in 2004 we found a 3 mm large yellowish-brown crystal of sphalerite on the IX<sup>th</sup> level. The crystal was overgrown by calcite and cinnabar. Sphalerite also precipitated in the form of fine grains together with cinnabar and pyrite in the Skonca beds. Rather interesting is the increased concentration of zinc in metacinnabar, which is according to SCHRA-UF (1891) related to the isomorphism between the two minerals. HERLEC et al. (2006) reported on 1 mm large crystals of galena from the Grübler Fault zone. Many authors rather awkwardly refer to the presence of auripigment (COLBERTADO and SLAVIK 1961; and subsequent citations). According to the original work, the presence of auripigment was determined only optically. The

Pentagondodecahedral crystals of pyrite with accessory forms from Grübler Fault zone. Sizes to 200 μm – SEM Photo: Α. Rečnik analyzed samples were from the Skonca beds at the X<sup>th</sup> level, where otherwise idrialine occurs. As auripigment was never confirmed by any other method and since no arsenic minerals occur in the Idria ore deposit, we can say with confidence that it is not present in Idria.





In massive ore, the crystals of cinnabar are rare. They formed in open fissures that crossed the massive ore, where the secondary crystallization of cinnabar took place. The image width is 2 cm. Mercury Mine Museum, Idria – Photo: A. Rečnik

#### **O**N THE IDRIA CINNABAR

In the Idria ore deposit, cinnabar crystals are found in all mineralized lithological units. The largest quantities of cinnabar were formed in the Upper Ladinian, when mercury-rich hydrothermal brines were injected into the marine swamps, where ample quantities of sulfide ions were produced by decomposition of organic matter and a reduction of sulfates. Despite the large quantities of cinnabar in the syngenetic ores the cinnabar crystals here are small and rare. They are found in pores and fissures of the cinnabar-rich ore, where open surfaces are only slightly recrystallized, and except cinnabar, generally no other minerals are present. The voids in the massive cinnabar ore were filled with heated meteoric waters, which dissolved cinnabar from the surroundings. On cooling, the cinnabar recrystallized in the exact orientation of the fractured grains. The surfaces of the voids appear as covered with platelets of flat cinnabar crystals. These specimens are characteristic for the earlier mining periods and were common in the eighteenth and nineteenth centuries. During deepening of the shafts the miners came across epigenetic ore bodies in Triassic carbonates, and specimens of well-crystallized cinnabar with the associated minerals started to appear in the mineralogical collections. Most of the cinnabar crystals have a beautiful ruby red color with an adamantine luster, only occasionally opaque, almost black crystals with a metallic luster are found. Frequently, cinnabar crystals in old collections become darker due to surface oxidation after long-term exposure to daylight. Similar phenomenon is sometimes observed in their natural environment, where bands of dark red crystals can be noticed in the vicinity of light red cinnabar crystals. Idrian cinnabars have a very complex crystal morphology. They are very rich in forms, no matter in which type of rock they have developed. One of the possible reasons is the recurring crystallization of cinnabar. Recrystallization, as already observed in syngenetic ores, is even more pronounced in open fissures in the Lower



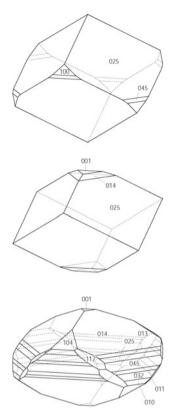
K. k. Naturhistorisches Hof-Museum. Mineralogisch-petrographische Abtheilung. Acq.-Post 9. 4834. II. 1896. Name Cinnabarit ... preachtvolle a his o. 5 mg. Kystalle Den hopefen auf schwargen Schiefer. 8 Fundort Decia, Hearing

Dark-red cinnabar crystals densely covering the surface of black Langobardian siltstone from the Skonca beds. The crystals developed in tectonically induced fissures lined perpendicular to foliation of the host rock. In the pockets between the crystals there are patches of native mercury. This 80 x 60 mm specimen closely resembles the one from the Desfontaines's illustration (see p. 14). It was bought for 2 florins from Mrs. Heger from Vienna in 1896. Collection of Natural History Museum, Vienna – Photo: A. Rečnik





Simple rhombohedral crystal of cinnabar with quartz crystals in a calcite-lined cavity. Primary rhombohedral form is modified by flat rhombohedra and a rugged pinacoidal face. Size 4 mm. X1<sup>th</sup> level, Delo shaft. Find and collection J. Klemenčič – Photo: A. Rečnik



The morphology of cinnabar crystals from Idria. Drawings are representations of actual crystals shown on the photographs

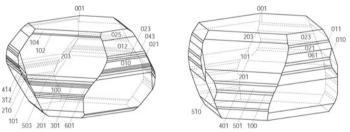


A cluster of simple rhombohedral crystals of cinnabar, partly overgrown by dolomite crystals from  $1X^{th}$  level. Simple crystals like this are not common. They belong to an older generation of cinnabar that grew relatively rapidly from saturated solutions. The size of the detail is 100  $\mu$ m – SEM Photo: A. Rečnik



Form-rich cinnabar crystal from a small cavity in Lower Scythian dolomite on IX<sup>th</sup> level. The crystal habit is defined by a flat rhombohedron truncated by pinacoid. Further it is modified by a series of rhombohedral faces, a hexagonal prism and a trigonal bipyramid. Crystal size 60 μm – SEM Photo: A. Rečnik

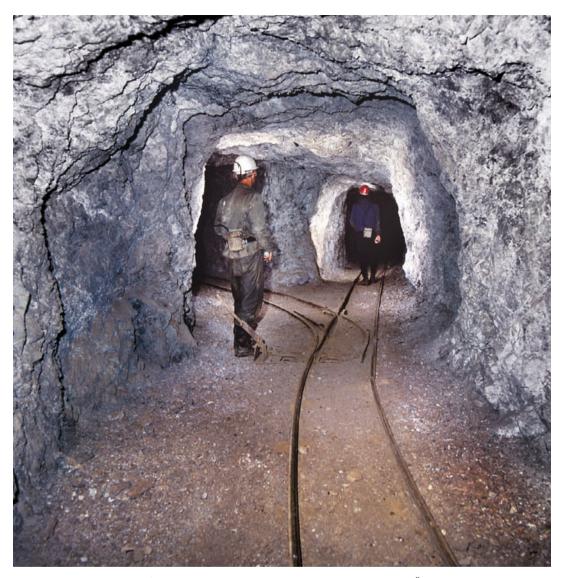




Numerous rhombohedral faces on cinnabar crystals are a true morphological challenge. Often there are so many, that they make the crystals virtually rounded. They can be best understood by finding their three fold axis, or basal pinacoid, as demonstrated on the drawings (left). The cinnabars on this specimen, dated from around 1900, closely resemble the illustrated crystals. Cinnabars on dolomite measure up to 2 mm. Collection J. Zavašnik – Photo: A. Rečnik

Drawings of complex cinnabar crystals, reconstructed after the morphological study of Idrian cinnabar by Magda Tratnik-Drolc (1957)

Scythian beds, where according to the study of Idrian cinnabar and metacinnabar published by Austrian mineralogist SCHRAUF (1891), cinnabar crystallized in several successive generations. Under different geochemical conditions of each mineralization cycle, completely new forms developed on the existing crystals. The simplest are the primary cinnabar crystals formed from saturated solutions, whereas the younger crystals, growing from diluted solutions, regularly display a more composite morphology. During slow growth, higher-index crystallographic forms, corresponding to the pertinent equilibrium conditions, develop on the crystals. The morphology of the Idrian cinnabars remains an open issue. In GOLDSCHMIDT's Atlas of crystal forms (1923), 24 different crystals of cinnabar are illustrated, but unfortunately it is not clear, whether they originate from Idria or Almadén. TRATNIK-DROLC (1957) carried out a morphological study of six cinnabar crystals from Idria and goniometrically determined over 40 different crystallographic forms, many of which were new.



Transportation gallery on the II<sup>nd</sup> level, near blind shaft August. Photo assistants are Jože and Aleš Čar (1988) – Photo: R. Podobnik

The most comprehensive study of open ore-bearing fissures was performed on the Grübler ore body in Lower Scythian dolomite by DROVENIK and coworkers (1991). The tectonically shattered zone in this strata is 25-30 m wide and it stretches along the contact with the Gröden sandstone (PLACER 1974/75). Individual fissures in this zone measured up to 30 m in length, and were up to 4 cm wide. They occurred at a relatively high frequency with lateral separations of 50–100 cm. The largest mineralized vugs and cavities, measuring up to 50 cm and more, were located in the shattered zone with a brecciavein texture that formed at the intersections of the fissures. According to high mining standards, the cinnabar mineralization in the Grübler Fault zone, extending between the X<sup>th</sup> and the XII<sup>th</sup> levels, was regarded as poor ore, or bašperh. Only in here and there they encountered fissures completely filled with massive cinnabar and even then, the width of the ore-bearing veins did not exceed 4 cm. On the other hand, these poorly mineralized fissures containing well-developed crystals of



(above) Specimen from some dolomite-lined fissure, densely crystallized with cinnabar. Size of the specimen 8 cm, detail 20 mm. Collection V. Pavčič – Photo: A. Rečnik

(right) Massive cinnabar covering crystals of calcite and quartz. The matrix is encrusted with a layer of black bituminous matter, which accompanies all mineralized fissures in Lower Scythian dolomites. Occurrences like this were considered poor for the miners and overly rich for mineralogists, as more sparsely, the cinnabar could have formed nice crystals instead of massively filling the fissure. Grübler Fault system, 8<sup>th</sup> stope on the XIII<sup>th</sup> level. Detail 4 cm. Find and collection B. Režun – Photo: A. Rečnik





Partly abraded simple rhombohedral crystal of cinnabar on quartz and calcite from Grübler. In this fault zone there were more abraded crystals than the intact ones. Specimen size is 1 cm. Collection of the Mercury Mine Museum in Idria – Photo: A. Rečnik

cinnabar and associated minerals were highly interesting to mineralogists. The largest cinnabar crystals in the history of the Idria mine, measuring 3 cm and more, were found right in this zone. They occurred in typical paragenesis together with dolomite, quartz, kaolinite, calcite, pyrite, barite, metacinnabar and gypsum. In 1986, a new mining field was opened on the 8<sup>th</sup> stope of the XIII<sup>th</sup> level (+39 m) in Grübler. The preparation drift intersected several mineralized fissures (DROVENIK et al. 1991). A detailed study of the ore-bearing brecciated dolostone revealed that mineralization occurred in several successive phases. During the pyrolysis of

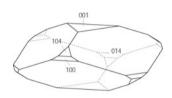


Typical heavily abraded specimen of cinnabar and calcite from the Grübler Fault zone. Specimens like this one were quite disappointing for finders, for us however, they represent an important part of the story. Size 3 cm. Collection B. Režun – Photo: A. Rečnik

the organic matter, sulfur for the formation of cinnabar was released from the neighboring rock. Since the fractures extended all the way to the surface, intrusions of cold groundwater were relatively frequent. Sudden temperature difference induced the formation of a convection cell and cyclic mineralization in the open fissures. The existence of the convection cells, and occasional turbulent flow of solutions through the narrow passages between the fissures is supported by the presence of eroded crystals in mineralized vugs. Vigorous exchange of fluids caused tumbling and abrasion of crystals and loose fragments of rock. Erosion-induced changes are



