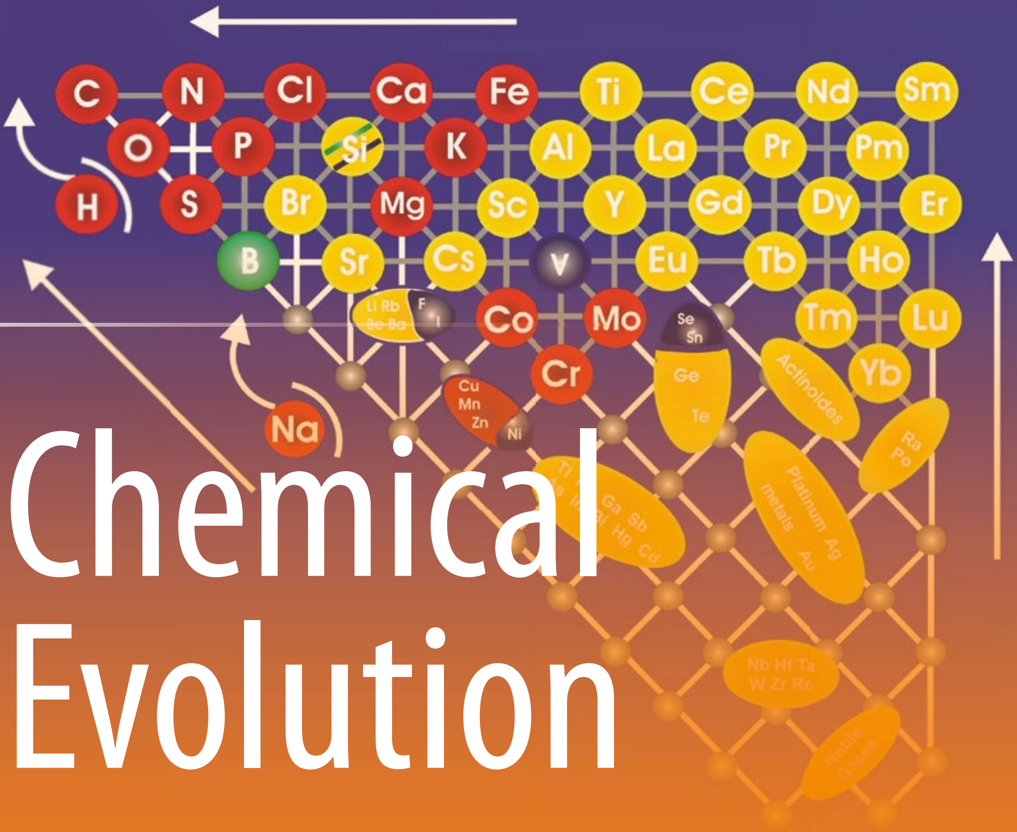
Bernd Markert · Stefan Fränzle
Simone Wünschmann



Chemical Evolution

The Biological System of the Elements

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Cover: The cover of the book represents The Biological System of the Elements (BSE) developed by one of these authors, Prof. Dr. Bernd Markert, in 1994.

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Preface

Generally speaking, we are concerned with the question: Where did organic-chemistry-based life come from?

This volume now in your hands was motivated by the attempt to discuss and to some extent explain chemical evolution from the point of view of physiological, essential, or at least beneficial activities of chemical elements in contemporary biology. From these chemical features, there may be hints to the pathway which eventually enabled biological evolution to start, using evidence from chemical evolution experiments as well as the Biological System of Elements (BSE) concerning present functions or roles of these elements.

Chapter 1 deals with considerations on the formation of chemical elements in cosmic systems and cosmochemistry providing building blocks for living beings within the Solar System, going back to astrophysical element syntheses ever since Big Bang took place some 13.8 billion years ago. Catalytic aspects observed in experiments on prebiotic chemistry and the presence of organics and HCN in interstellar medium, meteorites, and other celestial bodies all argue for a setting which is favorable for making chemical building blocks of biology right during aggregation of planets or large moons. Later on, requirements on the presence, properties, and interaction modes of environmental compartments such as atmosphere and liquidosphere in order to form life and be sustained somewhere will be discussed.

Thereafter (Chap. 2), chemical evolution would take place following pathways which are still much of a puzzle, but finally making living beings from organic molecules (and possibly additional components; *abiogenesis*). During Hadean ages ($\geq$4 bio. years from now), these processes preceded the evolution of organisms which are distinguished by a generally cellular organization. Ever since, biological evolution produced new living beings from already existing ones (*biogenesis*), chemical evolution is distinguished by the spontaneous formation of structures including chiral biases of organic molecules by chemical processes such as autocatalysis in some cases. For this to happen, there must be flow systems and throughflow equilibria. A possible (some say: most likely) reason and site for this are chemical and thermal gradients which exist around hot springs at the bottom of the oceans, better known as black smokers.

On a molecular level, biological processes follow physicochemical laws, but the actual outcomes may yet differ from “plain” chemistry due to adaptations of all organic living beings to an aqueous milieu. To start with a simple example, membrane passage dynamics of Na and K cations is the other way round than would be expected. This is unlike the hydratation of ions causing $Na_{aq}{}^{+}$ to have a larger diameter than $K_{aq}{}^{+}$ (and even $Rb_{aq}{}^{+}$) and thus pass through (nerve and other biological) membranes only in certain conditions while K and Rb ions could do so rather easily.

In order to account for physiological effects of chemical elements in living beings using some Biological System of Chemical Elements (BSE), the familiar Periodic Chemical System of Elements (PSE) according to Mendeleyev and Meyer (1869) had to be completed and modified also using the Geochemical System by Railsback (2003) which offered important hints and pieces of information.

The Biological System of Elements goes beyond accumulating essentiality investigations which have obvious technical and analytical limitations. In correlations among abundances of elements in different samples of biological origins, there are deep-rooted biochemical factors and relationships which these authors started to study and describe in more detail already in the late 1990s (Markert 1994, 1996, 1998; Fränzle and Markert 2000). Different features of chemical elements within the BSE produce the three edges of its graphic representation. These refer to the capability to form highly aggregated structures, salinity of milieu, and “organic-biochemical relatedness” of chemical species formed around this element; parameters linked to these dimensions, edges, or features accordingly have multiple implications.

In Chap. 3, the biological role of different chemical species (elements rather than their speciation forms) is discussed in more detail. Essentiality or toxicity depends on the impact on enzyme activities, far beyond coordination properties and preferences considered in bioinorganic chemistry. Beyond “simple” catalysis, biological reproduction, or it being compromised by certain elements, every protein which relies on metal ions inside or gets influenced by taking them up will influence its own reproduction in terms and manners of autocatalysis.

Stoichiometric Network Analysis (SNA), which was introduced by Clarke in the 1970s, explicitly deals with which principal modes of dynamics may be open to such autocatalytic systems in various circumstances (Chap. 4). This allows us to consider and analyze aspects of bioinorganic chemistry of metalloproteins including essentiality versus toxicity of element (speciation forms), testifying their roles as building blocks or controlling entities within or connected to autocatalytic feedback loops. The SNA theorems are used to produce a system of non-equations describing the possible or unlikely autocatalytic behavior of certain metals within the framework of biology. This is meant to enable detailed statements and even predictions whether a certain element may be essential or beneficial to physiology, and, if so, whether there are certain ranges of redox potential or binding forms such as complexes or biomethylation products which might enable such behavior.

Returning from chemical and biological evolution to the recent demands of humans, let us consider the possible role of chemical elements to be employed in medical research or health surveillance, including pharmaceutical applications of, e.g., Cr in type II diabetes or Li in a range of mental/psychical diseases. While neither element should be considered as essential for humans by now, both are obviously able to relieve severe disease symptoms in patients stricken by the mentioned illnesses.

Chapter 5 deals with the roles of water, soil, and atmosphere for chemical evolution.

Finally, Chap. 6 offers a glimpse on features of chemical evolution investigated by means of comparative (chemical) planetology, that is, we shall have a look at space research related to it, concerning both present and planned space probe missions. It is obvious that this field of research will continue to yield most exciting and informative results.

An extended and detailed Appendix gives relevant information on the functionality of singular chemical elements.

Many thanks ought to be given to all the colleagues who helped us to prepare this volume, answering numerous questions in great detail. In addition, many thanks to Springer and its staff for giving us the opportunity to publish this book and who supported us in many ways.

Dear readers, we hope to give you an impression of what chemical evolution might have been and worked like and look forward to your criticism of any kind.

Haren/Erika and Zittau
Autumn 2014

Bernd Markert
Stefan Fränzle
Simone Wünschmann

List of Abbreviations

AAN	Aminoacetonitrile
AAs	Amino acids
ATP	Adenosine Triphosphate
B&B	Bioindication and Biomonitoring Technologies
BAF	Biological Accumulator Factor
BCF	Biological Concentration Factor
BIF	Banded Iron Formations
BP	Years before the Present
Bq	Becquerel
BSE	The Biological System of the Elements
DM	Dry Matter
EDTA	Ethylenediaminetetraacetic
EUV	Extreme Ultraviolet
FTT	Fischer–Tropsch-Type
GC/MS	Gas Chromatography/Mass Spectrometry
GSE	Geochemical System of the Elements *originally:* The Earth Scientist's Periodic Table of the Elements and their Ions'
ICBM	Intercontinental Ballistic Missile
INTECOL	International Association for Ecology
IRC	Catalogue of Astronomical Infrared Sources
ISM	Interstellar Medium
IUBS	International Union of Biological Sciences
IUPAC	International Union of Pure and Applied Chemistry
KBOs	Kuiper Belt Objects
KT	Cretaceous-Tertiary
LMCT	Ligand-to-Metal Charge Transfer
LUCA	Last Universal Common Ancestor
MER	Mars Exploration Rover
MLCT	Metal-to-Ligand Charge Transfer
MT	Metallothionein
NA	Nucleic acid (RNA or DNA)

NIR	Near Infrared
NMR	Nuclear-Magnetic Resonance (spectroscopy)
NTP	Nucleoside Triphosphate
PEC	Photoelectrochemistry
PGMs	Platinum-Group Metals
ppb	Parts per billion
ppm	Parts per million
PRX	Viking Pyrolytic Release Experiment
PSE	Periodic System of the Elements
QMS	Quadrupole Mass Spectrometer
REE	Rare Earth Elements
RT	Room Temperature
RTG	Radioisotope Thermoelectric Generator
ROS	Reactive oxygen species
SETI	Search for Extraterrestrial Intelligence
SNA	Stoichiometric Network Analysis
SNC objects	Meteorites from Mars. Named after the first three (out of five now) which were actually observed while falling to Earth: **S**hergotty (India, in 1865), **N**akhla (Nile Delta, Egypt, in 1911), and **C**hassigny (France, in 1812).

Contents

Authors' Profile

Bernd Markert Born at Meppen, Germany, in 1958; Univ-Prof. Dr. rer. nat. habil., natural scientist. Finished his school education (by *Abitur*) at Maristenkloster (St. Mary´s Congregation) Grammar School at Meppen. After studying Chemistry and Biology at the Ludwig Maximilian University of Munich, he completed his PhD thesis in 1986, further advancing to obtain *venia legendi* (*Habilitation*) in 1993, both at the University of Osnabrück (Lower Saxony) supervised by Prof. Helmut Lieth. Then he had a postdoc stay with Prof. Iain Thornton (Applied Geochemistry Research Group, Imperial College London) to finally become an ICL alumnus. From London he shifted to Kernforschungsanlage (Nuclear Research Center) Jülich (North-Rhine-Westphalia) to become a scientific coworker in the team of Prof. Bruno Sansoni (Central Department for Chemical Analytics of KFA) in 1988. In this team, he got the position of Group Leader in charge of sampling and sample preparation. Reunification of Germany was soon to come; thereafter (in 1992) Prof. Markert took positions in the former GDR, first as Head of Department of Analytical Chemistry at Inland Waters Research Institute at GKSS (Magdeburg, Saxony-Anhalt). From 1994 to 2003, he was the Director of the International Graduate School (IHI) Zittau (Saxony), additionally heading the Chair of Environmental High Technology at IHI. Prof. Markert is now the head of the Environmental Institute of Scientific Networks (EISN; http://eisn-institute.de), located at Haren-Erika/River Ems next to the German-Dutch border. Since then, he does travel around the Globe to teach students and give talks and lectures dealing with his scientific hobbies. In addition, he authored/coauthored or was editor of a total of more than 25 scientific books and some 300 scientific papers. Besides attending numerous scientific conferences, Prof. Markert is a member of the Scientific Board of INTECOL (International Association for Ecology).

His research interests span biogeochemistry of trace substances across systems constituted of water, soil, plants, animals, and humans, instrumental analytic determination of chemical elements, pushing forward development and interpretation of the Biological System of Elements (BSE), eco- and humantoxicological features of hazardous substances, and pollution-level measurement by means of bioindicators and biomonitors, completed by development of waste management technologies, environmental restoration, and soil remediation. Apart from natural sciences, he is also concerned with economic and social sciences in an interdisciplinary manner, particularly for developing an ethical consensus by way of pursuing a dialogic educational process.

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Stefan Fränzle Dr. habil., born in Bonn in 1961, studied chemistry and astronomy at Kiel (Germany, next to Baltic Sea) in 1980–1986/1988–1991 (in between draft service [Zivildienst] as a conscientious objector). He was awarded a scholarship by Studienstiftung des Deutschen Volkes. He completed his graduation (Diploma) and Ph.D. (in 1992) in preparative inorganic (photo-)chemistry (Mo, Os, and Ir complexes containing CO and other ligands responding to it by switching binding modes) and discovery of two new methods to prepare transition-metal carbonyl complexes using aldehydes and visible light. Since 2001, he is giving classes in technical environmental chemistry (textbook publication in 2012), environmental chemical analytics, and other topics at IHI Zittau (Zittau International School), with an emphasis on chemical foundations of the effects and data gathered and used. He obtained his habilitation in 2008 (Hochschule Vechta, Lower Saxony) in “Environmental Sciences with a Chemical Focus”. His current emphasis of research is on the photochemical degradation of refractory pollutants in water and formic acid by different systems involving semiconductors, coordinative interaction of metal ions with biopolymers (mainly chitin from crabs), and the factors which influence the kind and extent of it (for purposes of more general modeling, biomonitoring of remote [lightless] sites, and device-construction alike), development of sensing devices to "look" into soil chemistry, and features of chemical evolution, organic cosmochemistry, apart from a continuous interest in understanding metal cycling in biota, identification/evaluation of new or uncommon bioindicators (with an emphasis on protection of organisms involved), and analysis of stability conditions/estimates of ecosystems and biocoenoses. He is the founding member of Cheesefondue Initiative and other institutions concerned with responsible, ethical work (and how to teach it, including peace research) of natural scientists.