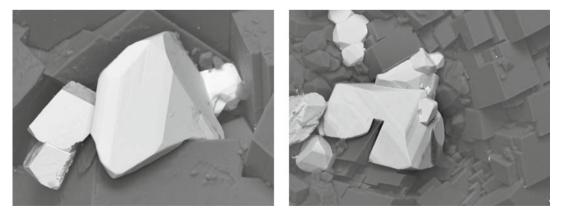
Flat rhombohedral crystals of cinnabar on dolomite from the XIII<sup>th</sup> level. The crystals have a simple morphology, a noble red color and are translucent. The cinnabar at the center of the photograph measures 4 mm across. On the back side of this 9 cm large specimen there is a cavity filled with pitch black pyrobitumen. Find J. Likar. Collection of the Faculty of Natural Sciences in Ljubljana – Photo: A. Rečnik



The morphology of simple flat rhombohedral cinnabar crystals from Grübler

also visible on the floor of the cavities. Some cinnabar crystals are so heavily abraded that their original forms are barely discernable (BANCROFT et al. 1991), and yet on some specimens cinnabar crystals with sharp edges and no visible signs of erosion are present. This indicates that the dynamic event was followed by a steady period in which a younger generation of crystals was grown from diluted solutions. A fine evidence of these

processes is the coexistence of completely abraded and fresh, virtually intact crystals of cinnabar in the same pocket (DROVENIK et al. 1991). Various factors confirm this crystallization regime. The presence of kaolinite in the vugs directly points to the intrusion of the surface waters. Each sudden drop of the temperature caused the supersaturation of the solutions and the rapid precipitation of minerals, whereas under



A closer look at the younger cinnabar crystals from Grübler reveals that they all have a very distinct flat rhombohedral trigonal habit. Their morphology is defined by the forms of negative flat rhombohedron and a wide basal pinacoid. This generation of cinnabar is overgrowing the dolomite crystals. The larger crystals measure about 100 μm across. Grübler, XIII<sup>th</sup> level – SEM Photo: A. Rečnik

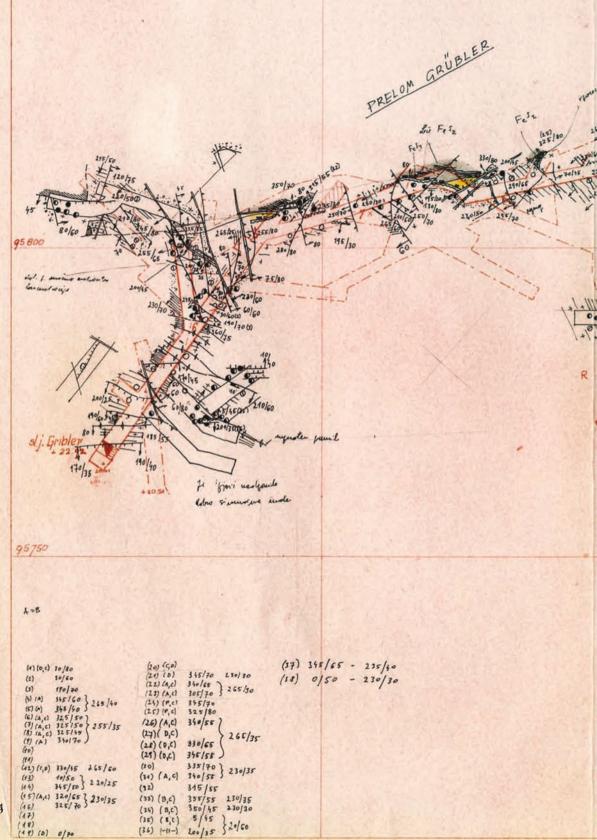


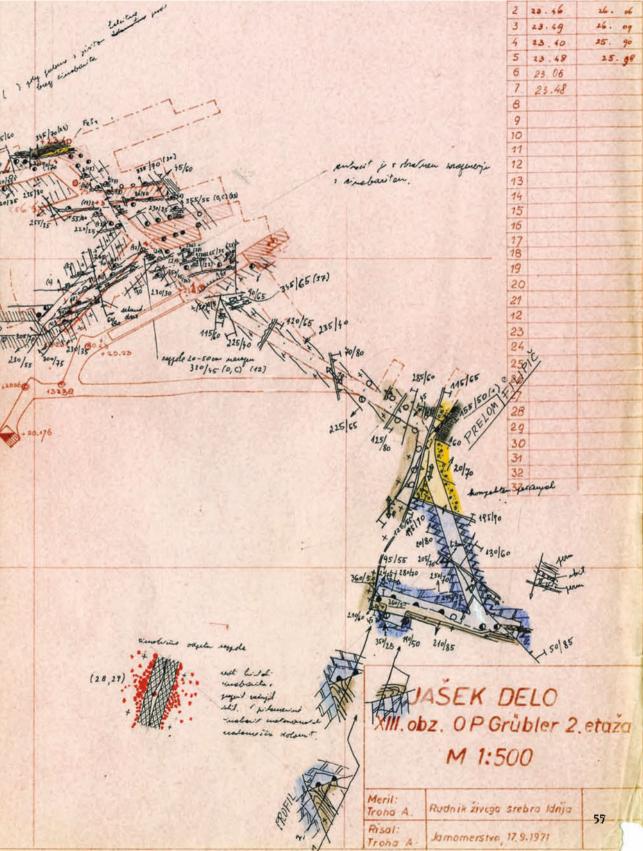
A fragment of Scythian dolomite overgrown by flat rhombohedral crystals of calcite, which were thoroughly abraded during the turbulent fluid exchange. Younger cinnabar crystallized from diluted solutions. This generation of cinnabar shows no mechanical damage. The specimen size is 5 cm. Find M. Drovenik 1987. Collection of the Faculty of Natural Sciences in Ljubljana – Photo: A. Rečnik

steady conditions crystals of a particular geochemically conditioned paragenesis were developed. The crystallined vugs in the Grübler Fault zone were entirely covered by tiny dolomite crystals, here and there decorated with isolated ruby-red crystals of cinnabar. The top of the overhanging walls was typically covered with fine-grained mineral dust, which after each sudden precipitation event settled on the exposed surfaces. The floor of the cavities was covered by crystalline rubble containing fragments of rock, crystals and pyrobitumen. In this crystalline rubble, also large cinnabar crystals were also found. Because of their weight and good cleavage they were first to break off the fissure walls during the tectonically active phases. In most of the cavities, mineralization ended in a quiet period of growth, when form-rich crystals of cinnabar and the accompanying minerals were developed.



Dark-red cinnabar crystals of the younger generation grown on dolomite and calcite. Grübler, XII<sup>th</sup> level. Detail 15 mm. Collection of the Mercury Mine Museum in Idria – Photo: A. Rečnik





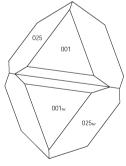


Laterally twinned cinnabar crystal on dolomite from Grübler. Twinned crystals of cinnabar are a specialty of the Grübler Fault zone. The crystal size is 4 mm. Find J. Likar. Collection of the Faculty of Natural Sciences in Ljubljana – Photo: A. Rečnik

## TWINNING OF CINNABAR

A close inspection of cinnabars from the Grübler Fault zone revealed that these are not regular crystals, but twins of a new type, which has not yet been described from Idria. This crystallographic peculiarity would certainly not have escaped the perceptive eye of SCHRAUF (1891), the mineralogist who had so carefully described the microscopic twins of metacinnabar. The fact that very observant scientists of the nineteenth century never mentioned twins of cinnabar strongly indicates that most probably they were not yet found at that time. It appears that the first cinnabar twins occurred much later, with the excavation of the Grübler ore body in the early 1970s. They appear in the form of contact, or asymmetrically developed lateral interpenetration twins. Their habit is rather unusual when compared to the twins from other localities. Interpenetration twins of cinnabar from famous localities such as Nikitovka in Ukraine and Tongren in China, for example, would be described by a 180° rotation of a steep rhombohedral crystal around the crystallographic c-axis, giving these twins a characteristic spindle-like appearance. In Idria this type of interpenetration twins is not observed. Instead, simple contact basal twins occur. In the initial stages of growth the twinned crystals grow exaggeratedly and anisotropically along the twin plane. Anisotropic growth leads to the formation of triangular platelike crystals with large pinacoidal faces. All the large crystals of cinnabar from Idria are in fact twins. Subsequently, when the conditions for twinning are interrupted, the crystals start to thicken and overgrow the inherent twin lamella. Depending on the supply of the material for growth the crystals develop various interpenetration forms. The main



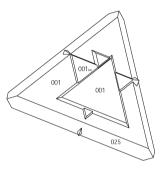


Lateral twin of cinnabar from the 9<sup>th</sup> stope of the XIII<sup>th</sup> level, Grübler. Based on their appearance we could infer that the crystal is twinned on a hexagonal prism, however, such twinning does not exist in cinnabar. Most likely we are dealing with interpenetration basal plane (001) twinning, while the cause for the observed translation is unknown. Crystal size 6 mm. Find and collection B. Režun – Photo: A. Rečnik





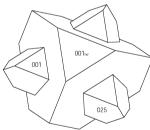
The largest known crystal of cinnabar was found by the miner Feliks Poljanec from Idria in 1971 when he was working on the  $3^{nd}$  stope of the XIII<sup>th</sup> level on Grübler. The crystal was originally broken in fragments parallel to the {100} cleavage planes. After reconstruction the crystal measures  $26 \times 23$  mm. With the bottom part (still missing) it measured more than 3 cm. The crystal with characteristic triangular twin domains is illustrated below. Find and collection F. Poljanec – Photo: A. Rečnik



Interpenetration twin of cinnabar from Grübler. The twin domains are rotated by 180° with respect to each other. Repeated twinning in the {001} planes gives the crystals a characteristic platelike appearance

reason for such twinning probably lies in the faulted stacking of basal planes in the cinnabar structure. The main cause for disrupted stacking in minerals is a local polymorphic phase transition. The presence of metacinnabar in Idria is certainly an interesting geochemical indicator that polymorphic transitions of HgS actually took place. Because metacinnabar is the closest polymorph of cinnabar, we may suspect that faulted stacking that leads to the twinning of cinnabar has in fact a metacinnabar structure. In favor of this hypothesis we find tetrahedral crystals of metacinnabar overgrown by an epitaxial layer of cinnabar in an orientation relationship, as expected in the case of twinning, where basal planes of cinnabar coincide with the tetrahedral planes of metacinnabar. The fact is, that specific geochemical conditions existed along the Grübler Fault, if these twins formed only here and nowhere else in the mine. By all means, Idria ore deposit still hides many challenges in the field of mineralogy. The actual cause of twinning in cinnabar, however, remains an unsolved problem. The largest known cinnabar crystals were found by the miner Feliks Poljanec from Idria, when he was working at the 3rd stope above the XIII<sup>th</sup> level of Grübler. According to his narration, he hit into a shattered part of the dolomite with a mattock and wide cavity opened in front of his eyes. The cavity was filled with a rubble in which he collected 30 cinnabar crystals larger than 10 mm and about a hundred smaller crystals. Many of these crystals were lost, but fortunately he kept the five largest specimens to our admiration until the present day. The largest crystal measures 26 mm and was naturally detached from matrix. This zone with cinnabar crystals (mostly twinned) was opened already at the 2<sup>nd</sup> stope and extended up to the 9<sup>th</sup> stope. We can only imagine how many pockets with cinnabar were found in the whole mineralized zone along the Grübler Fault. Some of the crystals were probably lost forever, whereas many of them were bought by (mostly Italian) mineral dealers, because Idria cinnabars were always highly esteemed among the collectors.



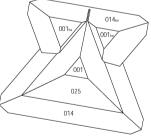


After twinning the two domains start to grow independently and develop characteristic reentrant angles. The above specimen, illustrated on the cover page, is composed of two twins in different stages of growth. The larger base crystal displays an initial stage of twinning, whereas the smaller twin shows a mature stage of growth. From the bottom side this floater specimen reveals a noble ruby-red color in transmitted light (right). Specimen size is 23 x 18 mm. Find and collection F. Poljanec – Photo: A. Rečnik









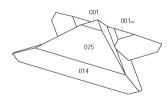
(above) 24 x 18 mm interpenetration twin of cinnabar. The asymmetric development is a consequence of repeated twinning in {001} planes. The exchanged positions of steep and flat rhombohedra is unusual. It was caused by the initial rapid growth of the twin plane, while steeper {025} rhombohedra distinctly developed in the later growth stages

(left) translucent 21  $\times$  16 mm large interpenetration twin of deep-red cinnabar



(above) Twinned cinnabar crystal from the opposite page viewed from its bottom side. All the crystals from this pocket are floaters. As a result of tectonic stresses larger crystals broke off and continued growing on the floor. At the original contact with the matrix we

see inclusions of dolomite and bitumen



(right) 25 x 23 mm twin of cinnabar. The growth of the crystals was initially dictated by the inherent twin plane and in the later stages a regular crystal morphology was developed through many vicinal faces.

Collection F. Poljanec – Photo: A. Rečnik



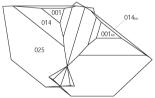




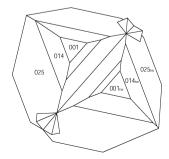
(above) 21 x 16 mm twin of cinnabar. In transmitted light the crystals flare up in an intense ruby-red color, whereas under reflected light they have an opaque submetallic luster. According to the miner, there were several dozen of such crystals in this 30 cm large pocket. Because they grew in the same geochemical environment, we can assume that they were all twinned. Lateral twins of cinnabar are not known from any other locality and are the true specialty of Idria. The cause of such twinning is probably repeated basal-plane twinning, which can be explained by a local polymorphic phase transformation into metacinnabar during the twin nucleation stage. Twins of cinnabar are found along the whole Grübler Fault system, even in poorly mineralized fissures on the IX<sup>th</sup> level. Find and collection F. Poljanec – Photo: A. Rečnik

(left) Basal twin of cinnabar perched on dolomite matrix. 9<sup>1/n</sup> stope, XIII<sup>1/n</sup> level of Grübler. Find and collection B. Režun, 1988

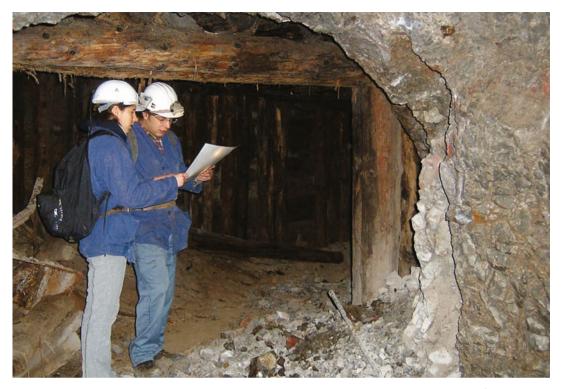




Lateral twin from the 3<sup>nd</sup> stope on XIII<sup>th</sup> level of Grübler. Size 21 x 15 mm. Find and collection F. Poljanec – Photo: A. Rečnik



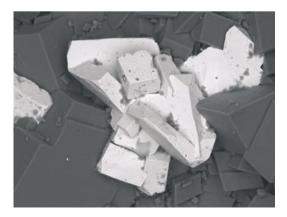


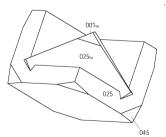


Geologists Janez Zavašnik and Saša Zavadlav on inspection of the outcrop of mineralized Scythian dolomite on the IX<sup>th</sup> level, where in 2004 we discovered several small cavities lined with crystals of dolomite, cinnabar, kaolinite and gypsum – Photo: A. Rečnik

## MINERALOGICAL EXPEDITION

To study mineralized vugs before flooding we made, during 2004–2006, a few experimental excavations in the poorly mineralized tectonically shattered zone in the Lower Scythian dolomite, that is crossed by transportation galleries at the IX<sup>th</sup> and XI<sup>th</sup> level. The vugs were covered by tiny crystals of dolomite, and only here and there was it accompanied by other minerals such as sphalerite, quartz, kaolinite, cinnabar, calcite and gypsum. Most of the finds were used for studying the paragenesis, but some were also quite attractive.





... continues on p. 74 ...

Very unusual (001) twin of cinnabar from  $IX^{th}$  level. After twinning the bottom crystal started to overgrow the upper half. This type of concave twins is known in rhombohedral carbonates, but not yet in cinnabar. Size 80  $\mu$ m – SEM Photo: A. Rečnik



One of the best specimens that could still be found in 2004 in fissures of tectonically shattered Scythian dolomite on XI<sup>th</sup> level, Delo shaft. The specimen with lustrous dolomite and cinnabar crystals is 45 mm high. Find and collection A. Rečnik – Photo: A. Rečnik





In 2004 the Idria mine was already undergoing shutdown works and therefore we organized a few mineral-collecting trips to rescue some of the last specimens of cinnabar. For our work we used pneumatic hammers that could be plugged to a compressed-air installation. Collected specimens were helpful in our study of the mineral paragenesis. The photograph shows a miner and enthusiastic collector of minerals Janez Klemenčič from Kanomlja and geologist Bojan Režun excavating a small outcrop of poorly mineralized Scythian dolomite on IX. level, Delo shaft – Photo: A. Rečnik

In poorly ventilated passages the rotting of wooden pillars additionally contributed to the lack of air; therefore, we had to be careful when exploring the abandoned tunnels. Accompanied by the experienced miners we could get a brief glimpse of the famous Idria mine – Photo: A. Rečnik



(above) Transparent crystals of dolomite with tiny clusters of cinnabar and kaolinite on the left-hand side of the specimen. We found few specimens of this kind in the ceiling of the main transportation gallery on the X1<sup>Ih</sup> level. These fissures are the upper extension of the Grübler Fault system. Their mineralization was just sufficiently rich that we could find a few isolated clusters of cinnabar on dolomite-lined fissure walls. The size of the detail is 10 mm. Find and collection A. Rečnik – Photo: A. Rečnik

(right) Translucent dolomite crystals overgrowing cinnabar from the X1<sup>th</sup> level. The matrix is covered by light-brown kaolinite crystals. This indicates that kaolinite is older than the cinnabar and dolomite. The specimen size is 15 x 20 mm. Find and collection A. Rečnik – Photo: A. Rečnik



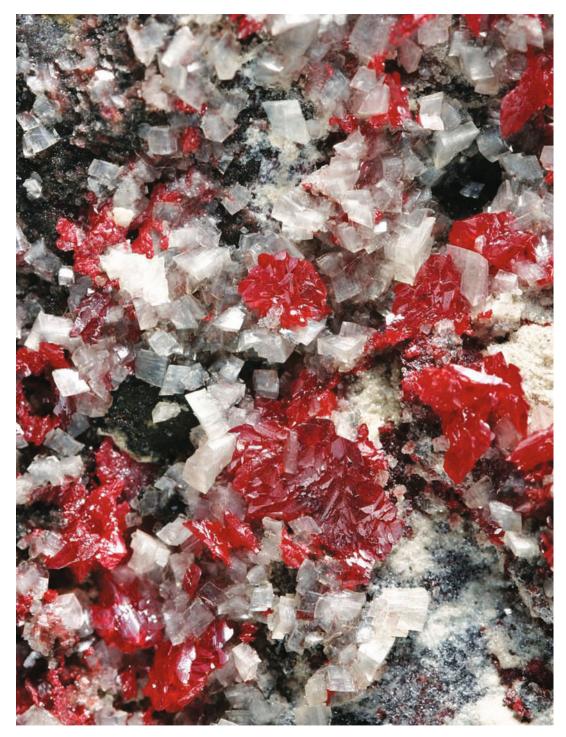




(above and on the next page) Ruby-red crystals of cinnabar on sparkling matrix of tiny transparent dolomite crystals from the mining field Bilek on the XIII<sup>th</sup> level. The morphology of these crystals is so complex that it seems virtually impossible to reconstruct. Countless stepped facets that modify the otherwise simple flat rhombohedral crystals are a consequence of repeated dissolution and recrystallization processes that took place after the crystals were already formed. The central crystal on the photograph measures not more than 8 mm, and yet it radiates in enchanting red color typical for Idrian cinnabar. Collection J. Klemenčič – Photo: A. Rečnik

J. Klemencic – I noto. A. Keenik

(left) Rhombohedral crystal of cinnabar with a stripe of smaller crystals in the cavity of dolomite crystals. Detail 10 mm. IX<sup>th</sup> level. Find A. Rečnik – Photo: A. Rečnik



White dolomite crystals intergrown with up to 2 mm large rosettes of cinnabar composed of several crystals slightly rotated with respect to each other. The reason for such growth is not known. The specimen dates back to 1900. Collection J. Zavašnik – Photo: A. Rečnik







Globular aggregates of metacinnabar on calcite. Specimen size 4 x 5 cm. Natural History Museum in Vienna – Photo: A. Rečnik