Simone Wünschmann Dr. rer. nat, natural scientist, born in 1967 in Heidelberg, Germany. She was former a scientific assistant at the International Graduate School Zittau, Germany, Department of Environmental High Technology, working group for Human- and Ecotoxicology. Dr. Wünschmann obtained her degree of a Diploma Engineer for Ecology and Environmental Protection at the University of Applied Sciences Zittau/Görlitz, Germany, and completed her Ph.D. in Environmental Sciences at the University of Vechta, Germany. In 2013 Dr. Wünschmann was an associate professor at the University of Vilnius (Lithuania). Presently she is working at the "Environmental Institute of Scientific Networks" (EISN-Institute), Germany, and joins as a board member the team of BIOMAP (Biomonitoring of Atmospheric Pollution). She is the author/coauthor of about 40 scientific papers and four scientific books. Her research interests include pollution control, human- and ecotoxicology, ecology and environmental protection, and environmental engineering with emphasis on renewable energy. Additionally to her scientific work she is integrating her hobby, painting of pictures, into the topic of "Science and Art".

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Chapter 1
Chemical Evolution: Definition, History, Discipline

Abstract People asked for origins of life much before discovering it would "normally" not come from non-living matter, accounting for its origins rather by myths or divine interference. Yet, while the term "chemical evolution" (denoting a phase of time and set of phenomena predating and preceding biogenesis) was coined only in 1959, there were many significant theoretical and experimental contributions before. Among these, many important works predated Stanley Miller's 1953 famous experiment while being more advanced than many later similar approaches in terms of both experimental design and yields. These dealt e.g. with formation of later-on going-to-be bioorganic compounds from very simple precursors (commonly C_1- or C_2 compounds, N sources where the $N{\equiv}N$ bond was already broken, hydride or oxide precursors of the other involved elements). While history of prebiotic chemistry is not the principal issue of this chapter, it must be pointed out that catalysis—beyond looking for enzyme-like activities of mainly polymeric products—by metal ions, autocatalysis and template-organized syntheses of many compounds otherwise hard to prepare at best, became a hot topic only some 15 years ago. Again including the older works, the present body of knowledge on catalytic (mostly by metal ions or -complexes) effects in prebiotic chemistry is summed up in a table, leading into the question in how far the corresponding range of catalysts is related (and why it should?) to contemporary essential element patterns which significantly differ among multicellular organisms except for a key set which in turn is not too closely related to the experiments. This may or may not indicate a thorough difference with respect to chemical conditions.

The term "**chemical evolution**" was coined by Calvin (1959) to denote the processes converting rather simple kinds of organic and inorganic compounds into an assembly of complicated and partly polymeric chemical compounds—which got eventually capable of reproduction including mutation and metabolism related to the former phenomena by matter exchange. Notwithstanding this origin, "chemical evolution" now has become ambiguous in meaning: if you introduce this search term into some Internet search agent such as Google™, you will find something quite different for most of the first 30 or so entries, namely, rather allusions to the processes of **astrophysical element synthesis**. The latter chain of processes did

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convert that mixture of hydrogen, helium and traces of lithium from a few minutes after the Big Bang into the about 90 elements now around us inside of stars, being then liberated by the eventual destruction of these stars in supernovae. It is about formation of atomic nuclei rather than of molecular assemblies, that is, two levels lower and smaller in organization of matter.

Stars, or their central regions, are the very sites—either during their "steady mode of operation" or when ending and disintegrating in most violent explosions—where chemical elements heavier than helium and lithium are made. As living beings mainly consist of elements C, N, O, P, S, Ca and some other metals besides of H, and one simply cannot have complex chemistry with just H, Li and He around, processing of the primordial baryonic matter in stars must have occurred **before** there were any preconditions for life: water contains O, solid (terrestrial) bodies and their dust precursors require Si, O, Al, Mg, Ca, or Fe. Nowadays about 1 % of baryonic matter in Cosmos consists of such heavier elements ($Z > 5$) while the rate of star formation decreased by a factor of 30 during the last 6 billion years. The stars which afford such elements are way more massive than Sun, and they last considerably shorter. Accordingly most of the nucleosynthetic work was done long before Sun and Earth came into existence by gravitational accretion and condensation some 4.57 bio. years BP. This suggests that, even given closely similar chemical foundations, life could have evolved elsewhere billions of years earlier. A visual timeline of Earth's history including the time of physical-, chemical- and biological evolution is given in Fig. 1.1.

Although Sun was and still is crucial for life here on Earth and perhaps (perhaps!) elsewhere in Solar System, other stars require attention too, justifying the above-mentioned double use of the term "chemical evolution". This attention must include many stars we shall never see as they vanished, exploded billions of years ago, thereby providing both building blocks (matter) and a shockwave compressing matter until gravity took over to make the Solar System and probably dozens of companion stars in an early cluster which then dispersed. Figure 1.2 shows the moons of the Solar System scaled to Earth's Moon as we know it today.

People felt related to stars in observing nighttime sky, recognizing figures of their myths there and implying celestial bodies in "explaining" their origins and possible fates for millennia, long before the considerations given above were outlined in the 1930s–1957. So let us change our point and perspective of view together with them:

Centuries ago, people became aware of the fact that at least some of the thousands of bright or weak, mobile or stationary light spots they observed by looking at night-time sky are in certain respects similar to earth, that is, bodies with a solid surface, rather than holes illuminated from behind some celestial sphere. Guessing there are likely to be many more of these hidden to the naked eye, they started assuming life to exist on these worlds also, maybe even intelligent life resembling or superior to ours. This assumption was pursued ever further (e.g. by Giordano Bruno in late sixteenth century) although strongly at odds with religious doctrines of their times, with several of these authors inferring both the universe and

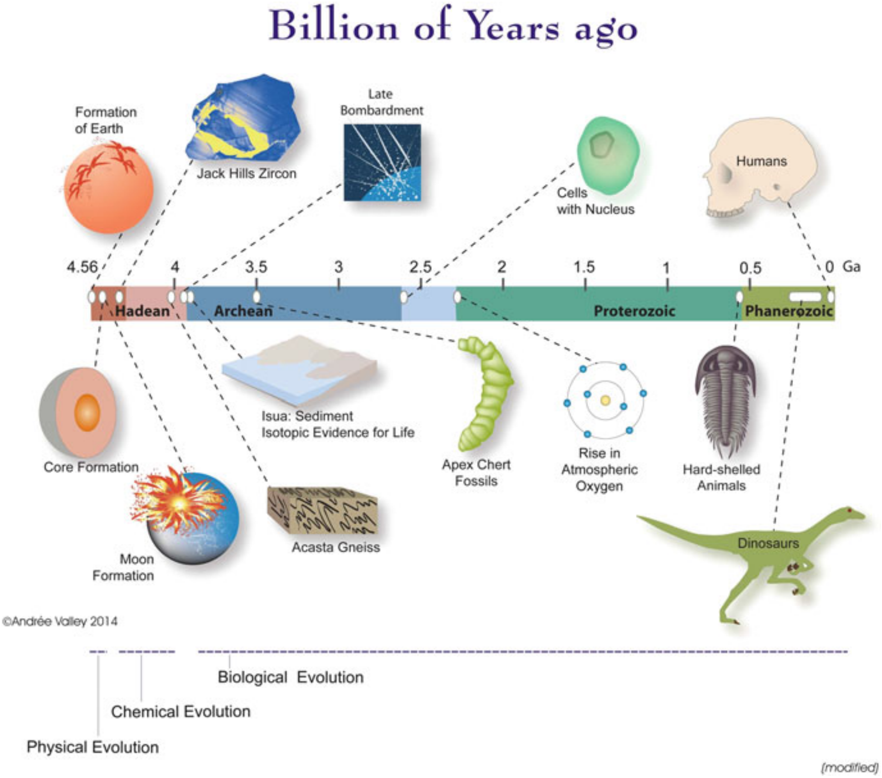

Fig. 1.1 Timeline of Earth's history, including the origin of microbial life 3.8 billion years ago and the evolution of multi-cellular life forms to the present day. Image courtesy of Andrée Valley, University of Wisconsin, Madison. Slightly modified by the authors

the number of planets inhabited by living and even intelligent beings to be infinite.[1] Soon afterwards, the telescope was invented, while there also were first experiments on the matter balance of biological processes (van Helmont), and chemistry of elements was done in a more scientific way owing to tasks of mineral and ore processing for making metals, likewise in seventeenth century. Then and after, a total of **two** chemical elements never seen before were first isolated from biological products (urine and charcoal and marine algae, respectively) around 1670 (phosphorus) and in 1811 (iodine). All others were detected elsewhere in minerals, salty

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[1] It should be pointed out that most (if not even all) of this infinite number of worlds were considered inhabited. The theological problem was not that this infinity would "compete" with (one single) God being almighty, but some notion of pantheism. Renaissance alchemists were not in a position to make any guesses on the chances of abiogenesis (which was not at all considered necessary according to Aristotle's teaching) for lack of both identity (this had to wait far into nineteenth century) and chemical properties, ways of preparation of biorelevant compounds. Accordingly invoking infinity or very large number of worlds suitable for life were not meant to overcome extremely small chances of certain events to happen: with an infinite number of sites and "runs", even miracles are not likely but sure to occur.

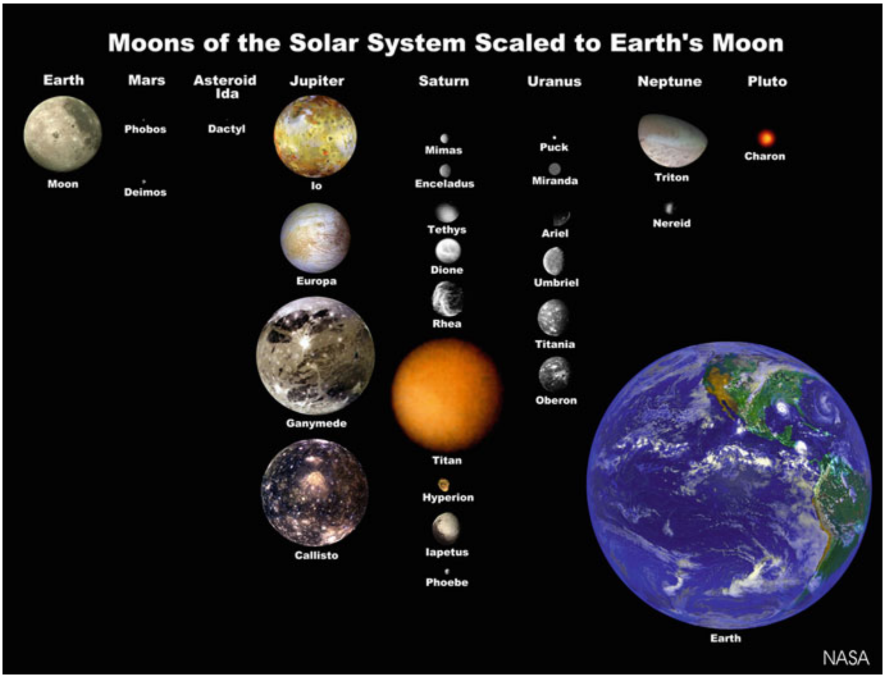

Fig. 1.2 A selection of our solar system's natural satellites are shown here to scale compared to the Earth and its moon. Image courtesy of NASA

waters, soil samples and the like or even collected as pure elemental specimen, including elemental gases[2] in the atmosphere.

But time was not yet ripe to consider the step from chemistry to biology in any modern sense of this word, even though chemical compositions of biomass were increasingly intensely studied: on one hand, it was considered sure that even complicated life-forms, such as flies, worms and even vertebrates (frogs, mice) could originate from rotting inanimate matter samples. The first ideas on this, advanced by Aristotle, began to be challenged by some scholars only in the seventeenth century. It should be pointed out that, while this was taken as evidence of life created from something else, all the most popular examples then considered made use of material which was biogenic itself, whether cotton rugs were supposed to turn into mice, slime into frogs or wooden logs deposited on ground of some lake into crocodiles. Thus, strictly speaking, the mentioned "experiments", omitting sterilization or exclusion of larvae of the animals said to form, did not give any

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[2] Even though the nitrogen content of biogenic samples/compounds like urea, potassium nitrate (niter, saltpeter), uric acid was detected very soon after N was identified as an element (amino acids and their composition were added to the list only after 1810 [asparagines] and 1820 [glycine]), the term "azote" (not compatible with life) was there to stay in French language until this day.

proof of forming organisms from anything else than other kinds of biomass. On the other hand many people maintained that there was a key feature of organic (carbon) compounds which would forever preclude their formation by human chemistry rather than biological activity (vitalism). That latter idea was refuted by experiments in the 1820s, making oxalic acid from cyanogene and urea from ammonium cyanate (Wöhler in 1824 and 1828[3]), the former took its final blow by thermal sterilization experiments of Redi, Spallanzani and later Pasteur. At about this time (1850–1870), also syntheses of certain amino acids, heterocyclic compounds including pyrrole (the sub-ring-structure of porphyrines including chlorophyll and haem) and pyridine from very simple compounds like HCN were demonstrated (Strecker 1850), as was a first synthesis of racemic sugars from formaldehyde HCHO[4] and its dimer, glycol aldehyde.

Thus a novel problem arose: there was a natural beginning to both the existence of Earth and hence to life on it. If true, processes making organic compounds which have roles in biology and biochemistry could occur without invoking any forms of life whereas the experiments of Pasteur and Spallanzani demonstrated it would not be simple or straightforward to endow the property of life to mixtures of such compounds, whatever their origins.

Moreover, regardless whether life-forms were here to persist forever or become extinct partly sooner or later, or underwent some evolution, their ultimate origins by something other than an act of divine creation had to be asked for once (a) production of organics including biorelevant compounds by non-animated systems was proven possible and (b) evolution was presumed to start with rather humble beings. Until far into twentieth century it was thought that green plants would likewise produce sugars from HCHO. Similarly, nitrate, cyanide, and formamide were considered biochemical precursors of amino acids and proteins. Even though both assumptions were erroneous, they prompted the first experiments which actually gave hints to possible pathways of chemical evolution (Löb 1913; Baudisch during the following years). Following the influential books by

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[3] Strictly speaking, the assertion of vitalists cannot be refuted at all: Wöhler, involved in doing the experiment, was obviously a living being, the ammonium salts he used for preparation of urea and cyanogene (via cyanide) were biogenic in origin, and even Miller and Urey in their seminal 1953 experiment on chemical evolution were alive and involved. But

1. we now know from radioastronomy samples of organics (HCN, $C_{2x}H$, CH_3OH, $HCONH_2$) which are older than Earth itself and
2. a thesis which cannot falsified for principal reasons of experiment and thus escapes falsification is not a scientific hypothesis at all (Karl Popper)! Thus the vitalist objection is not and never was a problem in our discussion, although certain biologists and philosophers tried to resuscitate it in various kinds of disguise (e.g. Bergson, "élan vital").

[4] This "formose" reaction was dismissed as irrelevant to chemical evolution for a long period of time as it apparently took very alkaline solutions ($pH > 13$) to operate and compete with Cannizzaro disproportionation into methanol and formate HCO_2^- ion. Now it is known that even rather dilute $HCHO + HOCH_2\text{–}CHO$ will react in presence of clay minerals or Ba^{2+} or Pb^{2+} ions to afford sugars and yields of glucose and ribose can be increased considerably by adding borate to this mixture. Prephosphorylated glycol aldehyde gives rise to "activated" sugars capable of binding CO_2.