#### METACINNABAR AND CALCITE

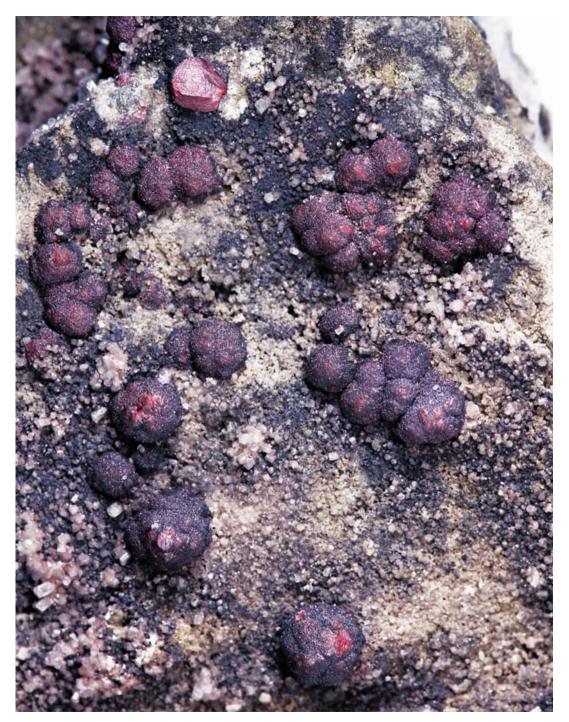
Metacinnabar is the cubic modification of mercuric sulfide and forms at higher temperatures than cinnabar. It is one of the specialties of the Idria ore deposit. Metacinnabar was already noticed by HACQUET (1781), but at that time it was not yet recognized as an independent mineral. Later, SCHRAUF (1891) described intergrowths of metacinnabar and cinnabar and frequent twinning of metacinnabar, which was aggravating during the determination of their morphology. He determined a relatively high content of zinc in metacinnabar. It is known that the increased amounts of iron and zinc in HgS significantly decrease the phase-transition temperature (DICKSON and TUNELL 1959). Metacinnabar crystals form up to 5 mm large, black, semispherical aggregates of metallic luster. The most beautiful specimens were found at the IX<sup>th</sup> and X<sup>th</sup> levels in mining field Barbara and at the VII<sup>th</sup> level of the blind shaft Lamberg (BERCE 1958). Its crystals from oolitic limestone in the Ruda ore body at the XII<sup>th</sup> level were described in detail by MLAKAR and DROVENIK (1971). Fine-grained cinnabar crystallizes as the first mineral on the fissure walls. Subsequently, cinnabar was covered by translucent to grayish prismatic crystals of calcite. Metacinnabar crystallized on the top of the calcite crystals, and in the final stage it was retrogradely Metacinnabar globules on crystalline calcite from the 3<sup>rd</sup> stope of the X<sup>th</sup> level, Delo shaft (formerly Joseph). The specimen goes back to the end of nineteenth century, when Austrian mineralogist Albrecht Schrauf studied Idrian metacinnabars. Specimen 90 x 65 mm, detail 30 mm. Natural History Museum in Vienna – Photo: A. Rečnik

K. k. Naturhistorisches Hof-Museum. Mineralogisch-petrographische Abtheilung Acq. Post J. 5520. 1890 . X41 Name Metacimabarit zablerich 1 Jelewary Hanfelen ster du uner Caleit Hrmete lemitischen Kall d. gitensteine . ang.2. Inschand

(below) Arrays of metacinnabar globules with calcite crystals. Fresh metacinnabar is pitch black and that altered to cinnabar is rusty red. Detail 40 mm. Natural History Museum in Vienna – Photo: A. Rečnik







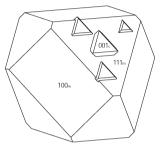
Clusters of globular aggregates of metacinnabar with transitions to cinnabar, perched on fine crystalline calcite. Their matrix is pyritized crystalline Langobardian marly siltstone from Skonca beds. Individual globules measure 3 mm across. Shown is a detail from a 55 x 50 mm specimen. Find J. Gostiša. Mineralogical collection of the Faculty of Natural Sciences in Ljubljana – Photo: A. Rečnik



Back side of the specimen shown on the previous page, densely covered by numerous clear crystals of calcite and tiny metacinnabar globules. The thickness of the siltstone slab crystallized from both sides is about 1 cm, which testifies to the original density of the mineralized fissures. The detail shown on the photograph is 24 x 32 mm wide. Faculty of Natural Sciences in Ljubljana – Photo: A. Rečnik

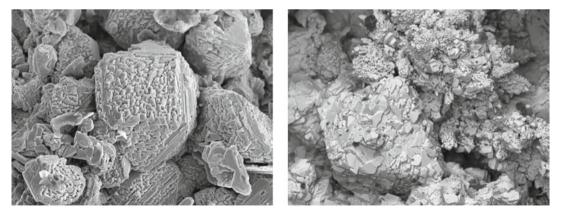


Compact layer of pitch black metacinnabar crystals on the surface of mineralized limestone-dolomitic conglomerate from the Lamberg-Ruda mining field on the IX<sup>1/h</sup> level. The host rock is cemented by cinnabar, which was probably the main source of mercuric sulfide for crystallization of metacinnabar in freshly opened fissures. Unaltered metacinnabar is considered a rarity. Shown is a 35 mm detail from a 13 cm specimen. Mineralogical collection of the Municipal Museum of Idria – Photo: A. Rečnik



Epitaxy of cinnabar on metacinnabar

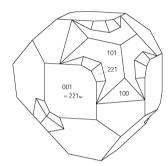
recrystallized to cinnabar. On unaltered metacinnabar crystals it is possible to recognize rhombic-dodecahedral and tetrahedral forms; however, in most cases their surface is covered by a thin epitaxial layer of cinnabar. On the top of cinnabar occasionally developed a second generation of microscopic metacinnabar crystals, which is characterized by the presence twin lamellas parallel to the tetrahedral planes. The reason why cinnabar does not transform to metacinnabar during crystallization of this otherwise higher-temperature polymorph lies in the incorporation of specific trace elements. Here, the coexistence of both polymorphs is enabled by the presence of zinc in the final stages of crystallization. Depending on the amount of zinc, cinnabar and



(left) Cubo-octahedral crystals of metacinnabar with a thin surface layer of epitaxial cinnabar. The orientation relationship between the metacinnabar and cinnabar is illustrated above. The other photograph (right) shows an octahedral metacinnabar crystal with a thick recrystallization layer. The widths of the micrographs are 130 and 330 µm. Faculty of Natural Sciences in Ljubljana – SEM Photo: A. Rečnik

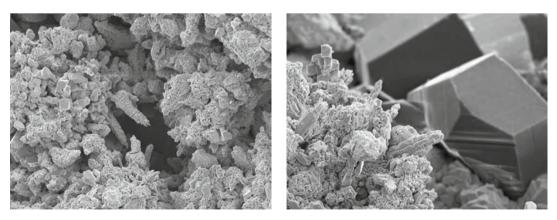
Metacinnabar clusters partly overgrown by translucent calcite crystals on oolitic limestone, X<sup>th</sup> level. Detail 15 x 15 mm. Collection of J. Klemenčič – Photo: A. Rečnik

According to Schrauf (1891), the additional reason for the complex morphology is twinning of metacinnabar. He measured several crystals of metacinnabar interpenetration twinned by {111} planes. Following this operation cube {100} faces are brought in parallel with deltoid dodecahedral {221} faces.



Metacinnabar twin after Schrauf (1891)

metacinnabar can therefore crystallize practically at the same temperature. Botryoidal crusts comprising alternating layers of cinnabar and metacinnabar were found on the calcite crystals in the vugs of Upper Scythian dolosparite in Grübler Fault zone form XI<sup>th</sup> to the XIII<sup>th</sup> level (DROVENIK et al. 1991). In the Idria mine, there are no reports about the existence of the hexagonal hightemperature polymorph of HgS, hypercinnabar (POTTER and BARNES 1978); however, it may be expected due to the high formation temperature of pyrobitumen (LAVRIČ et al. 2003). Lamellar twinning of metacinnabar (SCHRAUF 1891; MLAKAR and DROVENIK 1971), could therefore be a consequence of polymorphic phase transition to either hypercinnabar or back to cinnabar.



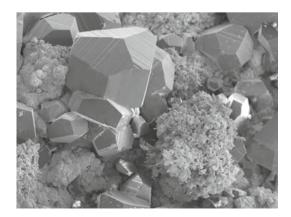
Occasionally cinnabar completely replaces metacinnabar (left). Recrystallization occurs on the invasion of low-temperature solutions that trigger the phase transformation. Metacinnabar and its cinnabar perimorphs commonly occur in association with short-prismatic calcite crystals (right). The image widths are 380 and 250 µm. Faculty of Natural Sciences in Ljubljana – SEM Photo: A. Rečnik





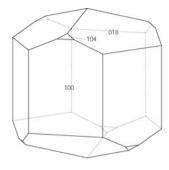
Zoned grayish prismatic crystal of calcite on Lower Scythian oolitic limestone. Through the transparent bottom part of the crystal the underlying fine crystalline cinnabar is visible. Crystal size 5 mm, specimen 12 cm. Municipal Museum of Idria – Photo: A. Rečnik

Calcite is the primary mineral in calcite-bearing rocks and is formed by local recrystallization of the constituent limestone. It is found in higher dolomite levels, in vugs of the Lower Scythian dolosparite, in oolitic limestone and in the Langobardian claystone strata. In the vugs of dolosparite it occurs in the form of white



or pale-yellow flat rhombohedral crystals, which rarely exceed 8 mm. Much more frequent are the calcite crystals in the fissures of dark-grey Lower Scythian oolitic limestone or in Langobardian claystones. Here they occur in the form of translucent short prismatic crystals with jagged terminations, densely overgrowing the fissure walls. In the mineralized zones, calcite crystals contain inclusions of cinnabar and are often accompanied by black globules of metacinnabar. It is interesting that metacinnabar almost always occurs together with the prismatic type of the calcite crystals, which implies a certain relationship between the two minerals that is not yet understood. Older calcite crystals, common for the eighteenth and nineteenth century (HACQUET 1781), have a scalenohedral habit. They are often overgrown by younger prismatic calcite that is transparent.

Short prismatic crystal of calcite with altered metacinnabar. The sutures on terminations run parallel with the primary rhombohedron {104}. Crystal size is 0.5 mm – SEM Photo: A. Rečnik



The morphology of calcite crystals form Idria. The crystal habit is defined by a prism and the flat negative rhombohedron

Calcite crystals with protogenetic inclusions of cinnabar from the fissures in oolitic limestone, XII<sup>th</sup> level. The overall specimen size is 10 x 8 cm, with crystals measuring up to 5 mm. Mineralogical collection of the Municipal Museum of Idria – Photo: A. Rečnik











An old specimen of scalenohedral-prismatic crystals of calcite. The primary crystals had a form of simple scalenohedron {214}, which were in the late growth stages homoepitaxially overgrown by younger prismatic crystals. Due to overgrowth the scalenohedra have a stepped appearance. Such specimens were typical for a period between eighteenth and nineteenth century. The specimen with the original label is from the mineralogical collection of the eighteenth century scientist Balthasar Hacquet, who worked about 12 years in Idria. These crystals are described in his book Oryctographia Carniolica (1781). The specimen size is  $12 \times 8$  cm. Collection of the Geological Museum of Jagiellonian University in Krakow – Photo: A. Rečnik





(above) Calcite with cinnabar from tectonic breccia in Langobardian limestone. The specimen shows a tectonic slide plane where fractured calcite crystals recrystallized and included precipitating cinnabar. Specimen size 12 x 8 cm. Hacquet's mineralogical collection, Geological Museum of Jagiellonian University in Krakow – Photo: A. Rečnik

(right) Short prismatic crystals of calcite perched on massive cinnabar. The host rock is brecciated Langobardian limestone. Lowtemperature solutions transported only calcite, while the cinnabar is only poorly recrystallized. Detail 35 mm, specimen 9 x 11 cm. Geological Museum of Jagiellonian University in Krakow – Photo: A. Rečnik





Simple crystals of dolomite with cinnabar, IX<sup>th</sup> level. Image width 15 mm. Find and collection A. Rečnik – Photo: A. Rečnik

#### **D**OLOMITE AND QUARTZ

Dolomite and quartz belong to the primary minerals that formed by local recrystallization from the bedrock and were not brought into the system by ore brines. They crystallized in fissures along the tectonically shattered dolomite, that served as pathways for descending meteoric waters. In the process of dissolution and recrystallization, simple rhombohedral or saddle-like crystals of dolomite developed in the vugs and open fissures. Leaching of the bedrock opened free paths for the percolation of other constituents from the bedrock into new opened fissures. At the temperature of the oil-window, hydrocarbons present in the bedrock started to migrate towards the open fissures, where they were mixed with heated meteoric waters and formed colloidal solutions. From such solutions quartz crystals do not grow on the fissure walls as usual, but rather homogenously precipitate within the whole volume until they gravitationally deposit on the exposed surfaces when a critical size

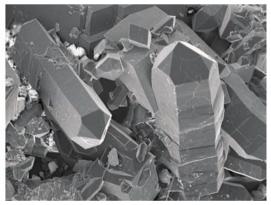
reached. Quartz crystals grown from non-polar colloidal solutions are usually doubly terminated. Often they are additionally twisted around the c-axis to form bow-tie like crystals and their clusters similar to those found in bituminous Triassic dolomites on other Slovenian localities, e.g. Vojsko, Zadobje, Crngrob and Turjak (REČNIK 2007). Quartz crystals from Idria are usually not larger than a few millimeters. Doubly terminated crystals of quartz with bituminous matter were found perched on dolomite crystals in the Lower Scythian dolosparite in the Grübler Fault zone (DROVENIK et al. 1991), and recently also in the main transportation gallery on the X<sup>th</sup> level of the Delo shaft associated with calcite, cinnabar and mountain leather. Occasionally, dolomite was replaced by cinnabar during the inflow of ore-rich brines. A good example of this process were pseudomorphs of cinnabar over saddle dolomite, found by F. Krantz from Bonn and described by VOSS (1895).



Clear crystals of quartz with lentiform calcite and cinnabar crystals on Lower Scythian limestone matrix. Black impregnations on the crystals are bitumen, which indicates the presence of hydrocarbons during crystallization. In this association cinnabar is the youngest mineral. The size of the quartz crystal in the center is 2 mm. Find and collection J. Klemenčič – Photo: A. Rečnik



Doubly terminated bow-tie crystals of quartz from the cavities in Lower Scythian dolomite, X<sup>th</sup> level. Similar quartz crystals can be found in bituminous Triassic dolomites elsewhere in Slovenia. Size 9 mm. Find and collection G. Velikonja – Photo: A. Rečnik



Doubly terminated quartz crystals are typical for the growth from colloidal solutions, rich in hydrocarbons. During their nucleation the crystals homogenously precipitate on the open surfaces. Image width is approximately 1 mm – SEM Photo: A. Rečnik





(above) Twisted dolomite crystals with cinnabar from the nineteenth century. Saddle dolomite crystals are a consequence of inherent dislocations, which cause twisting according to the rules of trigonal symmetry. Detail 30 mm – Photo: A. Rečnik



(left) The specimen is from the nineteenth century Jaklin's collection, later acquired by F. Krantz fom Bonn. Detail 15 mm. It may be possible that pseudomorphs of cinnabar after saddle dolomite reported by Zepharowich (1872) from the XI<sup>th</sup> level were from the same collection. Today in the Collection of V. Pavčič – Photo: A. Rečnik



(above) Translucent crystals of dolomite on cinnabar from IX<sup>th</sup> level. The specimen size is 7 x 8 cm; detail 15 mm. Find B. Stojanovič. Collection of the Natural History Museum in Ljubljana – Photo: A. Rečnik

(right) Dolomite with tiny red crystals of cinnabar from IX<sup>th</sup> level, Delo shaft. Only a few years ago it was still possible to collect such specimens in mineralized fissures and cavities of Lower Scythian dolomite. Detail 20 mm. Find and collection A. Rečnik – Photo: A. Rečnik







K. k. Naturhistorisches Hof-Museum. ineralogisch-petrographische Abtheilung Acq. Post A. K. 959. Name Kinno ber Va. M. new RHY . (") Fundore Jaria , Main

Large dolomite crystals on cinnabar from a vug of richly mineralized Langobardian dolomitic conglomerate. The interior of the crystals appears dull white to grey due to fluid inclusions. The outer zone of the crystals is translucent. This nineteenth century specimen measures 80 x 37 mm. Natural History Museum in Vienna – Photo: A. Rečnik



Ha. Zinables A. G. 3964 Fundort: Drie? Ranices. Dr. Baader's Sohn in Wien. 



Cinnabar with doubly terminated quartz crystal on fine crystalline dolomite in a vug of mineralized dolostone. The quartz crystal measures 5 mm, the size of the whole specimen is 75 x 50 mm. Natural History Museum in Vienna. The specimen was bought in 1862 from Mr. Ernst Baader from Vienna for 20 florins – Photo: A. Rečnik





Mountain leather (palygorskite) with cinnabar crystal from a small cavity in Scythian intraclastic dolosparite on the  $X^{th}$  level, Delo shaft. In addition to palygorskite, there were also several up to 10 mm long doubly terminated crystals of quartz and fragments of crystalline calcite and cinnabar. From the specimen shown above it is evident that the cinnabar crystallized after palygorskite. The size of the specimen is 22 x 12 mm. Find and collection G. Velikonja – Photo: A. Rečnik



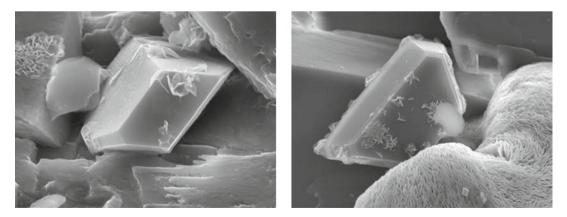
Translucent crystals of brown kaolinite on dolomite and quartz from  $XI^{th}$  level. The kaolinite is older than the calcite and cinnabar. Detail 10 mm. Find and collection J. Klemenčič – Photo: A. Rečnik

### SILICATE MINERALS

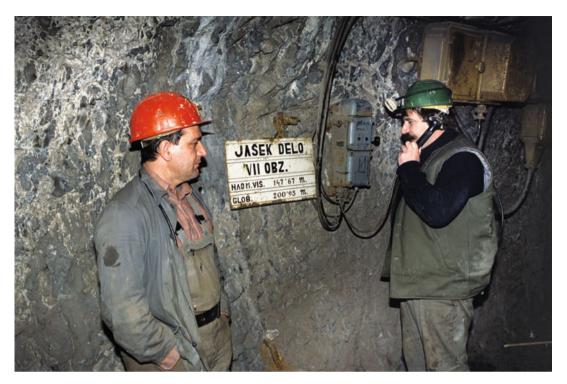
In addition to dolomite, calcite and guartz, also kaolinite crystals and fibers of palygorskite are found in the crystal-lined vugs of Lower Scythian dolostones (BER-CE 1958). Palygorskite occurs in the form of white fibrous crystals and tangled mats, known as mountain leather, together with quartz and cinnabar in the vugs of Lower Scythian dolosparite. It belongs to older minerals in the paragenesis. Kaolinite occurs in the form of white or brownish translucent crystals with a distinct cleavage along the basal plane. It formed from a glassy tuff in an acidic swampy environment and was brought in the system by descending meteoric waters. In larger quantities it was found in veins together with chalcedony in the Langobardian sandstones (MLAKAR and DROVENIK 1971) and in up to 15 m thick kaolinite sandstone beds in the lower part of the Skonca beds (DROVENIK et al. 1975).



Mountain leather on mineralized dolomite from mining field Talnina on the IV<sup>th</sup> level. In Idria palygorskite occurs in the form of fibers entangled into a few centimeters large cloth-like assemblies. It is found in fissures of silica-rich intraclastic dolosparite. In the past, this mineral has been also referred to as pilolite, xylotile or tuesite. The reason for the different designations is a quite variable composition. In the late 1990s we found mountain leather with quartz, calcite and cinnabar on the XI<sup>th</sup> level, Delo shaft. Specimen size is 13 cm. Find J. Čar. Mineralogical collection of the Municipal Museum in Idria – Photo: A. Rečnik



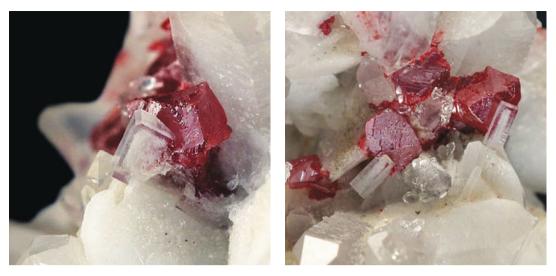
In mineralized fissures and vugs along the Grübler Fault system sand-yellow to light-brown crystals of kaolinite are found in association with dolomite and cinnabar. Kaolinite is considered a young member of the mineral paragenesis. Photographs show unaltered kaolinite crystals with an unknown silicate grown on dolomite. The size of the crystals is 20 µm. Find A. Rečnik – SEM Photo: A. Rečnik



Mining geologist Bojan Režun and supervisor Mirko Lukan calling the elevator at Delo shaft in 1994 – Photo: B. Kladnik

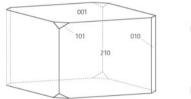
#### BARYTE AND CELESTINE

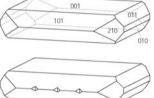
Baryte in the form of well-developed crystals is considered a mineralogical rarity in the Idria ore deposit. According to SCHRAUF (1891), the largest baryte crystals measured up to 2 cm in width and were only 3 mm thick. They originated from a very old find in the Theresia shaft. He also found 5 mm transparent baryte crystals at the VI<sup>th</sup> level of the Ioseph (now Delo) shaft in the immediate vicinity of the fissures with metacinnabar crystals. Probably the best specimen of tabular baryte crystals from Idria is kept in the mineralogical collection of the Natural History Museum in Vienna. The crystals measure up to 10 mm across and are extremely rich forms. They form various rosette-like intergrowths on fine-crystalline quartz matrix, covered by tiny reddishbrown cinnabar crystals. Cinnabar is also present along the growth-zones of these crystals. In the last century this type of baryte crystals was never found again. DRO-VENIK and coworkers (1991) reported on a find of beautiful baryte floaters from the Grübler ore body at XIIIth level. They determined two generations of baryte, of which the older is represented by white crystals with a simple rhomboidal appearance, while the younger baryte generation is transparent and rich in forms, indicating slow growth from diluted solutions. The crystals did not exceed 2 mm. Baryte sporadically occurred also at the higher levels of the Scythian dolosparite. At the end of the 1990s, a miner Janez Klemenčič from Kanomlja found a vug with small baryte crystals with calcite, guartz and cinnabar at the X<sup>th</sup> level of the Delo shaft. The crystals have a similar habit to those from Grübler and show zonal growth. Their core is white, whereas is their outer zone completely transparent. A study of the specimens from crystal-lined vugs of the Grübler Fault zone revealed the presence of microscopic celestine crystals (DOLENEC et al. 2005). Celestine appears to be one of the youngest minerals in the paragenesis. It is younger than calcite, pyrite and cinnabar. The crystals measure up to 20 microns across, and are covered only by nanocrystalline cinnabar. The source of strontium for the formation of celestine could be hydrothermal (BERCE 1958), but it might also be remobilized from the neighboring rocks (DOLENEC et al. 2005).