Oparin and Bernal (1920s), photochemical production of simple aldehydes and carboxylic acids from CO_2 started to be taken relevant for the question on origins of life early in the 1930s (Dhar and Mukherjee 1934; Groth and Suess 1938).

Then astronomy, spectroscopy (starting around 1860), geology (a little earlier), geo- and organic chemistry evolved parallel to each other which produced a fundament for a new synthesis of thinking on chemistry taking place “elsewhere”, and what it might have produced in long periods of time. Now knowing (Chladni 1756–1827) for some while that meteorites were actually samples from outer space, people started looking for both organic compounds, and traces of extraterrestrial life forms in them in the 1830s (Berzelius 1834). Later-on (about 1930), first data on chemical conditions in stars and planets were obtained by astronomical spectroscopy, while first experiments supported the idea that chemical changes caused by illumination or lightning bolts or silent discharges could produce amino acids, sugars and other compounds required for life besides of precursors thereof (Löb 1913; Oparin 1924; Haldane 1929). It was straightforward that both matters and lines of reasoning became considered related to each other.

What hitherto (until early last century) had been a topic of mere speculation, e.g. on intelligent life on Mars, literary fictional novels, augmented by scattered pieces of often misinterpreted observation, now could be turned into a reasonable combination of observation and experiment. The latter, already then challenged, discussed and differently interpreted apparent observations included “channels” on Mars (Schiaparelli, Lowell after 1877), clouds on Titan and likewise on the four big Jovian moons (Camas Sola 1908). Around 1970, finally, radioastronomy replaced optical spectroscopy[5] in looking for colloquial as well as exotic molecules and molecular ions in outer space, both around stars and in the diffuse and dense, dusty interstellar medium. Doing so, radioastronomers soon pinpointed some precursors and intermediates of chemical evolution such as formaldehyde, hydrogen cyanide, ammonia,[6] propyne nitrile, formic acid, or formamide (all discovered between 1968 and 1973) in interstellar clouds, even in remoter sites like in other galaxies. From such molecular clouds and dust shrouds around going-to-become stars other planetary systems were likely to form, while direct inspection by space probes changed our basis of information on the nearby celestial bodies beginning in 1962. Table 1.1

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[5] Both gaseous interstellar matter as such (atomic Ca, in 1904) and simple free radicals (methylidine, CH, its cation CH^+ [1937], cyanidyl radical CN [in 1941] and hydroxyl radical OH [in 1963]) were detected by optical or Near-Ultra-Violet (NUV) absorptions, while assignment of absorption bands in cm- to dm-wavelengths (already known since the early 1950s) to be due to presence of larger molecules and CO began only in 1968. Now some 170 molecules and molecular ions are known in interstellar medium (ISM), disregarding unidentified peaks and isotopomers.

[6] These first three (NH_3, HCHO and HCN) are the components required to make glycine by Strecker synthesis. However, their common condensation product aminoacetonitrile (AAN) was discovered in interstellar medium only recently (in 2008) in one particular gas cloud (“large molecule heimat”). It was found near the centre of the Milky Way, and there still (2015) is no evidence for interstellar glycine although it is both a little volatile, hence might be “seen” in gas phase and pretty abundant within meteorites.

Table 1.1 Epistemological key events of cosmochemistry and astronomical observation as well as their association with laboratory tests related to chemical evolution in a chronological order

Date (year)	Site (celestial body)	Compound involved or detected	Significance; conclusion	Remarks
Ancient (fourth to third century BC)	Mars	None (change of color of planet [red ↔ yellowish] observed in Greece, Egypt, China)		Later attributed to growth of vegetation and/or inundations
1870s	Orgueil meteorite (fallen in France in 1864)	Tarry, smelly organics, "strange" microstructures	Orgueil parent body probably harbored extraterrestrial life	"Strange" structures were later identified as Earthborne biological contaminations (uncommon kinds of pollen, bacteria)
1912	Experiment in lab	Glycine	Amino acids can be formed from either aq. formamide or $CO + NH_3$ by silent or spark electric discharges	Precursor compounds do exist in comet nuclei
1922	Mars	None	Looking for possibly intelligent signals from radio broadcasts by extraterrestrial beings by eavesdropping first (**Marconi**) at 150 km wavelength, taken to exclude human technical origins	Pioneering radioastronomy which later provided the fundaments/arguments of identifying interstellar medium molecules and gross structure/properties of Universe as a whole
1931 and following	Jupiter, Saturn	CH_4, NH_3 detected in atmosphere	"Heavy" ($Z > 2$) element content in gas planets similar to that in Sun	
1937–1941	Interstellar gas clouds	CH, CN, CH^+	First evidence for molecules (hydrocarbons, nitriles), precursors or fragments thereof to exist beyond the Solar System	
1944	Titan	CH_4	First identification of a molecule in an atmosphere of a moon (rather than planet)	Long-term photochemical stability of this atmosphere was soon put into question (a problem till today)

(continued)

Table 1.1 (continued)

Date (year)	Site (celestial body)	Compound involved or detected	Significance; conclusion	Remarks
1953	Experiment in lab	Amino acids, hydroxycarboxylic acids, HCOOH, hydrocarbons	Miller-Urey experiment: spark discharge in a moist $CH_4 + NH_3$ atmosphere	Intermediates identified point to Strecker synthesis as pathway into products; link to both radioemission (lightning bolts, synchrotron radiation) in and chemical composition of Jovian planets (rather than early Earth)
1959	Experiment in lab	Polypeptides	Biopolymer precursors, which moreover are liable towards introduction of functional side chains, can be produced from gas phase ($H_2N\text{-}CH_2CN$ or HCN in atmosphere) directly by contact with clays, other minerals	
1960	Radioastronomy	–	Start of SETI campaigns to look for purposely or unintended (“evaporation” of or Earthly TV and radio broadcasts) radio signals produced by some intelligent beings	By-products: 1967 discovery of pulsars (rapidly spinning tiny neutron stars); 1977 unique signal unaccounted for which would match the criteria but never was taken again (“wow-signal”)
1969–1970	Murchison, Allende meteorites (both fell in 1969)	Variety of organics	Many compounds significant in biology are already present in meteorites, even primitive ones which never were attached to a large celestial body such as Mars	
1968–1971	Interstellar gas clouds (ISM), particularly close to galactic center	HCHO, CH_3CHO, NH_3, HCN, $HCO\text{-}NH_2$,	Precursors/reactants of Strecker synthesis detected in interstellar medium (a little later HCOOH and	When comets and planets condense around young stars, amino acids will be formed to end up in

			alkylene amines R-CH=NH were added to the list which combine into amino acids directly when heated)	possible ponds, oceans or at clayey surfaces
1970	Moon	Organics	Organics found in analysis of lunar samples (both first Apollo landing missions and Luna 16)	Partly due to proton implantation into surface carbides like schreibersite Fe_3C by solar wind, partly produced by the landing rocket gear itself
Since 1973	Interstellar medium throughout the galaxy, lateron extending to nearby galaxies	Various molecules, mainly organic ones but also CO, SiO	Mapping of tendency of formation of larger molecules related to chemical evolution throughout galactic disc(s)	Learn where astrobiology is most likely (i.e., next to galactic centers) but there possibly subject to violent activities of central supermassive black holes; it does not make much sense to look for exolife at outskirts of galaxies, let alone surrounding dwarf galaxies or old spherical star clusters
1974	Jupiter	PH_3, ethyne, propyne, H_2O vapor, HCN	Jovian atmosphere contains everything required for photo-phosphorylations in reducing conditions → pathways into "energy-storing" as well as genetics-related compounds	Was supposed to be related to both coloration and chemistry ongoing in Great Red spot of Jupiter
1976	Mars	Unidentified organics (possibly glycolic acid) [PRX], CH_3Cl and CH_2Cl_2 [GC/MS]		Biology-related experiments onboard Viking lander probes
1976	Mars	Magnetic dust	Only **the very uppermost layers** of Mars are thoroughly oxidized, possibly destroying both extant life and infalling (meteorites	Viking probes

(continued)

Table 1.1 (continued)

Date (year)	Site (celestial body)	Compound involved or detected	Significance; conclusion	Remarks
			spotted on-site since then) organics likewise	
About 1985	Experiments in lab	Yellow solid forming by UV or ionizing irradiation of condensable solids found in ISM at 10 K (CH_3OH, NH_3, CO, water); product explodes on warming above some 35 K	HCN, aminonitriles identified among products; explosive properties indicate formation of high levels of free radicals and unsaturated small-ring nitrogen compounds like 2-H-diazirine, nitrene NH	Simulates processes in outer parts of circumstellar gas clouds; chemistry probably related to behavior and properties of comets and Kuiper Belt objects (KBOs) when very far from Sun
1986	Comet P Halley	Formaldehyde polymers, formamide, nitriles and others	T cycles in a comet nucleus give rise to oligocondensation of intermediates known from interstellar medium	First close-up account of chemistry in an (already highly evolved after dozens of close sun passages) comet
1989	Triton (satellite of Neptun)	CO, geysers emitting dark particulate matter	Violent chemistry after storage of radiation in surface matter (water ice, solid N_2, CO, hydrocarbons)	First close-up investigation (by space probe Voyager 2) of an sizable object having an atmosphere to evolve photo- and radiochemically at $T \ll 50$ K (see above) and representing biggest Kuiper Belt objects (KBOs)
1995	51 Pegasi		First exoplanet (gas planet larger than Jupiter) discovered orbiting a “normal” star	
1997; 2000	Murchison, Lake Tagish meteorites	2-methyl amino acids	Chiral bias (excess of one enantiomer); homochirality may have been induced by (smaller) impactors	Strecker precursors of chiral AAs are methyl ketones R-CO-CH_3 ($R \neq CH_3$)

2002; 2006	Interstellar medium (large molecule heimat)	$HOCH_2CHO$, ethane diol	First precursors and analogs of sugars detected in interstellar medium	$HOCH_2CHO$ (formaldehyde dimer) is a required autocatalytic intermediate in HCHO oligocondensation affording sugars (formose reaction, co-catalyzed by Ba^{2+}, Pb^{2+} or clays)
2003	Outer solar system	Extremely red-colored organics in Kuiper Belt objects (KBOs)	Organic photo- and radiochemistry in cryogenic conditions ($T < 60$ K) affords products which (and their spectra) were never seen before (cp. "yellow stuff")	Indicates formation of "interesting" products; big KBOs (dwarf-planets other than Sedna) are rather white than dark-red which indicates a steadily rejuvenating surface (geysers like on Triton, Enceladus?)
2005	Titan	Large organic ions in atmosphere	Hydrocarbons, nitriles can be volatilized from cold (94 K) surface; main product of pyrolysis-GC/MS is NH_3 [Huygens lander probe]	Range of chemical evolution in unpolar cryogenic conditions?; what will happen (additionally) when there is liquid water due to impacts, volcanoes?
2006	Interstellar Medium	Mg-NC, Mg-CN, Al-NC	First interstellar molecules detected which might act as both templates (by charge transfer and Mg^+ release, followed by addition to another CN, HCN or nitrile molecule) for making "prebiotic" molecules and (Mg, Al-rich) dust	Around an old, carbon-rich dust-clouded giant star
2007	Surroundings of several stars	CH_4, C_2H_2, HCN, CO, $H_2O(g)$, NH_3	Transmission spectra of gas exoplanets ("hot Jupiters" transiting in front of their stars)	Compounds are related to Strecker synthesis yet there is neither a solid surface nor extended liquid volumes to form and process amino acids in

(continued)

Table 1.1 (continued)

Date (year)	Site (celestial body)	Compound involved or detected	Significance; conclusion	Remarks
2008	Interstellar medium (large molecule heimat)	aminoacetonitrile $H_2N\text{-}CH_2CN$		Direct precursor to both glycine and polypeptides
2009	Around several stars, Gliese 581 and others		First exoplanets found which possess a solid surface (“super-Earths”) and probably both an atmosphere and liquids on surface	No information yet on their atmospheric composition
2009	Comet (dust tail)	Glycine, alcohols, other organics	Several μg of dust particles obtained by “Stardust” probe flyby of a cometary nucleus (implanted into niobia aerogel) were isolated and analyzed	
2010	Very remote sources (cosmological distances)	CH_3OH	Laws and coupling constants of Nature did not change during the last > 7 bio. years	Chemical evolution might have worked much the same way as probably during biogenesis on Earth much before this planet or the Solar System came into existence at all (likelihood of extra-terrestrial life)
2012	Mars	Chlorinated methanes up to $CHCl_3$, HCN, CH_3CN	Cl isotopic composition linked to other Martian samples, that of C in between the range of Earth and Mars; attributed to oxidation of local organics by heating besides of perchlorate (detected before by wet extraction)	Curiosity lander/rover, cp. Viking results
2013	Mars	Clay minerals, hydrated salts like jarosite	Martian environment once was rather moist, water pools were long-lived and neither strongly acidic nor loaded with oxidants	

gives an overview of epistemological key events of cosmochemistry and astronomical observation over time.

Now, experiments on chemical evolution guided by both geo- and cosmochemical facts and settings, to the best of reconstructions possible at the time, became indispensible to understand the often puzzling data, accepting that

(a) knowledge on local chemical conditions is still limited in scope and, which is more important, in time. These bodies, their atmospheres and possible liquidospheres[7] already underwent chemical processing from outside (UV and cosmic radiation, impacts) for billions of years and inside (volcanoes, mechanochemistry). We only can investigate the present state of affairs with the most diverse and intriguing processes possibly dating far back in time, whereas
(b) the very chemical and planetological effects involved in a possible chemical evolution might have removed most of the traces (such as "chemofossils") of it since long.

Reactive intermediates are key in chemical evolution, but this is exactly why they would also have undergone additional reactions when buried in sediment. The case for a warm, dense-atmosphere wet[8] early Mars now is derived from erosion features by running waters and structures of sediment formation, not by chemical remains. It is outright impossible to say whether the absence of organics seen there is due to either

- secondary consumption by living beings while changing conditions reduced or terminated replenishment of these organics,
- reactions taking place during analytical procedures, which might destroy "fossil" organic residues altogether, or
- inorganic reactions with sediment which on Earth also prevail over formation of fossil organic fuels.

Any attempt to estimate the extent of chemical evolution which did or might have occurred somewhere, must begin with considering whether photolysis did thoroughly change chemical composition of an atmosphere with time. If so, both a changed extent of greenhouse effect, e.g. when gradually turning CH_4 into CO and

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[7] Summarizing all liquids which possibly cover larger shares of a planet or moon surface, except for molten rock (lava). The liquid might e.g. be water (Earth, Mars in earlier times), molten sulfur (Jovian moon Io), a mixture of cryoliquified aliphatic hydrocarbons (Titan), liquid SO_2, N_2, CO (possibly the latter form [-ed] lakes on either Triton or Pluto, maybe covered by thin ice layers), or something else consisting of rather abundant elements. Glaciers made of, say, water ice or creeping rock salt are likewise not considered to be a liquidosphere as they, though slowly flowing, will not dissolve salts or chemical compounds in about the same manner; a liquid would do but rather will mechanically erode the bedrock.