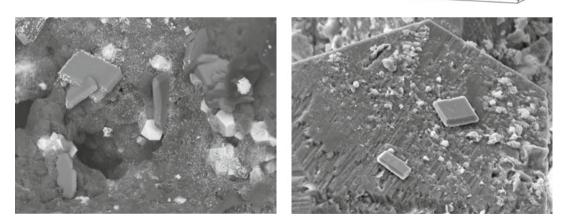


Baryte is not very common in Idria. It is younger than quartz and calcite but older than cinnabar. On the photograph, the core of the crystals measuring up to 1 mm is white, while their outer zone is clear. X<sup>th</sup> level, Delo shaft. Find and collection J. Klemenčič – Photo: A. Rečnik

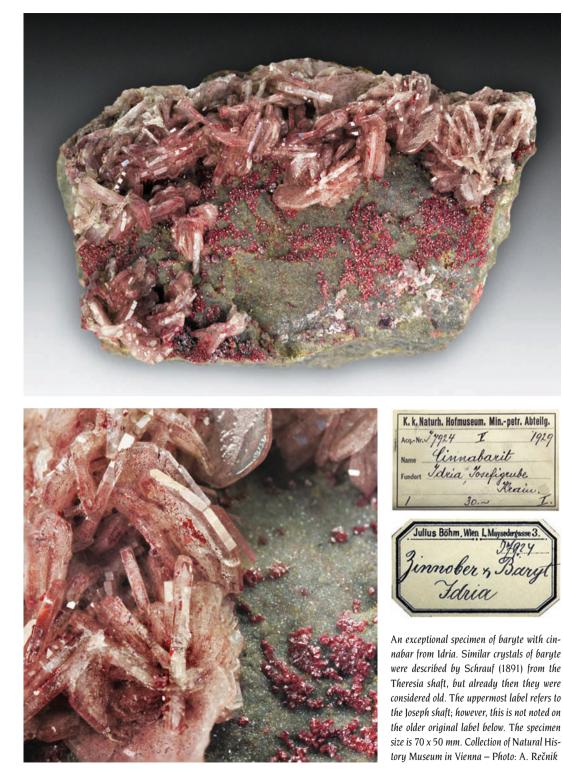
The morphology of baryte and celestine from Idria. Baryte crystals are dominated by base pinacoid {001} and prism {210}, contributing to their rhombic shape. The celestine crystals are flattened by {001} and modified by prisms. Often they have reentrant angles visible on the front pinacoid





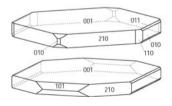


Microscopy of the samples from mineralized vugs in brecciated Lower Scythian dolomite of the Grübler Fault system revealed the presence of strontium sulfate celestine. Crystals of celestine measure up to 20 μm and appear similar to baryte. They are tabular on base pinacoid, as shown in the drawing (above right). The crystals are jagged on the edge of frontal pinacoid and they often form clusters. Celestine is one of the youngest members of the mineral paragenesis and is found on dolomite, calcite, cinnabar, pyrite and gypsum. Sometimes it is overgrown by nanocrystalline cinnabar, as shown on the micrograph (left), where it is associated with white cubooctahedral crystals of pyrite. Another photograph (right) shows celestine crystals perched on a rough rhombohedral termination of calcite. Find T. Dolenec. Collection of the Faculty of Natural Sciences in Ljubljana. Widths of the images are 88 and 176 μm – SEM Photo: A. Rečnik





JAPEY Xi 525. Tinnober f. 30. mit Barys Kee Chi Elg Idria, Fundort: Krain



Baryte crystals from older finds have a tender pink coloration due to banded inclusions of cinnabar. Morphologically they are quite similar to microscopic celestine crystals from Grübler. The crystals measure up to 10 mm and are 1 mm thick. The specimen is kept in the collection of the Natural History Museum in Vienna – Photo: A. Rečnik





Gypsum from Hacquet's collection of minerals. Geological Museum of Jagiellonian University in Krakow – Photo: A. Rečnik

#### $M_{\text{INERALS OF THE OXIDATION ZONE}}$

The most abundant sulfate mineral in the ore deposit is gypsum. The vast majority of gypsum was present already before the formation of the ore deposit in the form of intrastratified layers in the Upper Permian and Lower Scythian dolomite. Here, gypsum formed as a result of intense evaporation in a lagoon environment. The individual lenses measure up to 2 m in thickness and their lengths can be up to several tens of meters. In these lenses gypsum is fine grained and sporadically contains crystals of purple fluorite (ČADEŽ 1977). Like in all sulfide-ore deposits, also in Idria the sulfide minerals oxidize and release sulfate ions, which react with the rock-forming and other ore minerals to form various sulfates and vitriols. In Idria, most of the sulfate ions were produced by the decomposition of iron sulfides in the overburden. Acidic sulfate ions from the oxidation zone are transported by descending meteoric waters through the strata of sedimentary rocks where they react with the present minerals. One of the reaction products is gypsum. It forms in a reaction of descending sulfate ions with calcite. In open fissures and vugs filled with carbonate clay well-developed crystals of gypsum can be found. In a gray limestone at the X<sup>th</sup> level, it is present in the form of slightly corroded, translucent, up to 4 cm long twinned crystals. In the fissures and vugs of the Lower Scythian dolomite it appears as the youngest mineral of the paragenesis. The gypsum crystals in these cavities are sharp, water clear and usually smaller than 1 mm. Occasionally, they are overgrown only by the youngest generation of cinnabar.

MUZEUM MINERALOGICZNE UNIWERSYTETU JAGIELLOŃSKIEGO Dr. inw. IV.d Rok inw. 1932. 4364. svat. Sips- skupienie droknych kryse. Kraina Idrja. Corla + 2420. jednoskas; kl. stupa jednoskas. C. 2 3 stary.

(on the previous page) Gypsum crystals from a fissure in mineralized limestone-dolomitic conglomerate. The crystals are covered by a thin layer of limonite, which is responsible for the brown coloration of the specimen. The specimen with the original labels is from Hacquet's collection of minerals, which was founded during his employment in Idria (1766–1778). Specimen 8 x 9 cm. Geological Museum of Jagiellonian University in Krakow – Photo: A. Rečnik





In carbonate hosted sulfide ore deposits gypsum crystallizes in reaction of sulfate ions with calcite from the host rock. It is commonly collected in clayey fillings in open tectonic fissures that serve as open paths for oxidizing meteoric waters. Limonite, as the least mobile product of iron sulfide oxidation, often accompanies gypsum. Until recently, it was possible to find up to 3 cm long gypsum crystals in a fissure of Scythian limestone on the VI<sup>th</sup> level of Delo shaft. The photograph (above) shows a 2 cm long transparent crystal of gypsum in limonite. Find and collection G. Velikonja – Photo: A. Rečnik



Water clear crystal of gypsum on cinnabar in a dolomite-lined vug in Lower Scythian dolostone. Gypsum is one of the last minerals of the paragenesis and therefore it overgrows most of the minerals in usual associations. The crystals of gypsum in these vugs are rarely larger than 1 mm. Detail on the photograph measures 10 x 7 mm. Find and collection A. Rečnik – Photo: A. Rečnik



Corroded gypsum overgrowing dolomite rhombohedron. The crystals on gypsum are cinnabar, which is a rather unusual situation. In the lower part of the micrograph are altered kaolinite crystals. The specimen comes from a vug in Lower Scythian dolostone on the IX<sup>th</sup> level of Delo shaft. Width of the detail is 1.2 mm. Find and collection A. Rečnik – Photo: A. Rečnik



Long fibrous crystals of epsomite in an abandoned tunnel on the IV<sup>th</sup> level. Photographed in 2003 – Photo: B. Režun

In the Idria ore deposit, oxidation processes forming vitriols are still active today. The most widespread vitriols are magnesium and iron sulfate-hydrates epsomite and melanterite. Their formation is related to the oxidation of iron sulfides and dedolomitization of the overlaying dolomite strata. Iron and magnesium, which are leached from the host rocks by percolating meteoric waters react with the sulfate ions to form epsomite and melanterite (HERLEC et al. 2006). They crystallize from saturated solutions by water evaporation, similar to aragonite stalactites in karstic caves. As vitriols are soluble in water, they quickly migrate into the lower parts of the ore deposit. According to BERCE (1958), epsomite covers the walls of newly dug tunnels in only a few weeks. It occurs in the form of tender pearly-white fibrous crystals measuring several decimeters length. In poorly ventilated tunnels, impressive stalactite formations developed, consisting of various crystalline vitriols, most of which is epsomite. Melanterite occurs in the form of thick crystalline coatings and stalactites of translucent green, pink, yellow or brown color. The crystal grains of melanterite in dripstones measure up to 10 mm. The beauty of these crystalline formations can be admired only in the mine, because they need just the right moisture and temperature for their existence. Brought to the surface, the vitriols lose crystalline water and soon transform



Epsomite grows relatively rapidly on the walls of poorly ventilated tunnels and blind shafts. It forms by the reaction of acidic descending waters with dolomite from the host rock. In the reaction with magnesium, sulfate ions cause dedolomitization of the rock, resulting in an abundant generation of epsomite. In a similar way other vitriolic salts are formed. The most common are hydrated sulfates of iron, such as melanterite, szomolnokite and siderotil. In addition to silvery fibers growing on the humid dolostone outcrops epsomite also forms up to several meters high stalagmites

Photographs show up to 20 cm long aggregates of fibrous epsomite in an abandoned tunnel on the X1<sup>th</sup> level on Delo shaft. Photographed in 2004 – Photo: A. Rečnik

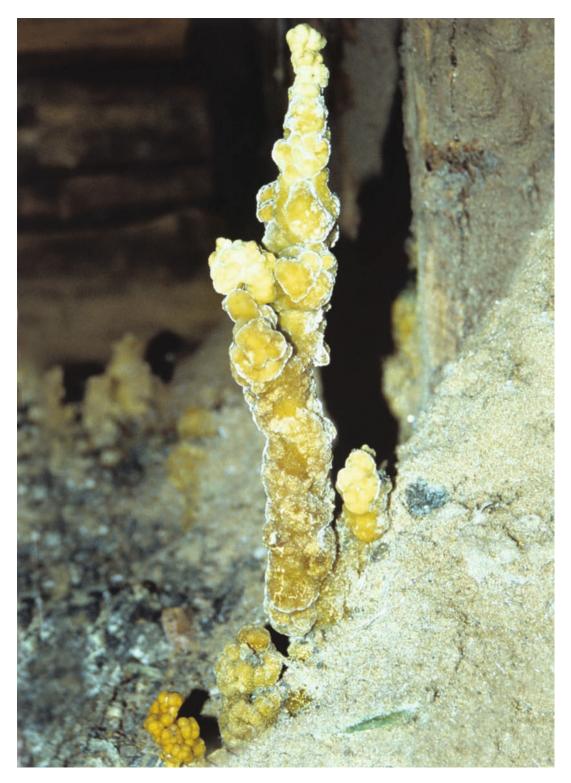




(above) A blind shaft Zergoller with rotting wood and epsomite stalagmites on the IV<sup>th</sup> level. – Photo: R. Podobnik (on the opposite page) 40 cm tall velvety yellow melanterite stalagmite on the VI<sup>th</sup> level. Photographed around 1988 – Photo: R. Vidrih

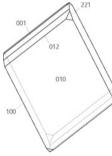
into dehydrated white sulfate powder. In the second part of the nineteenth century, the mineralogists devoted a lot of attention to the vitriols from the Idria ore deposit. In addition to epsomite and melanterite, ZEPHA-ROWICH (1893) described halotrichite, whereas SCHRAUF (1891) discovered the first valid type-mineral from Idria, the iron sulfate-hydrate siderotil. The type-material was collected on the IV<sup>th</sup> level in the north-western part of the ore deposit. Siderotil occurs in the form of white or pale-yellow needle-like aggregates on green melanter-ite crusts. Recently, we have determined another ferrous

vitriol, szomolnokite, occurring together with pyrite and idrialine in Langobardian siltstone at XII<sup>th</sup> level. In spite of a thorough research of the 19<sup>th</sup> century scientists, vitriols of mercury were never observed in the ore deposit. A canary-yellow mercuric sulfate schuetteite, however, can be found on the bricks of the mercury ore smelters. In Idria, it was first described by SEYFRIEDSBERGER (1890). This supergene mineral crystallizes under highly oxidative conditions, which rarely occur in a natural environment. Commonly it forms on oxidation of cinnabar in sunlight (BAILEY et al. 1959).





A real surprise was the discovery of bluish vivianite crystals by the mineral collector Goran Velikonja from Idria. They occur in fissures of the Lanaobardian sandstone in the immediate vicinity of coral-ore beds on the IV<sup>th</sup> level. In spite of the fact that vivianite was not yet described by the previous authors, it is an expected member of the oxidation zone in the phosphate-rich Skonca beds. Based on this find also some other phosphate minerals could be expected. A thin red vein of cinnabar winds through the matrix next to the vivianite cluster. The size of the larger crystal on the photograph is 2 mm. Find and collection G. Velikonja in 1994 – Photo: A. Rečnik



The morphology of vivianite crystals from Idria. They are flattened by the side pinacoid {010}, parallel to the cleavage planes of the mineral. Their simple habit is further defined by the front {100} and base {001} pinacoids. Other accessory forms are somewhat rounded. The crystals occur individually or in rosette-like groupings



In the samples of tectonically shattered Langobardian sandstone, located not far from the coral-ore stratum, a mineral collector Goran Velikonja from Idria found tiny bluish crystals of iron sulfate vivianite. It forms simple translucent crystals and crystal aggregates measuring up to 2 mm across. They cover open surfaces of the orebearing sandstone. Since the nineteenth century it is known that the coral-ore is rich in phosphates (JAHN and KLETZINSKY 1780); however, no crystallized phosphate minerals were reported. According to the analyses, the shells of the Discina brachiopods consist of interchanging layers of calcium phosphates and carbonates (MLAKAR and DROVENIK 1971). Given the fact that ore solutions migrated through these rocks, repositioning of phosphate components into the open fissures could occur. Under oxidizing conditions, the phosphate ions reacted with the ferric ions, released by the decomposition of iron sulfides, to form vivianite. Given the prevalence of these basic components, we could expect a number of other interesting phosphate minerals in these beds.



The old mining town Idria with castle Gewerkenegg in the background today - Photo: J. Peternelj

## GEOLOGICAL AND TECHNICAL HERITAGE OF IDRIA

After 500 years of mining history, the last batch of ore was excavated in 1995, and in 2009 the mine was finally shut down. Through all that time, many ore, fossil and mineral collections were formed. Collecting became very popular during the Enlightenment, when several renowned scientists were working in the territory of Slovenia. Many of these collections have been preserved until the present day. The famous researchers GIOVAN-NI A. SCOPOLI (1723-1788) and BALTHASAR HACQUET (1739-1815) collected ores and minerals from the Idria mine as well as from other known Carniolan localities. Their contemporary, the founder of Slovenian mineralogy, Baron SIGMUND ZOIS (1747-1819), also made a large collection of ore specimens from Idria. The most important of all these collections is certainly the HACQUET's mineral and ore collection, now at the Geological Museum of the Jagiellonian University in Krakow, Poland.

His mineral specimens are not only well documented and preserved, but they are also described in detail in his monograph on the natural treasures of Carniola (Oructographia Carniolica 1781), which gives us an invaluable insight into the mining conditions and findings of mineral specimens of that time. Collecting kept pace with the bloom of the natural sciences in the nineteenth century. From this period, a part of the Idrian geologist MARK V. LIPOLD's (1816-1883) collection is preserved and displayed in the Municipal Museum of Idria in the castle Gewerkenegg. Along these known collectors, there were probably many other private collectors that were forgotten over time, but fortunately, the very tradition of mineral collecting survived until today. Without the miners who kept some very precious specimens, it would not be possible to evoke the whole beauty of the Idrjian minerals presented in this book.







Gewerkenegg castle was built in the early sixteenth century. Today it hosts the Municipal Museum of Idria – Photo: A. Zelenc

A small part of the historical collections of ores and minerals is now incorporated within the Geological Collection of the Municipal Museum of Idria. A total of 2,690 specimens are organized into geological collection of rocks and fossils of the Idria-Cerkno mountain range, a collection of ores from the Idria mine, and the mineral collection. The collection of ores includes polished cross-sections of all the syngenetic ore types that would be difficult to find in the ore deposit today. Of particular interest within the collection are the minerals of Idria and the surroundings. Among many specimens the visitors can see a nice sample of a Carboniferous claystone with droplets of native mercury, an iron ball floating on mercury, and can try themselves how heavy the cinnabar-rich steel-ore is. The side showcases feature some old specimens of crystalline cinnabar and metacinnabar, the kind that any mineralogical museum would be proud of. Next to them are exhibited some elderly calcite crystals that could not be found in the mine after the nineteenth century. The exhibits are quite instructive for schoolchildren as well as for geology students. The latter can find excellent material for their science projects. A walk through the museum rooms in the sixteenth century Renaissance castle Gewerkenegg, built to serve as mercury and cereal storage and then became the main mine administration building, takes the visitors through the history of the town and acquaints them with all the famous people that worked and lived in Idria through the centuries. Numerous black-and-white photographs let anyone feel the real beat of the town at the turn of the twentieth century, whereas exact models of timber floating, reconstruction of underground shafts and tunnels, and replicas of ore smelting give us a precious insight into the work involved with ore mining. The oldest part of the mine in the hinterland of Anthony's shaft is restored and accessible for visitors. The former mine facilities are now hosting many technical, geological and mineralogical exhibits that were preserved after the operation of the mine. The cornerstone of Antony's shaft was

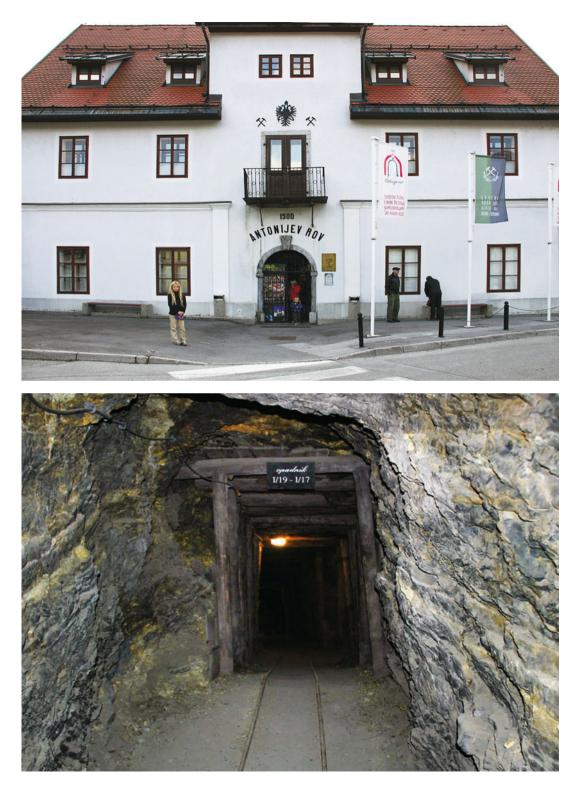


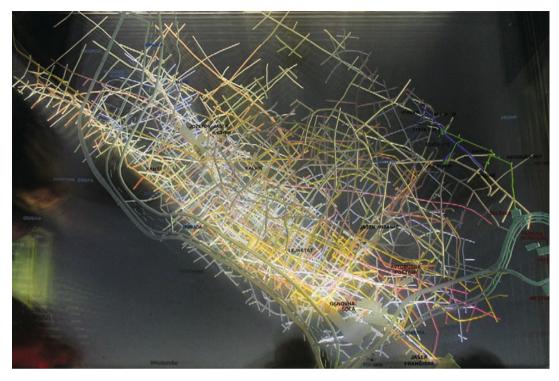
Backyard of castle Gewerkenegg. In the showrooms the visitors can see various collections related to mining and the life of the Idrian inhabitants through its history. The collection of ores and minerals from the Idria mine and other localities has more than 2,600 exhibits – Photo: A. Rečnik

(on the previous page) An abandoned tunnel with epsomite stalagmites on  $IV^{th}$  level behind the blind shaft Zergoller at the end of the 1980s – Photo: B. Kladnik

In reminiscence of the life with mercury in Idria acad. sculptor Jožef Vrščaj constructed an installation of a plexi-glass cube with floating bubbles of native mercury that defy gravity. It is displayed in the basement of the museum – Photo: A. Rečnik







laid already in 1500, just a few years after the discovery of mercury in Idria, which makes it the oldest preserved underground object of the Idrian history. Visiting the very old tunnels leaves a lasting experience. Here we learn that in the early times the tunnels and shafts were hand-dug. The most skilled miners had to work a fullday to excavate 15 cm of a tunnel. In expectation to hit a rich ore vein they often had to dig whether there was any ore in the rock or not. With the progress of mining, a new science about rocks was evolving, being able to predict ore occurrences and thus save some hard work to the miners. Because Antony's tunnel is dug into the unstable Carboniferous claystone, it had to be well supported by wooden timbers. No wonder why skilled carpenters were always so highly prized in Idria. In 1766, the tunnel was reinforced with limestone blocks in order to assure long-time stability. For many centuries, the miners used Anthony's shaft to access the lower levels of the mine. On passing through Anthony's tunnel, visitors will enter the oldest parts of the mine, whereas more recent tunnels, situated deeper underground, are no longer accessible. On the 1,200 m long walk through the mine, you will pass the original Carboniferous claystone with native mercury, learn about the miners' work, and see the former mining areas. The way through the mine is properly secured and suitable also for the voungest explorers.