[8] There are all morning fogs, orographic clouds, polar ice caps, and even snowfall on Mars, but not all of these phenomena represent condensed pure water, rather CO_2 hexahydrate or even dry ice in many cases.

CO_2, and production of less volatile compounds relevant to chemical evolution can be anticipated. However, such extant photochemistry can likewise alter or even destroy a possible liquidosphere: oceans or lakes consisting of water or ammonia or methanol would experience photolysis into highly volatile gases [H_2 and O_2 or N_2 or CO] of which N_2 is highly inert towards reconstitution of NH_3; H_2 readily escapes to outer space or reacts with sediment. In stark contrast, hydrocarbon lakes like on Titan are converted into an oily slick of higher-melting and less volatile hydrocarbons, likewise loosing H_2; HCN and other nitriles which possibly fill up pools also will undergo photochemical polymerization.

1.1 What Do We Know About Chemical Evolution on Earth, Other Planets?[9]

Life is assumed to be some kind of end-point of chemical evolution, but by now the steps of development which link production of rather simple compounds in simulation experiments to formation of first reproducing entities can be inferred only vaguely. Accordingly, nobody knows which kinds of “sophisticated” intermediates were produced on Earth which were then either consumed and transformed by first and early living beings or underwent chemical changes upon heating while introduced into sediment.[10] Hence the only possible evidence of chemical evolution—unless analyzing tiny volumes of salty water included in minerals from Isua (Greenland) or stromatoliths (Australia, Fig. 1.3), and other sides—would be to look for the most distinctive feature of those organics formed during chemical evolution: their tendency to form increasingly stable complexes with metal ions.

Apparently, atmospheric pressures on early Earth were not significantly higher or lower (prior to massive later volcanic venting) than today. How can one estimate this? The “father” of geology, Charles Lyell pointed out already in 1851 how it could be done even though the actual experiment was done only recently (Som

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[9] Here, the term “planet” does not intend a restriction to considering bodies of certain size ranges which orbit the Sun directly but also refers to such moons (planetary satellites) sizable to withhold an atmosphere and liquid condensate layers (e.g. Titan, Ganymed, Triton, Io). Likewise exoplanets are included. For some of the latter, such as Henry Draper Catalogue (HD) 189733 b, information on atmospheric composition is available from differential spectra taken when transiting in front of their central star.

[10] E.g. polyphosphates which can be made starting by heating NH_4 monophosphates or photochemically from HCN, phosphate and hexacyanoferrate (catalytic if some oxidant is present) would produce simple phosphates like apatite or vivianite ($FePO_4*8H_2O$) in sediment rapidly while the CN heterocycle components would undergo hydrolysis. Amino acids and porphyrines are more stable. Isua mica and similarly old sediments are strongly metamorphic, leaving behind an isotopic signature (decrease in ^{13}C) at most which may or may not indicate that the carbonaceous solids found there already represent samples of biogenic organic matter. However, simple abiotic sources of organic matter, such as Fischer-Tropsch-Type (FTT) CO hydrogenation, can also give rise to isotopically highly anomalous methane and other compounds.

Fig. 1.3 Stromatolithes at Lake Thetis, Western Australia. The oldest fossil records of life are stromatolithes produced by an archaic form of bacteria about 3.4 billion years ago. Image courtesy of Ruth Ellison via Wikipedia

et al. 2010): falling raindrops get a limited size otherwise being torn apart by wind drag, and thus can only attend a limited speed of falling in drag-weight equilibrium. When such a falling drop of maximum size hits some soft ground, it will leave a mark (actually a little impact crater) the size of which corresponds to the speed of impact and the drop size which both are related to gas (air) density.[11] Such soft surfaces in which traces are produced and which, moreover, readily undergo fossilization to preserve e.g. footprints or the cavities made by worms or roots forever include mud (river shores, limnetic sediments) and tephra (fine-grained volcanic ashes, preferably moist). Recently very old raindrop imprints were discovered in Namibia in either material (Fig. 1.4).

Rainwater is not an inert liquid but can alter or destroy mineral surfaces by chemical attack as well as mechanical impact/fluvial erosion. Thus partial dissolution of the solids rain falls on will dissolve certain chemical elements in some oxidation states. E.g. alkali and alkaline earth ions as simple aquated cations or dications, halogens as anions, many other non-metals and some metals as oxoanions

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[11] It is just the density of the gas which matters; resistance and thus maximum speed shortly before impact do not depend on chemical composition of atmosphere but just on the superposition of pressure, temperature (likely somewhere between freezing point [there is no indication we deal with hailstones here] of 273 K and some 320 K) and average molar mass of gases (between 28 [N_2 dominating] and some 40 [with CO_2 prevailing]). Another factor of 2 comes from terrain (we do not know whether these raindrops ended in a depression like Dead Sea or somewhere up in the mountains) but the guess nevertheless is telling.

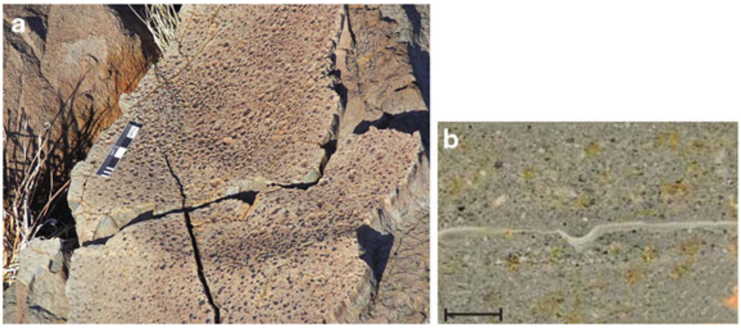

Fig. 1.4 Raindrop imprints in moist slick (**a**) and (cross-section) freshly fallen volcanic tuff dust (**b**), produced and fossilized some 2.69 bio. years ago. The size of marks depends on the speed falling raindrops attend in drag-weight equilibrium in atmospheric gas and thus to density of the atmosphere, and the sizes of the marks in these fossils are quite similar to contemporary ones. Accordingly the density of early biotic atmosphere was about the same as today, which, given an atmosphere still dominated by CO_2, that is, an average molar mass of 35 or more would mean a surface pressure of some 800 mbar. Very high CO_2 partial pressures are incompatible with the existence of carbonate minerals (which then would dissolve in the same way caves are formed in calcite, dolomite, or ferrocalcite rocks now). Source of the figure: Som et al. (2010)

which then run off with the former rainwater as dissolved species. These species can influence the chemical behavior of yet other entities they come along.

For C or N and some other elements, it is hard to guess which kinds of compounds would end up in rain- and runoff waters, except for the simple fact that simple carboxylic acids[12] or aldehydes will dissolve in water much more readily than hydrocarbons do. F.e.,

- halide ions may cause complexation of metal ions,
- acids can dissolve carbonate bedrocks,
- the dissolved ions, complexes can both undergo secondary reactions with minerals, clays, organics located somewhere downstream,
- and also catalyze chemical transformations of third substrates besides or instead of the above stoichiometric reactions.

Water is not the very best solvent to do catalytic chemistry in but it will do for very many purposes, including most of biochemistry. Aquatic transport of such dissolved reactants or catalysts will enable secondary, tertiary… reactions to take place at remote sites, far from the sites where they were produced or leached. With the products concentrated by evaporation, catalysis thus can increase both yields and selectivities of pertinent organic transformations at sites where otherwise nothing would happen at all. Precipitation of corresponding solvents (water here and probably earlier on Mars, liquid hydrocarbons on Titan), combined with runoff in lines (creeks, rivers) through intermittent pools thus links different reaction sites

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[12] There are no formates or acetates or glycolates (or nitrates) which are little or insoluble in water, excluding secondary precipitation of any salts once the acids got into water.

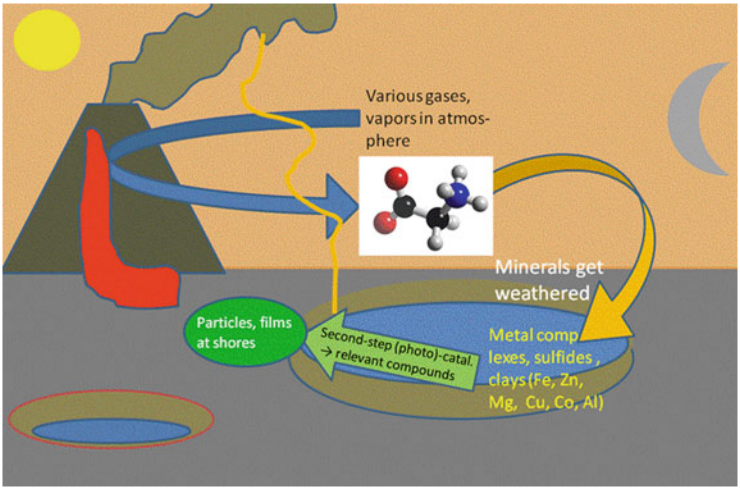

Fig. 1.5 During chemical evolution, the ability of the products to mobilize and catalytically activate metal ions from sediments or tuff would steadily increase. Besides, metal (Fe, Zn) sulfides bring about photoelectrochemical transformations. This is required to promote a sufficient number and diversity of catalyzed prebiotic reactions. Notwithstanding the relative width of the three arrows in the picture, only some small share of the previous compounds will undergo the next step in each case rather than ending in "degraded" by-products. For colors and sizes, see text. Glycine is shown just as an example although it can be considered a key intermediate in certain conditions, providing a sizable number of interesting secondary products

owing to solution properties. Moreover rainwater impact alters primary minerals to create yet other catalysts: clays, aquated Fe oxides, to name but a few.

Possible catalysis of prebiotic reactions by different compounds, complexes, and solids identified by simulation experiments or invoked from theoretical considerations, must be kept in conditions where the various catalysts can stably co-exist. The general pattern might look like demonstrated in Fig. 1.5.

Figure 1.5 is a kind of sketch, of course: the arrows show the spatial *and* chemical pathway of compounds from the atmosphere, exposed to energy sources like heat (running lava [red line to the left]), lightning bolts, UV radiation via up-concentration by preferential dissolution in water. Glycine,[13] shown in the insert in the center of the picture, is hardly volatile but most readily soluble in water. Then some pool of water (an impact crater in this example) "accommodates" the intermediates formed so far in either gas or liquid phases. Heterogeneous catalysis are taking up reactive gases (HCN, hydrogen halides, CO) from or at hot tephra, volcanic ash or pumice—then offering both medium and setting for all homogeneous and heterogeneous catalysis and photocatalysis which will link parts of the

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[13] Its Strecker reaction precursors HCHO, NH_3 and HCN all are gases [or HCN is a very volatile, almost boiling (bp. ≈ 26 °C) liquid] which all really violently dissolve in water to yield 15–20 M solutions at ambient pressure.

material into polymers. Most of these polymers, and in addition long-chained carboxylic acids which also form in secondary thermal reactions, are insoluble in water. They tend to form either "bubbles" (vesicles, micelles, microspheres and so on) or films on some surface. The orange color of the sky is the most likely one both judging from common colors of processed organics ("tholin" aerosols) and comparison with the other terrestrial planets and Titan likewise. As Earth and Moon exchange rotational momentum by tidal coupling, now increasing the average mutual distance by some 4 cm/year, the young, early Moon of "chemical evolution ages" is depicted considerably larger than Sun. Minerals, especially if containing Ti, Cu or Zn, at pool shore are likely to contribute to processing by photoelectrochemistry (PEC). PEC can be involved in making polymers, too, including peptide linkages while the mechanism based on photooxidation is uncertain (green arrow on left side of pool; maybe condensation agents are formed by oxidation of cyanide or primary amines[14] including amino acids).

When this is accomplished by solid (mainly sulfide) phases photoelectrochemically, a solid basis is needed—some kind of "soil", at least on "continents" or larger islands, not just as an atmospheric dust/aerosol—besides a hydrosphere or volcanoes next to which the sulfides are precipitated. Volcanoes by definition imply presence of some semi-molten lithosphere next to a solid crust which, however, need not be made from silicates. Yet, in all cases the fate of these compounds depends on how to deal with released hydrogen **and** oxygen from water or CO_2 photolysis, simply speaking, whether there are sinks for either as both may compromise chemical evolution.

1.1.1 How Far Might Chemical Evolution Take on Some Celestial Body?

To put it into a nutshell, the extent of chemical evolution in terms of production rates of certain compounds or of maximum complexity achieved in chemical structures cannot be determined with any reasonable precision. This applies even for early Earth and Mars, since on neither planet there is sufficient information on chemofossils which are known to predate the local origins of life. The only rather reliable statements are such that chemical evolution is precluded by either total absence of volatiles or by conditions existing in gas planets. Besides, there are few chances to find out which kind of chemistry happens below a surface "propelled" by ionizing radiation, upwelling of hot reduced compounds or of magma melts.

While we know not too much about what was going on planetary surfaces or in moderately dense atmospheres, more can be said for the stage predating accretion

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[14] NCO^- from cyanide and imines $RCH = NH$ both are condensation agents; effective (generally n-type and thus photooxidizing) photocatalysts include Ti phases rutile, anatas (both TiO_2), perovskite $SrTiO_3$, but also In_2O_3, ZnO, GaP and InP. All cyanate, imines, and cyanoamides/-imides were shown to efficiently produce peptide linkages even in dilute aqueous solution.

of the said celestial bodies: interstellar gas clouds from which stars and their planetary systems form by gravitational collapse, contain many compounds. Trace components among these compounds are either intermediates of chemical evolution, such as HCN, HC_2CN, $HCONH_2$, HCHO, and NH_3 or represent more advanced stages such as aminoacetonitrile (Loew et al. 1972). Upon being locked up in water ice or CH_4- or CO hydrates, they remain available for further photochemical processing and for delivery to planets or moons by asteroid or comet impacts.

Before discussing certain celestial objects, let us first consider the technical (astronomical, spectroscopical) advances. Together with direct visits by space probes, these advances turned little dots of nocturnal light into worlds like or unlike, but almost as differentiated as the one we live on. The changes of our conception of fairly remote surroundings and the rate this change occurred can only be compared to that Renaissance people were exposed to during the Golden Age of Earth exploration between about 1490 and 1680. Just like people then looked for gold and minerals and gems in newly discovered lands, we now ask what chemistry—including mineral formation—is like there. We can actually do statements on this problem since there was a tremendous increase in instrument sensitivity permitting to pinpoint trace and ultratrace compounds in atmospheres of weak, remote dwarf-planets and sometimes even exoplanets just about 80 years after detection of minor components of extraterrestrial atmospheres started with work by Rupert Wildt on Venus, Jupiter, and Saturn in the early 1930s. Within the last some 80 years, spectroscopic detection sensitivity for simple molecules in planetary atmospheres increased by a factor of about one trillion (10^{12} [!]) although it makes a difference whether

- a molecule is identified in near infrared (NIR) as Wildt did (absorption from the weak sunlight reflected from a distant planet in a spectral region far off the emission maximum of the Sun) or else
- by transmission spectroscopy (the exoplanets so far investigated for their atmospheric composition do transit regularly in front of their star, and some of the trace components of Neptunian, Titanian, and Plutonian atmospheres likewise were first seen and quantified during stellar occultations).

Trace components in various atmospheres are given in Table 1.2, but notice, the data do not refer to detections from orbiters or landing probes but from Earth of Earth-orbiting telescopes!

When we start to collect and consider and compare results of chemical evolution we must consider both pathways and chances of preservation of products of chemical evolution. They strongly depend on all size, structure, presence of liquids on and flux density of UV and ionizing radiation of the objects. The first and most important distinction is the classical four-kinds-classification of objects in the Solar System:

Table 1.2 Major (‰ range) or trace components in various atmospheres of well-studied bodies in- and outside the Solar System

Object	Compound in atmosphere	Approximate mixing ratio	Brightness of object	Brightness of object relative to Jupiter, Venus	Brightness of object times relative mixing ratio	Remarks, date of paper
Jupiter	NH_3	10^{-3}	−4 mag	1	1	Wildt (1932), NIR
Saturn	CH_4	10^{-3}	−1 mag	0.08	0.08	Wildt (1932)
Titan	CH_4	3×10^{-2}	8.3 mag	10^{-5}	3×10^{-4}	Kuiper (1944)
Jupiter	PH_3, GeH_4, CO	About 10^{-9}	See above	1	10^{-6}	1970s
Saturn	AsH_3	5×10^{-10}	See above	0.08	About 10^{-8}	
Triton	CH_4, CO	10^{-4}	13.5 mag	10^{-7}	About 10^{-8a}	Earthborne astronomy during 1990s
Neptune	HCN	2×10^{-9}	7.7 mag	2×10^{-5}	4×10^{-11}	
Pluto	CH_4, CO	Several 10^{-3}	13.7 mag	10^{-7}	About 10^{-7a}	
Mars	CH_4	10^{-8} (variable)	1 mag	0.1	10^{-7b}	Formisano et al. (2004)
Exoplanet HR 189733 b	CH_4, CO	About 10^{-4}				Transmission spectroscopy during stellar transit
Exoplanet HR 8799 c	C_2H_2					

The main components of the gas planet atmospheres are H_2 and He, and this probably also holds for the two exoplanets mentioned in the list while atmospheres of Titan, Triton, and probably Pluto mainly (>90 %) consist of N_2. Especially for the gas planets, data are for stratosphere conditions and $p_{total} < 100$ mbar (observed above the uppermost cloud decks) so signal intensities and relative sensitivities are influenced/increased by pressure broadening in neither case (there can‘t be any in atmospheres of Pluto or Mars down to the surface)

[a] Atmosphere some 10^4 times less dense than “standard”, hence actual positive detection threshold $< 10^{-12}$ of Wildt‘s work

[b] Atmosphere some 50 times less dense than “standard”, hence actual positive detection threshold $< 10^{-9}$ of Wildt‘s work

NIR near infrared; mag: unit of visual brightness (derived from magnitude)

- **gas planets**, which mainly “are” their atmosphere,
- **terrestrial bodies** with fairly light atmospheres (even with Venus, it is less than 0.01 % of total mass), and a hard, solid surface, sometimes (Earth, Titan, outer Jovian moons, Mars) partly covered by liquids and/or ices,
- **asteroids** lacking any atmosphere since being too small to keep it by gravitation, and
- **comets**.

In general, the maximum of an atmosphere which could develop around some terrestrial object would be produced by complete evaporation of ice layers, decomposition of gas hydrates or hydrated minerals or salts, CO_2 venting from heated carbonates, and so on. Liquid or solid water deposits on Earth and big Jovian or Saturnian satellites, the amount of carbonate minerals on Earth etc. suggest for such atmospheres utmost pressures of several 100 bar. Regardless of adiabatic heating in falling wind systems, partial to almost total collapse by condensation would be unavoidable for principal gases consisting of ≥ 3 atoms unless the entire atmospheric column is hotter than the critical temperatures of all the gases. This holds for Earth ($N_2 + O_2$) and the gas planets, but not for Titan, Mars or even Venus[15]: in the stratosphere at $p < 2$ bar, $T < 31$ °C, that is, $< T_{crit.(CO2)}$. Whether photochemistry occurs high in the atmosphere or rather close to the surface, obviously influences conditions of chemical evolution, and so does the chance of some product to be precipitated along with some liquid (H_2O on Earth, CH_4 and admixtures on Titan, probably liquid sulfur on Venus) or solid (dusts; CO_2 hydrate on Mars) matter.

Satellites of planets can be counted among terrestrial bodies or asteroids, depending on their size. There are just two satellites which retain a substantial atmosphere now (Titan and Triton), however, photochemistry or radiochemistry, and thus, chemical evolution, can also occur in solid phases, that is, ices covering a rocky or other surface. Generally speaking, the difference between terrestrial and gas planets lies with the

- limited extents of the atmospheres of **terrestrial planets**; the most massive atmospheric covers on terrestrial-size objects Venus ($p_{surf} \approx 92$ bar) and Titan ($p_{surf} \approx 1.5$ bar) correspond to gaseous matter covers of some 1.05×10^6 and 1.1×10^5 kg/m^2 above an average-level surface, respectively. The smaller relative difference owing to the grossly different strength of gravitational attraction.
- In **gas planets** there is a massive layer of gaseous, then (below) highly-compressed gaseous species including several solid or liquid-particle cloud decks which gradually convert into quasicondensed (supercritical) states. When getting downward and eventually into a dense plasma, they produce first

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[15] Now surface pressure of Venus is controlled by wollastonite + CO_2/calcite + quartz equilibrium: 470 °C/90 bars (Lewis and Prinn 1984). Crater statistics show that there was a phase of even more pronounced greenhouse effects some 700 mio. years ago, when CO_2 levels of some 300–500 bar (complete decomposition of carbonate minerals) meant heating–and global melting–of the Venusian surface to some 1,000 °C. Calcite reformation meant partial removal of this super-thick and superhot atmosphere, allowing the surface to solidify and be cratered again.

(if seen from above) molecular ions, then plasma containing atomic ions and finally they are becoming a kind of metal ("cold" degenerate matter). There is **no real surface** below this oversized atmosphere.

Notwithstanding this, except for some hypothetical scenario in "super-Earth" planets of some five Earth masses which in fact were detected among the hundreds of known exoplanets, the very existence of such a surface is crucial: there are considerable differences between terrestrial objects. This term includes planetary satellites of planetary sizes like Titan (which presently has a massive atmosphere), or Jovian moons Ganymed or Callisto (which apparently develop some much less dense ones more or less periodically) or Triton and dwarf-planet Pluto[16] (both having tenuous but weather-supporting atmospheres). The much more massive gas planets of the outer Solar System are very limited with respect to actual as well as possible extents of chemical evolution. These differences are due to both different chemical compositions and gravitation plus the existence of solid or liquid reactive layers underlying the atmosphere. These circumstances combine to permit or preclude permanent chemical changes in some atmosphere and a possible liquidosphere after their being caused by energy inputs. Parts of this energy input will simply translate to cleavage of EH- rather than EO- or ECl bonds,[17] thus causing net oxidation and dehydrogenation of gases, up to the level where there is photochemical dioxygen (and ozone, nitric acid) formation. Some small part of the free radicals and ions formed by UV and ionizing radiation, lightning bolts and so on, however, will go on to recombine to produce novel CC- and CN bonds while maintaining some of the hydrogen content of the precursors, making CHNO compounds and more complicated ones.

Concerning the importance of a solid surface and traces staying there, recently the Curiosity lander examinated martian mineral samples. Besides of just digging into fine-grained matter (thereby sometimes hitting permafrost layers or salt or amorphous silica crusts), the Curiosity lander sampling device is capable of drilling right into rocks or petrified sediments, up to a depth of several cm (Fig. 1.6).

There organics might be protected from oxidation or photodecomposition they would undergo right at the surface or in places where dust covers are regularly removed by wind. Heating such rock drilling powder produced several compounds, including NO, CO_2, SO_2, H_2S, chlorinated hydrocarbons, particularly CH_2Cl_2 and $CHCl_3$ with a shifted chlorine isotopic composition, HCN, O_2 and many other compounds, water vapor of course, not all of which are already identified. The Cl isotopic composition is identical to that observed in Martian meteorites while $^{13}C/^{12}C$ cannot be distinguished from terrestrial values. The source of SO_2 is unknown while O_2 might come from peroxides, halogenates upon wetting whereas a direct oxidation of water by some component of the soil is unlikely, given (a) the

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[16] The other Kuiper-belt dwarf-planets Sedna, Eris, or Makemake (diameters from 1,500–2,300 km) have, if any, only extremely tenuous atmospheres ($p \ll 5$ nbar), far from any saturation (resublimation) equilibrium with the known kinds of surface ices.

[17] E: Element; H: Hydrogen; O: Oxygen; Cl: Chlorine.

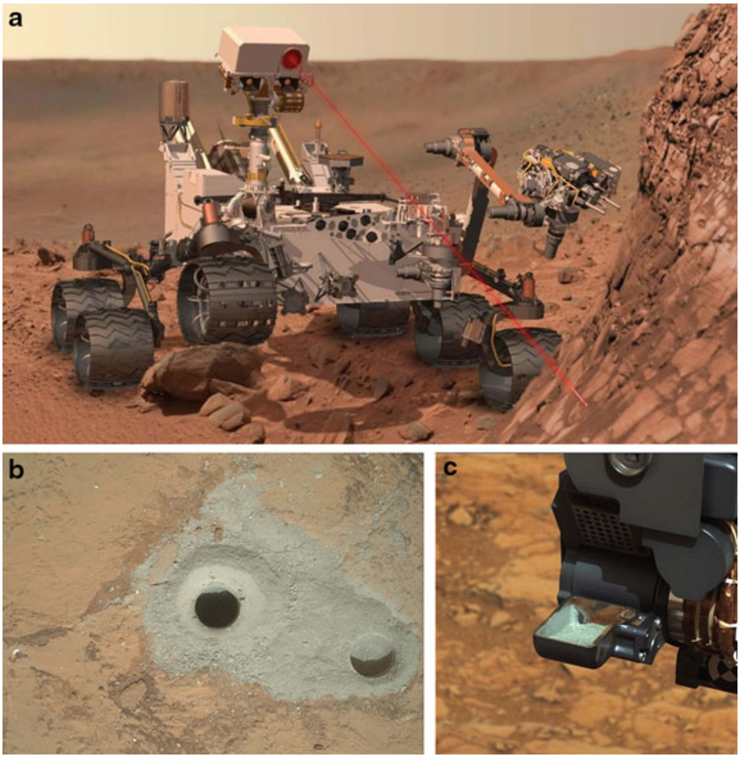

Fig. 1.6 Curiosity taking samples from Mars. (**a**) (drawing by NASA): "Curiosity" rover using its laser ablation system for evaporating samples and doing on-line optical emission spectroscopy (of both atoms and molecules). Range of device some 7 m, size of evaporated spot about 1.5 mm. The system is bright and sensitive/selective enough as to permit obtaining spectra not just during Martian night (which is not really enlightened by its moons); by now, several 100,000 (!) such spectra were taken; (**b**) two holes drilled by Curiosity rover into the same rock inside Gale Crater, covered by Fe(III) while the excavate is grayish. For the gaseous products obtained by heating such samples, see text. Diameter of drilling holes is one inch (2.54 cm). Such drilling would not have been feasible in any earlier missions because on the one hand the rovers or landers simply were not heavy enough, making them start moving (rotating) themselves rather than pressing the drill cone into the petrified or rock sample, and on the other hand electric power was insufficient at earlier stations/landers for doing such tricks (Curiosity has a constant [including nighttimes, winter] 125 W from a ^{238}Pu-powered RTG to be augmented by a Li buffer accumulator). (**c**) the Curiosity sample obtaining system. Image courtesy of NASA

presence of both reduced S and Fe and (b) the very high redox potentials of possible agents which then had to be produced by some probably photochemical process.

All six principal non-metals of Earth-borne biology were shown to be present in Martian minerals containing clays formed in neutral water, and gypsum, rather than acidigenic jarosite (K, Fe(III) hydroxysulfate), including some compounds of nitrogen, by pyrolytic GC-MS. The identity of these compounds, precursors of

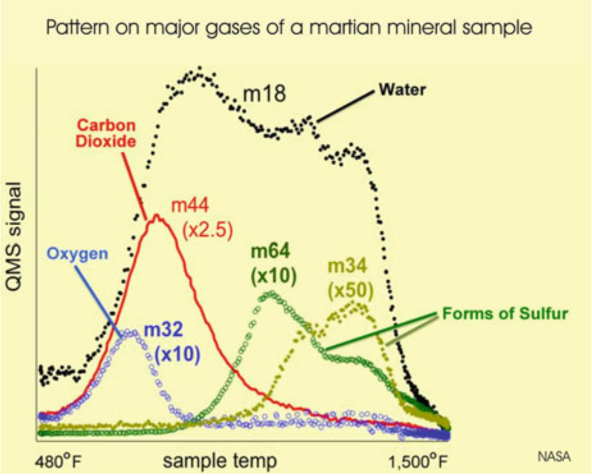

Fig. 1.7 Pyrolysis product pattern of a Martian mineral sample obtained by rock drilling and consecutive heating from 250 °C up to some 820 °C (while hundreds of compounds were identified so far, just five [H_2O, CO_2, SO_2, H_2S—"two forms of sulfur"—and O_2] are shown here). The low values of release maximum argue for thermal decomposition of peroxides including H_2O_2 peroxosolvates rather than that of alkali nitrates, perchlorates or even Fe(III)- or Ce(IV)- or similar oxides. SO_2 is released before H_2S is baked out. Sulfur release as SO_2 prior to (at lower temperatures than) that of H_2S means somewhat acidic sulfates do react with reduced carbon or labile sulfides by reduction in fairly moderate conditions. Heating gypsum or other alkaline earth sulfates such as $BaSO_4$ with carbon, organic matter, or CO affords the respective acid-labile sulfides ("fluorescent stones from Bologna") besides of CO_2. Organics were not detected in significant amounts but consider the release of dioxygen which occurs before that of SO_2 which might burn most of them at $T \approx 500$ °C within hours; this includes polymers also, the method being used for determination of organics content of terrestrial soil samples likewise. QMS: quadrupole mass spectrometer. Image courtesy of NASA

the respective gases, is still partly unknown, however. Figure 1.7 shows how the different compounds are evaporated (whether simply baked out or released due to thermochemical reactions, including release of acids then to attack carbonates and sulfides) with temperature increasing.