At the entrance to Anthony's tunnel the visitors can see an impressive three-dimensional colored glass reconstruction of the tunnels on different levels of the mine. In the half-millennium-long history of mining over 700 km of tunnels and shafts were excavated to a depth of 36 m below the sea level – Photo: A. Rečnik







Systematic geological collection of the Idria and Cerkljansko area can be seen in the Mercury Mine Museum in Idria. The ore and rock samples of the Idria mine are classified by individual lithological units – Photo: A. Rečnik

In conjunction with intensive geological research in the Idria mine in the twentieth century, a very important, specialized geological collection was built. The main aim was to gather and systemize all the rock and ore types of the Idria ore deposit and so preserve this part of the natural heritage for generations to come. The Idria deposit is considered genetically and tectonically one of the most complex ore deposits in the world. It took decades of research to reconstruct its formation. The geological collection of the mine allows us to learn about the structure and characteristics of the host rocks and mercury ores found in the ore deposit. This collection is important for understanding the geological processes during mineralization, while the particular specimens of rocks and ores helped geologists to reconstruct the formation of the deposit (ČAR 2010). Nowadays, the collection is displayed in the rebuilt mine administration quarters. It is divided into seven subunits. The first unit represents a lithostratigraphic collection of rocks of the Idria and Cerkno mountain range, which was at the time of mineralization tectonically highly active and accompanied by intense volcanic activity during the Middle Triassic. In that period, the major sediments of the Idria deposit were being deposited and the rocks along the Idria Fault were mineralized. This is followed by the host rock samples from the ore deposit itself. Geologically, the most outstanding among these are the rocks from the mineralized Skonca beds. The mercury-bearing ore unit represents the core of the geological collection. It is divided into syngenetic and epigenetic ores classified after individual lithological units. The very importance of this collection is the detailed documentation about the provenience of the specimens. The mineralogical collection is still sparse: however, in a collaboration with other museums, it will be possible to improve this in the future.

# **REFERENCES:**

AGRICOLA G: De Re Metallica. Basileae. (1556).

BAILEY EH, HILDEBRAND FA, CHRIST CL & FAHEY JJ: Schuetteite, a new supergene mercury mineral. American Mineralogist 44 (1959) 1026-1038.

BAJŽELJ U: Underhand cut and fill stoping experiments in carboniferrous schists at the Idria Mine. AIME Symposium, New York (1984) 163-183; I.c. LIKAR J, CIGALE
M & REŽUN B: Long-term deformation processes ... Rudarsko metalurški zbornik 53 (2006) 103-120.

BANCROFT P, ČAR J, ŽORŽ M & KOBLER G: The Idria Mines Slovenia, Yugoslavia. Min. Rec. 22 (1991) 201-208.

BERCE B: Geologija živosrebrnega rudišča Idria. Geologija **4** (1958) 5-62.

COLBERTADO DI D & SLAVIK S: Il giacimento cinabrifero di Idria in Jugoslavija. Rendiconti della Societa Mineralogica Italiana 17 (1961) 301-327.

ČADEŽ F: Sadra in anhidrit na Idrijskem. Geologija **20** (1977) 289-301.

ČAR J: Geološka zgradba idrijsko-cerkljanskega hribovja: Tolmač h Geološki karti idrijsko-cerkljanskega hribovja med Stopnikom in Rovtami v merilu 1:25.000. Geološki zavod Slovenije. Ljubljana (2010) 127 pgs.

DICKSON FW & TUNELL G: The stability relations of cinnabar and metacinnabar. American Mineralogist 44/5-6 (1959) 471-487.

DOLENEC T, REČNIK A, DANEU N, DOBNIKAR M & DOLE-NEC M: Celestine – A new mineral from the Idria mercury ore deposit (Western Slovenia): Its occurrence and origin. Rudarsko-metalurški zbornik **52**/2 (2005) 429-436.

DROVENIK M, ČAR J & STRMOLE D: Langobardske kaolinitne usedline v idrijskem rudišču. Geologija 18 (1975) 107-155.

DROVENIK M, DOLENEC T, REŽUN B & PEZDIČ J: O živosrebrovi rudi iz rudnega telesa Grübler v Idriji. Geologija **33** (1990) 397-446.

DROVENIK M, PLENIČAR M & DROVENIK F: Nastanek rudišč v SR Sloveniji. Geologija 23/1 (1980) 1-157.

FERBER JJ: Beschreibung des Quecksilberbergwerks zu Idria in Mittel Cräyn. Berlin (1774) 76 pgs.

GOLDSCHMIDT VM: Atlas der Kristallformen. Band 9 (1923) 96-101.

HACQUET B: Oryctographia Carniolica. Band II (1781) 34-133.

HERLEC U, REŽUN B, REČNIK A & POLJANEC S: Rudišče živega srebra v Idriji. JERŠEK M: Mineralna bogastva Slovenije. Ljubljana: Natural History Museum of Slovenia, Scopolia suppl. 3 (2006) 15-27.

JAHN E von & KLETZINSKY V: Idrianer Korallenerz. Verhandlungen der k.k. geologischen Reichsanstalt 11 (1870) 203-204. JANDA F: Einige idrianer Mineralien und Gesteine. Österr. Zeitschr. für Berg. und Hütt. **40** (1892) 483-485.

KOSSMAT F: Geologie des Idrianer Quecksilberbergbaues. Jahr. geol. R.A. **61**/2 (1911) 339-383.

KROPÁČ J: Die Lagerstättenverhältnisse des Bergbaugebietes Idria. Berg und Hütt. Jahrbuch 60/2 (1912) 97-146.

LAVRIČ JV, SPANGENBERG JE & REŽUN B: Organic and inorganic records of hydrothermal alteration at Idria mercury deposit, Slovenia. Geologija **46** (2003) 129-134.

LIPOLD MV: Erläuterungen zur geologischen Karte der Umgebung von Idria in Krain. Jahrbuch der k.k. geologischen Reichsanstalt **24** (1874) 425-456.

MIKLAVIČ B, REČNIK A & SCHMIDT G: Markazitno-piritne konkrecije z Matajurja. V: Nahajališča mineralov v Sloveniji. Jožef Stefan Institute. Ljubljana (2007) 345-354.

MLAKAR I: Geološke razmere idrijskega rudišča in okolice. Geologija **5** (1959) 164-179.

MLAKAR I & DROVENIK M: Strukturne in genetske posebnosti idrijskega rudišča. Geologija 14 (1971) 67-126.

MOHORIČ I: Rudnik živega srebra v Idriji: zgodovinski prikaz nastanka, razvoja in dela: 1490-1960. Municipal Museum of Idria (1960) 476 pgs.

MUCHA W: Anleitung zur mineralogischen Kenntniss des Quecksilberbergwerks zu Hydria im Herzogthume Krain. Wien (1780) 76 pgs.

PALINKAŠ LA, STRMIČ S, SPANGENBERG JE, PROCHASKA W & HERLEC U. Ore-forming fluids in the Grübler orebody, Idria mercury deposit, Slovenia. Schweiz. Mineral. Petrogr. Mitt. 84/1-2 (2004) 173-188.

PLACER L: Reconstruction of the nape structure of the Idria-Žiri region. Geologija 16 (1973) 317-334.

PLACER L: Strukturna analiza epigenetskega rudnega telesa Grübler v idrijskem rudišču. Rudarsko-metalurški zbornik 1 (1974/75) 3-28.

PLACER L & ČAR J: Srednjetriadna zgradba idrijskega ozemlja. Geologija **20** (1977) 141-166.

PLACER L: Tektonski razvoj idrijskega rudišča. Geologija **25** (1982) 7-94.

POPE W: Extract of a Letter, lately written from Venice by the Learned Doctor Walter Pope, to the Reverend Dean of Rippon, Doctor John Wilkins, concerning the Mines of Mercury in Friuli. Philosoph. Transactions 1-2/1 (1665) 21-26.

POPIT A: Vpliv seizmične aktivnosti na geokemične in geofizikalne lastnosti termalnih vod v Sloveniji. PhD thesis. Department of Geology of the Faculty of Natural Sciences, University of Ljubljana (2004) 215 pgs.

POTTER RW & BARNES HL: Phase relations in the binary Hg-S. American Mineralogist **63** (1978) 1143-1152. REŽUN B, PELJHAN M, ČAR J, STUPAR M, KAVČIČ M, ER-ŽEN U, HLAD B & HERLEC U: Geopark Idria. Geološki zbornik **20** (2009) 134-135.

REČNIK A: Nahajališča mineralov v Sloveniji. Jožef Stefan Institute. Ljubljana (2007) pg. 6; chapters on the occurences of doubly terminated quartz crystals in Triassic dolostones on pgs. 40, 194, 219 and 231.

REČNIK A, REŽUN B & HERLEC U: Die weltberühmte Quecksilber-Lagerstätte Idria. Mineralien Welt 21/3 (2010) 20-39.

REČNIK A, ZAVAŠNIK J, DOLENEC T, REŽUN B & HERLEC U: Az Idriai higanylelčhely (Szlovénia). Geoda 21/3 (2011) 12-31.

SCHRAUF A: Ueber Metacinabarit von Idria und dessen Paragenesis. Jahrbuch der k.k. geologischen Reichsanstalt **41**/2 (1891) 349-400.

SCHROEKINGER VJ: Fluorit als neues Mineralvorkommen in dem Quecksilberbergwerke zu Idria. Verh. Geol. R. A. Wien (1877).

SCOPOLI GA: Tentamen de Hydrargyro Idriensi. Venezia (1761). Flora Carniolica (1760).

SEYFRIEDSBERGER G: Über Quecksilbersulfate aus dem Mauerwerke eines Idrianer Ofens. Zeitschrift für Kristallographie **17** (1890) 433-444.

SPANGENBERG JE, MEISSER N & HERLEC U: Compound specific isotope analysis of the organic minerals hatchettite and idrialite in geodes, coal, and mineral deposits. V: STANLEY CJ: Mineral deposit: processes to processing. Rotterdam: AA Balkema 1 (1999) 275-278.

TRATNIK-DROLC M: Kristali cinabarita in metacinabarita iz Idrije. Diploma thesis. Mineralogical-petrographic Institute. University of Ljubljana (1957) 31 pgs.

VALVASOR JV: Die Ehre dess Hertzogthums Crain. III/16-18 (1689) 402-413.

VILLEFOSSE HERON DE AM: De la Richesse Minérale. Treuttel et Würtz Libraires, Paris. Vol. II (1819) str. 335.

VIDRIH R, PELJHAN M, MIKUŽ V & KLEMENČIČ T: Idrijsko rudišče in njegove rude. Proteus **57**/6 (1995) 229-236.

VIDRIH R, MIKUŽ V, PELJHAN M & KLEMENČIČ T: Minerali idrijskega rudišča. Proteus 57/7 (1995) 269-276.

VIDRIH R & MIKUŽ V: Minerali na Slovenskem. Tehniška založba Slovenije, Ljubljana (1995) 379 pgs.

VOSS W: Die Mineralien des Herzogtums Krain. Mittheilungen des Musealvereines für Krain (1895) pgs. 10 (pyrite), 17 (cinnabar), 77 (fluorite), 78 (idrialine).

ZEPHAROWICH VON VR: Mineralogisches Lexicon für das Kaiserthum Österreich. Wilhelm Braumüller. Wien.
Band I (1859) pg. 213 (idrialite) & Band II (1872) pg.
349 (cinnabar after dolomite) & Band III (1893) pgs.
133 (idrialine), 163 (metacinnabar).

ŽIBRET G & GOSAR M: Koliko živega srebra je akumulirano v poplavnih sedimentih Idrijce? Geologija **48**/1 (2005) 97-105.