There are implications for a possible or likely pathway of chemical evolution in these terrestrial bodies which directly depend on their size and different surface-near structure.[18] It was pointed out by many authors before that this implies—even if Sun is so remote and thus weakly shining and photolyzing as in Saturnian (Titan)

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[18] Deeper layers may influence events as well: mixing and convection in a silicate mantle will cause volcano activity and create some internal planetary magnetic field, while introducing compounds to the atmosphere by volcano venting. Composition of which gases and condensable fluids (H_2O, HCN, SO_2,…) in turn depends on temperature and redox state of the mantle will release lots of internal heat. They produce massive ice-covered oceans above a stony central region in outer-solar system objects. This ocean then can permit chemical evolution in a dissolved medium only insofar as a) hydrolysis does not compromise the products and b) there is some energy source available below the ice covers to propel chemical evolution.

or even Neptunian (Triton) orbits—the gross atmosphere will be photochemically processed within **periods of time which are very short compared to the age of the Solar System**. "Energy-rich" products of photolysis were noted to accumulate in both Titan's atmosphere and, due to the low temperature, also on its surface, e.g. ethyne, propyne, nitriles like HCN, HC_2CN, C_4N_2, or benzene. Hence, contrary to popular assertions that "non-equilibrium gas mixtures in some atmosphere are indicative of life existing on the celestial body", **non-equilibrium is quite common** due to photochemical processes. A prerequisite for this is that the temperature is not so high as to enhance rapid re-establishment of equilibrium: in any worlds where there is UV radiation, even water (liquid or vapor) or hydrogen chloride will be photolyzed into the elements hydrogen + oxygen or chlorine, respectively. They can re-unite violently while stable, exothermic alkanes methane and ethane are transformed into highly endothermic compounds like ethyne (acetylene, C_2H_2) and propyne by UV radiation. Likewise they have a very pronounced tendency to re-absorb molecular hydrogen—or react with something else. In either case, non-equilibrium is maintained by UV irradiation as long as the H_2 does not completely escape the system (atmosphere) into outer space. What is left behind will chemically attack and alter any kind of surface, then, producing tell-tale traces which might be spotted unless for total destruction much more easily and for longer periods of time than the "original" products of chemical evolution. It may be pointless to look for organic compounds, rather, "strange" minerals or ions included in them will tell the story which happened long, long ago. An example of this might be the perchlorates[19] detected on Mars which, moreover, are capable, of "masking" the possible presence of organics by oxidizing them into chloromethanes.

Moreover, non-equilibrium situations use to be related to chemical evolution in some broader sense of this word provided there is some sink for oxidizing products of water or CO_2 photolysis. It protects the other products from immediate photo-assisted reoxidation. This even holds for Mars (once again): O_2 is absorbed by the uppermost soil layers, allowing some CO to pile up in the atmosphere with ongoing CO_2 photolysis. It arises a thin, literally rust-red cover on layers containing an appreciable share of reduced (divalent) iron. Here, time-scales are several years to decades while O_2/CO, which should be 0.5 if oxygen would be derived from CO_2 photolysis according to $2CO_2 + h\nu \rightarrow 2CO + O_2$ only, in fact it can vary from <0.3 to >2 (data from Curiosity surface analysis]). The present composition of main components of the Martian atmosphere is given in Fig. 1.8.

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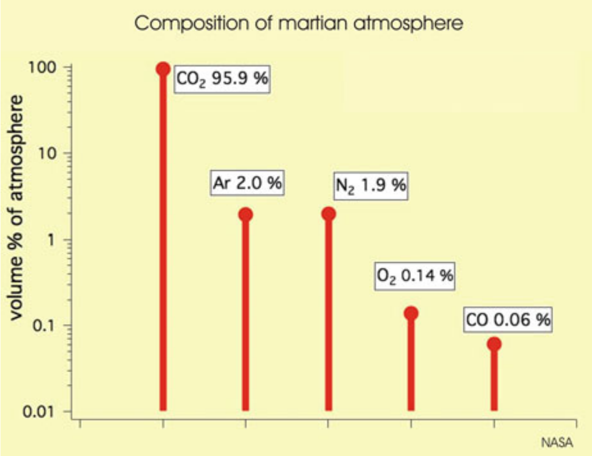
[19] Salts or minerals which contain the anion of perchloric acid, ClO_4^-. Chlor**ide** salts would be completely stable under a CO_2-dominated atmosphere like existing on Mars, and be only partly oxidized by nitric acid vapors, however, OH radicals and ozone would soon oxidize them eventually to produce fairly stable (it is a very poor, sluggish oxidant unless strongly heated) ClO_4^-. So perchlorates which use to be very soluble unless for high K contents will migrate into deeper soil layers and leave behind traces of non-equilibrium caused by UV photochemistry. On Earth, once again, there are lots of organisms which can also use ClO_4^- as a biochemical oxidant replacing nitrate or O_2 and, hence, except for some sites in Atacama desert (Peru/Chile), they are as gone as organic remains of chemical evolution.

Fig. 1.8 Present composition of Martian atmosphere (end of 2012, variable within few years). Only main components are given; trace gases like CH_4, H_2O_2 are also subject to variation. Image courtesy of NASA



So CO is **presently** (unlike the 1970s!) considerably decreased by attack by OH radicals accordingly to $CO + OH \rightarrow CO_2 + H$ which means OH photochemical precursors water, H_2O_2, and HNO_3 now control abundances of reduced gases on Mars. Even methane which should last hundreds of years there, yet is spatially scattered and sometimes even completely absent at the <1 ppb detection level (Curiosity Rover spectrometer), so its actual lifetime is of order of some weeks, rather. This does indicate the system of Martian tropospheric chemistry is somewhat unstable. This means that the "excess" oxygen, notwithstanding CO level decrease by OH, likely is due to interactions among OH and H_2O_2, e.g. $2OH \rightarrow O_2 + H_2$, with H_2 rapidly being lost to outer space. In phases of low OH production or presence of efficient OH sinks (such as recombination at Fe-rich dust) both CO and CH_4 might reach higher concentrations and enhance efficacy and product complexity of chemical evolution which however, if still in operation is more likely to take place near to and beneath the soil surface. The composition of the Martian atmosphere is variable on short timescales (Mumma et al. 2009; Encrenaz et al. 2010; Sellentin 2012).

On Mars, there are chloromethanes detected in soil samples, among them CH_3Cl, CH_2Cl_2, and $CHCl_3$. The soil layers below the immediate surface are darker in color, ferromagnetic (i.e., consist of Fe-containing phases less oxidized than Fe_2O_3). It can be uncovered by digging or by Aeolian activity (dust devils), leaving behind black lines of exposed reduced Fe-containing matter (Fig. 1.9). Dust devils on Mars are known to have been crucial for literally keeping the photovoltaics-driven rovers "Spirit" and "Opportunity" (Fig. 1.10) moving and working (both landed in 2004, with Opportunity still going on having covered almost 40 km now). General maintenance of basic functions in the rovers takes some 180 Wh/sol[20] with

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[20] One sol is a local (Martian) day, lasting about 24.66 (Earthly) hours. The above power requirement, which does not permit any movement of the rovers or even taking photographs etc., thus amounts to 7.3 W. Just compare what amount of electricity even your netbook- or tablet computer will take for operation, and the demands of the central computers of the rovers are way

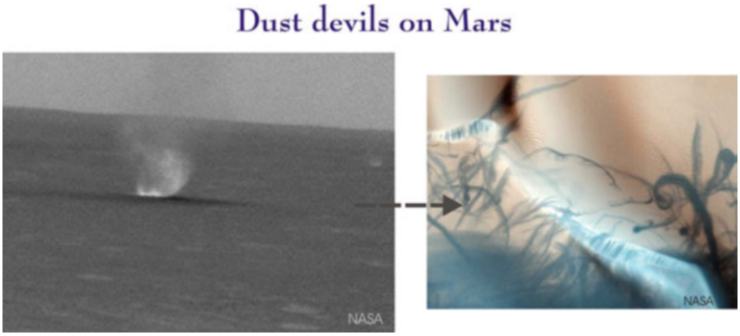

Fig. 1.9 Martian "Dust devils" eroded the thin uppermost fully oxidized (i.e., Fe(III) only) surface layer to uncover black matter a few mm beneath which then apparently is stable for some months at least. Image courtesy of NASA (*left*); NASA/JPL/University of Arizona (*right*)

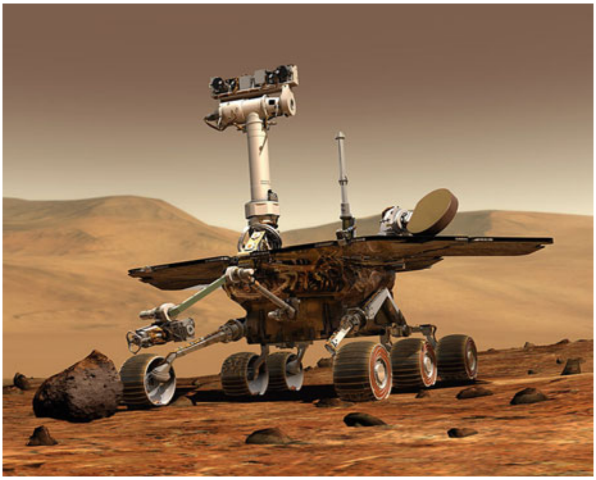

Fig. 1.10 An artist creation of Mars Rover Spirit (MER-A: Mars Exploration Rover), active from 2004 to 2010. The Mars Spirit Rover is the twin of Opportunity rover (MER-B). While the latter is still active since 2004 there was a loss in communication with Earth of Mars Rover Spirit on March 22, 2010. Image courtesy of NASA

only the "bonus" provided by sunlight (neither rover does operate in Martian tropic regions so seasonal variation of solar energy is an issue) applicable for actual fieldwork. These dust-devils periodically cover most of the surface and thus

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more ambitious, processing complex orders for proper driving in hazardous surroundings, e.g. next to crater edges, keeping radio contact to orbiters and controlling itself! Normal supply was 210 Wh/sol at just 25 % of sunlight penetrating the dust on the photovoltaic devices, so little more than 1 W (!) was available on average for driving and scientific activities before dust devils improved the situation which limited driving ranges to some 10 m/sol. The rover weighs in at some 150 kg, some 600 N weight on Mars.

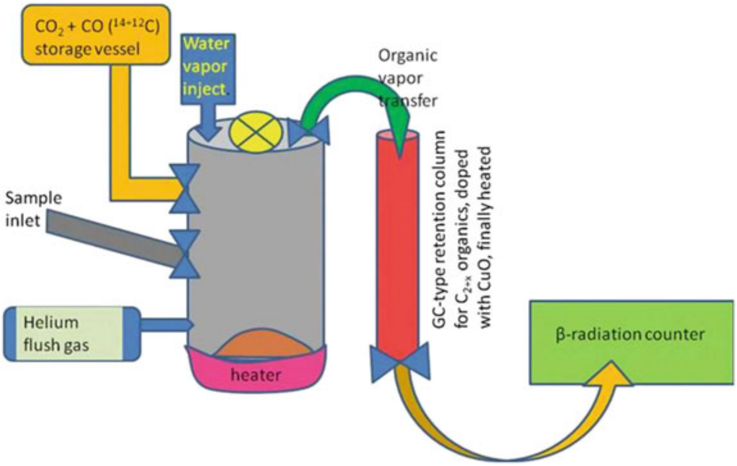

Fig. 1.11 A schematic representation of the process of "metabolism" in soil samples (Viking Pyrolytic Release Experiment [PRX]). The soil sample (several hundred mg, sieved to remove larger pebbles and coarse gravel which might block the device [meant to be used twice per cell at least]) is located above the heating plate; it may be exposed to light (bulb in *top* of cell). CuO does oxidize the organics adsorbed by the column at right when heated above 90 °C $\left(C_{org(ads)} + x\ CuO\ \Delta \rightarrow n\ CO_2 + y\ H_2O + x/2\ Cu_2O\right)$. The soil sample was obtained several cm below the surface, that is, below the super-oxidized layer (explanation in the text)

partially clean the photovoltaic devices also as they do with every other dust-loaded surface on Mars. In such systems, Fe(II) and similar reductants may intercept oxidizing byproducts of chemical evolution and thus keep it going "forward".

The process of "metabolism" in soil samples (Viking Pyrolytic Release Experiment [PRX]) was investigated by a device the function of which is depicted in Fig. 1.11. The Viking PRX was criticized for reasons of experiment design making assumptions taken from Earthly life uncritically. Yet the device worked in a way and sensitivity sufficient to

(a) detect soilborne metabolic activities wherever at least some bacteria were around and
(b) its results could but partly be reproduced in a "Mars analogue" sample system, hence should be more complicated.

The lamp (yellow) was equipped with a $\lambda \approx 320$ nm cutoff filter to preclude photochemical or photoelectrochemical production of organics; some experiments, each lasting 2–5 sols, were conducted in darkness. The heater pad (dark pink, below sample compartment) served both to test for heat-sensitive (perhaps biological) processes (after prior moderate heating to 50–160 °C) and to eventually "bake out" (evaporate) organics possibly formed or decomposition products thereof (T approaching 500 °C in the end). Helium (lower left) was added to move introduced and produced gases/vapors to the analyst assembly. In peak 1, ^{14}C-labeled carbon oxides (+ possibly present methane [orange]) were flushed and passed the column without being adsorbed; this might include CO_2 which just had undergone (isotopic) exchange with carbonates (typical peak size about 1–4 kBq). In peak 2, labeled gases (green) which had been retained by the CuO-loaded column and released after its heating were detected (typically, some 5 Bq activity of ^{14}C). F.e., notwithstanding plausibility of respective formation in the experiment, both oxalic acid $\rightarrow$ $CO + CO_2 + H_2O$, besides some HCOOH) and numerous methylmetal compounds sensitive to thermohydrolysis with water vapor according to $\left[M(CH_3)_n + x\, H_2Og \rightarrow M(OH)_n + n\, CH_4\right]$ would thus mostly or completely escape detection. As the sample compartments were not cooled, device operation was to heat them somewhat above ambient which is, sufficient to convert alkali or alkaline earth chloride hydrates into brines but not to dehydrate clays.

The experiments done onboard the Viking probes (within a small experiment box limited to some 15 kg and <30 l volume) were the first designed to search for extraterrestrial life or metabolic traces thereof which were done beyond Earth,[21] that is, on spot. For more than 30 years, no similar work would be done wherever beyond Earth (Fig. 1.12). Partly owing to this, interest in the results still is not just historical but represents an ongoing scientific debate: up to this day, complete reproduction of the results was not accomplished either in sterile conditions using various minerals and other possible catalysts nor by deliberate addition of bacteria. Among four different approaches towards the problem, the PRX is particularly important as it looks for organic chemistry linking together at least two C atoms from locally available C_1 compounds (CO and CO_2) without any assumptions of the specific pathways to do so.

If the PRX reading interpretation involves some kind of local (Martian) biochemistry/extant life, there are just three assumptions associated with this extant biota which are pertinent to detecting it:

- it is based on carbon;
- some part of the products or of their pyrolytic successors either is volatile or gets so in the conditions of the second part of the experiment. Remark: biology produces polymers, of course, but heating up them produces lots of typical volatiles you shall smell while frying some organism sample or doing a barbecue, including furanes, pyrroles, isoxazoles and other heterocycles besides of aldehydes;
- the reactions take place near freezing point of water within several sols at most (i.e. rather fast kinetics suggesting effective enzymes [in organisms adapted to local climate] are involved).

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[21] The three different devices flown on Viking Landers had originally (around 1960) been developed by the very scientists who later would be involved in the Viking experiments to look for traces of **metabolism on Earth** in places where it was presumably very low-level (such as interior regions of the Antarctic) or even unwanted (looking for bacterial contaminations of ground- and drinking waters). While some of the apparatuses were also tested on meteorites, their sites of origin then were unknown. These meteorites had been on Earth for a while already, hence such tests were not conducted beyond Earth and possibly (if not probably) susceptible to post-fall biological contaminations.

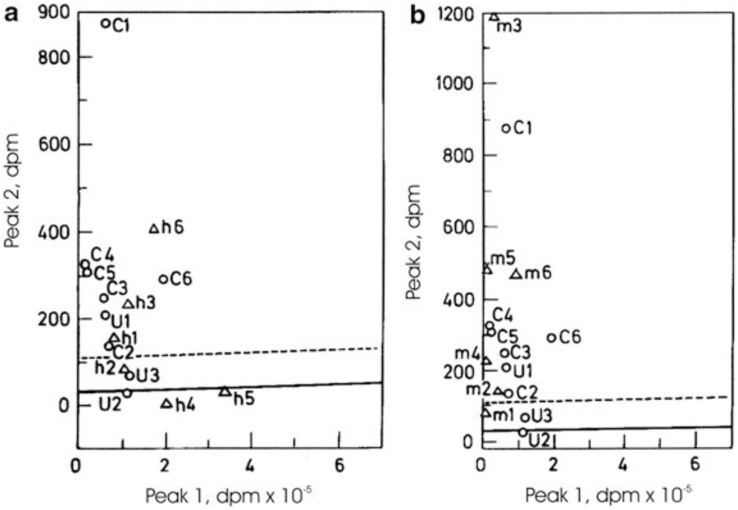

Fig. 1.12 Earth lab-based PRX model experiments with (**a**) hematite (labeled "h") and (**b**) magnetite (labeled "m") exposed to identical conditions to soils obtained and tested on Mars (C = Chryse Planitia = Viking 1 landing site, U = Utopia Planitia = Viking 2 landing site), including and comparing both Martian and model results. Except for Utopia, all the tests were considerably above the background readings. Note the different scales for the second, organics-derived ^{14}C decay signal (60 dpm [decays per minute] = 1 Bq) in both diagrams. While peak 2 in hematite samples uses to be <4 Bq, readings in magnetite (Fe_3O_4) may be up to 20 Bq, which suggests Fe (II) actually to be the primary reductant (which would work both with and without illumination: moist $Fe^{II}CO_3$ yields hydrocarbons upon heating also) (Hubbard 1979)

While now (in 2014) some terrestrial biota is known which grows and buds much more slowly, the other assumptions do still hold. While then no organics more complex than C_1 compounds were detected by GC/MS, it is not at all clear how to interpret the set of results from all four experiments—consistently in either chemical or biological/biochemical terms and from theoretical points of view. Except for halomethanes, HCN (which actually are there on Mars) and CH_3OH, dimethyl ether, -sulfide which do not either contain CC bonds, other C_1 products would (could!) not be detected either for lacking adsorption to the column (CH_4, CO) or being too labile to leave behind anything which might be detected (HCHO, HCOOH, metal formates).

Moreover, the perchlorates now known to exist in Martian soil (like in Atacama Desert and several other comparable sites on Earth) would degrade organics down to chloromethanes upon heating while non-volatile organics (polymers, carboxylate salts, amino acids) would escape either experiment completely. Salts containing organic cat- or anions will not evaporate, while acetates or higher carboxylates can only decompose into something detectable (symmetrical ketones) if present in very high levels. When, which is more likely, organics do exist (extant biology, chemofossils) or form (PRX setup) in traces, no such volatiles can be produced while e.g. oxalate, glyoxylate $HCO{-}COO^-$, formate and disperse acetate (or malonate) afford such pyrolytic products only which escape both PRX detection or mass spectroscopy likewise (CH_4, CO, CO_2).

Meanwhile, after Vikings were launched in 1975 really lots of new metabolic pathways were discovered, especially in the field of chemolithoautotrophs, and entirely new ecosystems turned up in deep sea or rock, but the above assumptions would still hold. However, they are not fully sufficient to distinguish "life"—given there is an unequivocal yet broad definition of it—from pure organic chemistry involving CO_x reduction on/by mineral catalysts or perhaps photoelectrochemistry. Notably, up to now, apparently nobody succeeded in designing experiments which come around these pitfalls.

Why Are There No Gas Planets Under Consideration Related to the Experiments?

In order to permit biogenesis rather than stop somewhere during a simple processing of organic and other (e.g. NH_3, H_2O, CO, HCN, PH_3) compounds by photochemistry, cosmic radiation, lightning bolts and so on, intermediates and (polymeric or insoluble and solid) products must take up metal ions. They must be concentrated in limited liquid volumes and adsorbed on a solid surface (or at a liquid-liquid interface). Both such liquid "pools" or ponds or puddles which might accommodate life precursors can exist on a solid surface only. Starting chemical evolution with fully hydrogenated compounds like CH_4, NH_3, water, H_2S means formation of amino acids etc. is tantamount to dehydrogenation, e.g.: $2\ CH_4 + NH_3 + 2\ H_2O\ h\nu \rightarrow H_2NCH_2COOH$ (glycine) $+ 5\ H_2$

Moreover, gas planets do not only lack a solid surface (there are most likely liquid drops in clouds and fog layers somewhere in the atmosphere, except for "hot Jupiters"), but most of the gaseous shrouding is H_2 [22]. Intermediates of chemical evolution like CO, HCHO, higher aldehydes and HCN are susceptible to hydrogenation in the H_2-dominated dense, hot lower atmospheres of gas planets (given the H_2 partial pressures, temperatures and Fe-, other metal oxide phases in the lower atmospheres, even N_2 is likely to react, affording ammonia).

Steady and irreversible loss of H_2 is essential to chemical evolution, hence, and chemical evolution can take place only in small bodies which have both an atmosphere and solid surface, with smaller or larger pools of some liquid around. These celestial bodies might be either planets, dwarf planets or large moons among which the latter offer the best chances given they cannot become locked up into bound rotation with the star in the center of the system. In turn, gas planets cannot offer the surroundings in which chemical evolution could go on, however. If there is little internal heat production in a gas planet, like with Uranus, its atmosphere will

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[22] In smaller gas planets (Neptune type), H and He constitute $< 30\ \%$ of total mass. There may or may not be a large metal/silicate core in them (that of Uranus is about 0.7 Earth masses [some 5 % of total]) but shares of heavier elements C (probably producing a solid layer of diamond [!] inside the planet), N (there is substantial N_2 in Neptunian atmosphere, guessing from the density, scale height and HCN abundance likewise), O, S, Ar are much higher than in Jovian planets ($>70\ \%$ in total).

be stably stratified, meaning whatever is going to become a liquid or solid after photochemical processing will just sink down and be buried for ever; that is why Uranus appears so clean and somewhat boring in the telescope as well as in close-view inspections. If, however, there is convection, the above hydrogenation processes which give rise to compounds like PH_3, AsH_3, GeH_4, and CH_3PH_2 will simply reverse the primary processes of chemical evolution. So there would be nothing left to be accumulated by adsorption or undergo further processing.

The **lower limit** of size for a possible abode of life depends on retaining an atmosphere at all, while the maximum size is given by solids being present at parts of the surface (not completely covered by water or other solvents) and hydrogen getting lost to outer space. In cases of doubt, this latter might soon be proven by determining the deuterium[23] content of volatiles in the atmosphere against the background star. This D content should be substantially larger than that of gas planets (some 35–40 ppm of H in Jupiter, Saturn and Neptune), e.g. it is 156 ppm on Earth, a similar value on Titan (143 ± 16 ppm in CH_3D) and even 1.5 % (15,000 ppm!) in both water vapor and sulfuric acid on Venus. For Mars, the D content of soil/clay waters was recently determined, here $H/D = 1,284$, that is, $D = 778$ ppm, meeting the expectation that H depletion on Mars went further than on either Earth or Titan. Obviously there cannot be any direct conclusion from the respective D levels on how far chemical evolution went but $D > 40$ ppm is a necessary indication that it could occur at all.

Planets (terrestrial planets) are nice things but have some disadvantage to grow life on at least when judging from the presently known sample of exoplanets: in long-lived, low-mass/low-luminosity[24] stars suitable celestial bodies which orbit them directly (planets) or indirectly (moons) must be close to the stars. Hence they tend to be tidally locked into bound rotation. Then a planet faces its star always by

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[23] In chemical terms, deuterium behaves much like "normal" hydrogen although it does react some five times slower as a rule. C-D- or O-D bonds are somewhat stronger than their CH, OH counterparts meaning in a dense atmosphere with close-to saturation absorption of the latter photo dissociation of elem.-D bonds is effectively shielded, causing relatively fast enrichment of deuterium in the remaining volatiles. In high atmospheres (around the respective exobase), element-H and element-D compounds can undergo dissociation by reacting with either excited argon (which is abundant, having a metastable excited state) or various cations, ejecting either neutral or cationic H/day at energies of several eV. Then the ejected H atom or proton is close to escape speed in larger terrestrial planets (let alone Mars or big moons, of course) while D, being twice as heavy and more strongly bound before, will move some 30 % slower, thus is likely to be (better or totally) retained by the planet or moon. Accordingly, insofar as the possibility of H loss to outer space is significant for progressing chemical evolution, an enrichment of D in the celestial body suggests **one** condition of chemical evolution is met: the object is not too large (although this yet does not imply there is a solid surface: we now know $<4\ M_e$ gas planets ["sub-Neptunes"] as well as $\approx 10\ M_e$ solid bodies ["super-Earths"] in the sample of exoplanets observed so far).

[24] Along the hydrogen main sequence, luminosity goes approximately with $M^{3.5}$ for the stellar mass range $M = 0.1–10$ solar masses, implying the former is some 3,000 times less luminous than Sun while the latter is 3,000 times more luminous. Hence in this mass range which covers >99 % of all stars the distance star-solid object (planet or moon) at which appreciable temperatures exist, e.g. maintaining liquid water at the surface do vary with $M^{1.75}$.

the same side while a moon would do so with respect to its planet only. Except for the unlikely case that both orbital periods are identical, a moon will be lit from every side periodically regardless whether its planet is locked into bound rotation while there are seasons on the moon. They correspond to the orbital period of the planet for any rotational axis of the moon which is inclined towards the orbital plane of the planet. But this does make an advantage only if there are both an atmosphere and liquids on the moon for long periods of time which means it must be really big.

The most interesting case is Titan (see also Sect. 6.4). On **Titan**, aerosols are formed along large negatively charged ions in the atmosphere which attract intermediates such as HCN to grow into yet larger particles. As the atmosphere is way too cold to contain any significant traces of water vapor, ethyne is made to trimerize in such cloud particles, yielding benzene rather than undergoing hydrolysis, and some acrylonitrile $CH_2{=}CH\text{-}CN$ rather than acetaldehyde. During its parachute descent towards Titan surface in January, 2005, Huygens probe pyrolytic GC/MS apparatus "swallowed" several larger neutral or anionic particles pyrolysis of which mainly afforded ammonia, not HCN. This renders it likely ammonium salts are also present in the aerosols while the level of N organics capable of eliminating HCN is low. Condensation of unsaturated hydrocarbons and HCN into such a mixture continuing to be exposed to UV radiation while hydrolysis is excluded would be a prolific source of aminonitriles, carbamidines, and cyanamide. Evaporation of shallow lakes mainly consisting of liquid CH_4 and C_2H_6 leaves behind thin layers of more complex organics which are no longer volatile in these conditions, with similar films covering "rocks" which most likely consist of water ice (Fig. 1.13). There are rather high mountains on Titan while craters use to be flat, i.e. largely filled up with soft or even liquid matter or by some kind of "sand" forming dunes (sand rather consisting of water ice and organic particle). At 450 km above average surface level T and p are about 180 K (almost twice the temperature at the surface) and 5 μbar pressure; that is, e.g. HCN, CO_2, or C_3H_4 would be volatile enough to remain gaseous and be detected[25] all the time unless being bound to haze particles.

When comparing Cassini photographs to former Voyager and Pioneer photos and Earth-bound high-resolution Titan pictures, the higher-level hazes likewise appear to vary in density, extent, and color within months to years. Of course, accordingly the chance to adsorb the above volatiles after their formation in the upper stratosphere will vary as well. The general structure of atmosphere and liquidosphere on Titan and its effects on a possible chemical evolution are given in Fig. 1.14. While the stratosphere of Titan is rather warm (up to some 160–190 K), allowing even to suspend some water vapor, T in tropopause goes down to some 70 K, precluding an exchange of C-containing volatiles other than CH_4, CO (both are present in Titan's atmosphere at some 4 % and 50 ppm next to the surface) in gaseous state through this layer. Compounds forming above by EUV or cosmic

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[25] By present Earth-bound spectroscopy and local gravitational acceleration on Titan, detection limits would be about 10^{-10} bar or 20 ppm at 450 km.

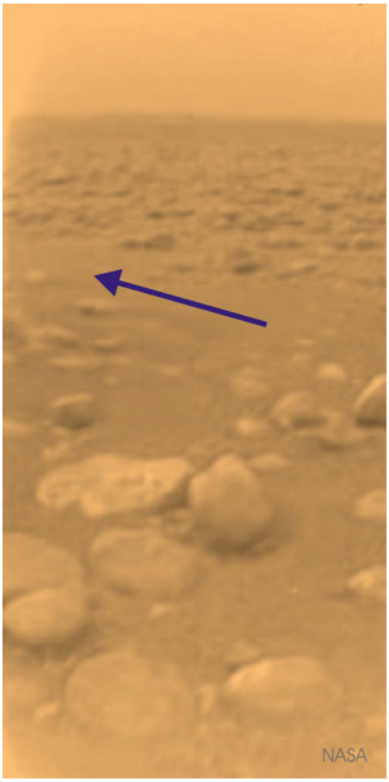

Fig. 1.13 The surface of Titan at Huygens landing site, January 14th, 2005. Note the similarity of surface cover and atmospheric colors and that of the latter with the atmospheres of Mars and Venus. Huygens lander probe touched down in the offskirts of a then inactive fluvial delta; the shallow ditch not covered by “pebbles” or “rocks” a few m away might belong to this structure (*arrow*). Size of forefront pebbles: about 15 cm. As the heat shield remained attached to lower end of Huygens probe, hot material came into direct contact with the soil, volatizing different compounds which had condensed among the grains of water ice. Thus, benzene, ethyne, propyne, and nitriles were identified right on the surface. The hydrocarbons are soluble in liquid CH_4, C_2H_6 at some 94 K to get into deeper-located basins. Fluvial activity caused by rare but massive liquid methane rainshowers would wash out those of the above compounds, plus aminonitriles and possible products of photochemistry including water ice (E.g. methanol, formamide HCO-NH_2, HCN, ethane diol (= ethylene glycol), formic and glycolic acids. However none of these would dissolve in aliphatic hydrocarbons even at room temperatures or readily mix with benzene, let alone if much colder. As a result, the water ice pebbles would cover with some polar “wrapping” to which solutes from the creeks or rivers would be adsorbed if being a little more polar themselves, much in the manner of classical chromatography (not, reversed-phase). Further chemical evolution on Titan then should take place on these ice pebbles rather than in the spectacular lakes around its North pole). Image courtesy of NASA

radiation (Titan moves outside Saturn’s radiation belt, unlike the big Jovian moons) such as HCN, $C_{2x}H_2$, or HC_2CN would trickle down as solids and possibly polymerize thereby rather than be re-evaporated in the lower troposphere where

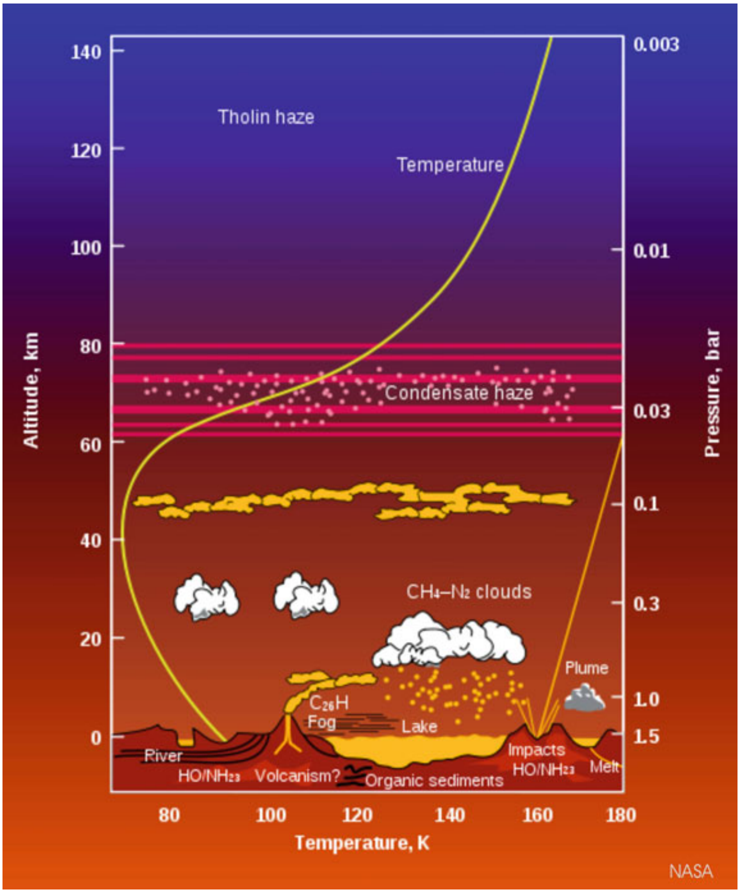

Fig. 1.14 Titan's atmosphere and weather phenomena. Description in the text. Image courtesy of NASA

T increases back to 94 K at 1.6 bar surface pressure. There is a haze layer right at the minimum of temperatures in the atmospheric column. In the troposphere, methane can exist in all three states and thus produce weather phenomena much like water does on Earth, including clouds, rain, and snow. The three haze/fog layers in the warmer lower stratosphere (pink in this diagram) are due to photochemical polymer production rather than reversible condensation, except for HCN enrichment.

We do not have a satisfying knowledge of how far chemical evolution could get on the four outer large terrestrial objects of the solar system. Except for knowing its most positive outcome on Earth, that any possible products of chemical evolution were just burned away near the surface of Venus,[26] there is no atmosphere or hydrosphere on the Moon (and apparently never was).

Mars remains a puzzle despite most arduous and ardent attempts to find out till today. But what can be said is that the atmosphere of early Mars (and Earth, Venus alike) was not too strongly reducing, meaning that the fate of an atmosphere which contains or once contained substantial hydrocarbons under continuous photochemically changing insolation must be studied elsewhere. Gas planets destroy everything which is produced beyond the very first products (like HCN, HC_3N, C_2H_2, propyne and benzene) soon after by re-hydrogenation. Smaller bodies having a solid surface, that is, moons of these gas planets might behave differently. In our Solar System, there are two such moons. They have appreciable dense atmospheres although both are exposed to truly cryogenic conditions and thus weak photochemical activity and little volatile abundances and variation widths, e.g. NH_3, amines, HCN or water would not remains gaseous to any significant extent. These two bodies are Titan, the biggest satellite of Saturn and its counterpart with Neptune, Triton, which is even much colder than Titan, limiting the density of its atmosphere; either is dominated by molecular nitrogen N_2. Table 1.3 gives a summary of most "advanced" products of chemical evolution observed on different bodies of the Solar System.

1.2 Where Is Life Coming from (Time, Site, Setting)?

This is to say that life originated once, somewhere on Earth or nearby, while all contemporary living beings are fairly closely related in terms of their biochemical and genetic-information-storage fundamentals while the setting is much less clear.

Interfaces are superior to dilute solutions; photochemistry in a homogeneous system (atmosphere, clouds, clear near-surface waters without substantial vertical mixing) would be destructive rather than constructive in the long run and so on. Nevertheless, some parts of the setting might be reconstructed by asking which kinds of intermediates and solid or dissolved catalysts would be required to obtain several key components of biochemistry. Furthermore, in which conditions these catalysts might co-exist to process the intermediates side-by-side to permit further mutual and cross-wise "constructive" reactions. Suffice this to say for now. A more detailed description from the above reasoning, also addressing the issue of "primeval" essential elements, is given later-on.

The idea that life originated in chemical conditions rather different from the present ones found on Earth while life, moreover, then removed both the chemical

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[26] Surface temperatures are some 450–470 °C on Venus while amino acids decompose at 200–300 °C rapidly and hydroxypolycarboxylic acids and sugars are way less stable, especially if exposed to concentrated sulfuric acid (sugars turn into carbon, hydroxypolycarboxylic acids into unsaturated compounds like acrylic acid, acetone, however formic and oxalic acids decay just into CO, CO_2).

Table 1.3 The most “advanced” products of chemical evolution observed on different bodies of Solar System (second and third column from the left)

Body	Atmosphere	Sub-surface	Radiation sources	Catalytically active minerals present?	Remarks
Meteorites	None existing				
_common chondrites		Amino acids, ketones, long-chain hydrocarbons and alcohols			
_from Mars		Traces of amino acids (Nakhla meteorite)		Mainly basalt, some clays, carbonates which promote condensation and hydrogenation reactions	
_stony irons				Metal phases can act as FTT catalysts, producing hydrocarbons and amino acids, alcohols from presolar nebula	
_others					
Mercury	None existing ($p \approx 10^{-14}$ bar)	Unknown, but evidence for local volcanoes, very high average density			
Venus	rapid equilibration in hot atmosphere; SO_2 and COS possibly from recent volcanoes	Organics would be unstable under such a hot CO_2-based atmosphere			
Earth	Atmosphere processed by biota to become enriched by O_2 while CO_2 was distinctly depleted			Abundant but partially indirectly biogenic; many active minerals would not exist unless for a high-O_2 atmosphere	Life exists here

(continued)

Table 1.3 (continued)

Body	Atmosphere	Sub-surface	Radiation sources	Catalytically active minerals present?	Remarks
Moon	None existing	Diverse organics at ppm- to ppb levels			
Mars	CO, CH_4, HNO_3	Chlorinated methanes, probably simple carboxylic acids, maybe more complicated precursors of either which underwent solid-state oxidation during sample extraction	UV light from Sun, no filter by ozone but absorption from Fe oxide aerosols	Fe oxide aerosols, clays on surface	Subsurface chemistry and origins, variation of CH_4 are poorly understood but investigated now
Jupiter	Higher hydrocarbons, C_6H_6, CH_3CN, HCN, HCP	No surface			Earlier (1950s and 1960s) prebiotic simulation experiments in fact came close to Jovian atmosphere conditions: presence and retention of excess H_2, much CH_4 and NH_3, some H_2S
Io	Various gases of volcanic origin (SO_2, COS, CO_2) but no evidence of further photochemical or similar processing			Silicates, molten sulfur, sulfates	
Europa		H_2SO_4		No, covered by ice and liquid water	
Ganymed	O_2-based (photogenic or radiogenic) atmosphere which presumably changes density between two states (about 10^{-5} and $<10^{-11}$ bar surf. pressure)			No, covered by thick water ice layer(s)	

Callisto	Like Ganymed			No, covered by thick water ice layer	
Saturn		No surface		–	
Titan	N compounds which release NH_3 upon pyrol. GC/MS, large organic anions, aerosols	C_6H_6, N compounds, alkanes up to > butane and unsaturated ones (in lakes)		?	
Enceladus	No static atmosphere	Organics co-ejected with water, NaCl by “geysers” at South pole		?	
Uranus	Massive atmosphere, but there are no trace gases from (photochem-)ical evolution	No surface		–	
Neptune	HCN	No surface		–	
Triton	Components of inversion layer $[(CN)_2]$**?**	Colored, probably N-containing intermediates likely to undergo violent decomposition upon solar warming		? (no information on thickness of volatile ice layer over rock; geysers eject unidentified dark dusts)	
Pluto	Ice components indicate photooxidation (e.g., CO_2) but too cold to maintain them in atmosphere	Colored spots (rather red to yellow) of unknown composition, ices include N_2, CH_4, and CO		?	

products of these processes as kind of nutrients and the very conditions, at least dates back to nineteenth century. A famous letter by Charles Darwin (1871) [directed to Robert Hooker] reads as follows:

> It is often said that all the conditions for the production of a living organism are now present, which could ever have been present. But if (and oh! what a big if!) we could conceive in some warm little pond, with all sorts of ammonia and phosphoric salts, lights, heat, electricity etc. present, that a protein compound[27] was chemically formed ready to undergo still more complex changes, at the present day such matter would be instantly devoured or absorbed, which would not have been the case before living creatures had formed.

This very difference between early-Earth conditions and contemporary state of matters, where such products, protolife or chemical intermediates would either not be formed at all, readily oxidized or devoured by more evolved organisms, was re-emphasized in 1924 by A.I. Oparin, a Russian biochemist. His book essentially re-shaped thinking on the entire problem.

Later-on substantial chemical differences were pinpointed which distinguish sediment samples about as old as the origins of life from younger ones and especially those revealing enrichment of dioxygen (produced by algal photosynthesis) in the atmosphere. Accordingly the former might give an idea what geochemistry was like during or soon before or after origins of life on Earth.

Life as we know it could not have originated soon after the Big Bang anywhere in the Universe since no C, N, O, P did not yet exist anywhere but were produced in stars only about half a billion years later. Chemistry then had to evolve, and life had to come only later. This statement is a general one, even permitting for panspermia however unlikely this may be. Accordingly this chemical evolution eventually leading into biogenesis had to take place somewhere and somehow. Concerning life on Earth, it is likely to have happened right here or at least within the Solar system.

The timescale of crucial events of developments (Table 1.4) is as follows; provided life evolved on Earth independently this happened > 3.6 bio. years ago. Whether there was "impact frustration" destroying previously originated life-forms during or before the "Late Heavy Bombardment" like demonstrated in Fig. 1.15 (see below), is doubtful as Earth, unlike Moon (the maria on its front side), Mars

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[27] Keep in mind that then and much into twentieth century (Avery et al. 1944) inheritance, and the capability to transfer genetic information to the phenotype and undergo inheritable mutations, was not attributed to some chemical entity other than protein, that is, while nucleic acids were known already their actual function and importance was completely ignored. Proteins were then known to form most of biomass while their role as enzymes was neither yet identified in Darwin's times: the first set of enzymes operating outside of living cells or larger organism bodies, "zymase" involved in glycolysis and ethanol (+ CO_2) formation from glucose was obtained by Buchner in 1897 (15 years after Darwin's death). Up to this obvious change of a carbon backbone structure, the role of enzymes was held to be restricted to causing hydrolysis (E. Duclaux [1840–1904], quoted after Mason 1991). Later-on, zymase was shown to be a mixture of enzymes, with the first crystallinic enzyme isolated only in 1926 (urease from beans, much later found to contain and operate by using substantial Ni; animal urease is unrelated to this enzyme complex altogether).

Table 1.4 Developments in Solar System and shaping Earth in geochemical and -morphological terms: dating versus implications

Mio. Years BP	Event	Traces left behind	Remarks	
4,568	Supernova triggers collapse of presolar cloud	Decay remnants of hardly volatile radionuclides like ^{44}Ti, ^{26}Al, ^{32}Si, ^{60}Fe in primitive meteorites, producing "anomalous" Ca, Mg, S, and Ni located in the most refractory phases	Collapse produced not Sun alone but a loose cluster of stars some of which were likely identified	
4,527	Impact of a Mars-sized other protoplanet ("Theya") produces the Moon	Moon and its chemical similarities with Earth's upper mantle		
4,403	Oldest dated zircon $ZrSiO_4$ crystal found on Earth so far	The very mineral grains	Was probably formed in contact with liquid water already	
Before 4,200	Large pools of water form on Earth			
Around 3,950	Late heavy bombardment by medium-size asteroids		Deduced indirectly from comparison with neighbor celestial bodies (Moon, Mars, Mercury); there are no huge impact basins on Earth like on any of these bodies, and no larger areas on Earth being so old as to represent the respective astroblemes	Time range of biogenesis
About 3,850	Oldest rocks traced to sediments	Isua, Akilia shists, greenstones (Western Greenland)	Highly metamorphic material, no clear chemical residues of (biogenic?) organic matter; $^{13}C/^{12}C$ ratio probably too much modified in petrogenesis to draw conclusions on biological carbon contributions	
Between 3,950 and 3,700	Onset of plate tectonics		Created magnetic field of Earth thereafter protecting atmosphere from being removed by solar wind; reason	

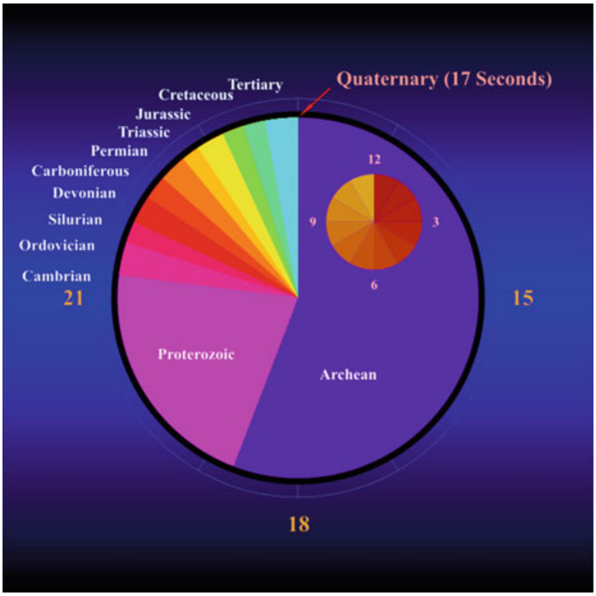
(continued)

Table 1.4 (continued)

Mio. Years BP	Event	Traces left behind	Remarks	
			of (fairly late) onset of mantle convection is not obvious as heat-flow from Earth core to crust is likely to steadily decrease with time going on (formation of aqueous phases or certain minerals with low viscosity and poor heat conduction in mantle or even origins of novel deep-mantle heat sources?)	
About 3,450	Onset of large-scale photo-synthesis	Oldest stromatoliths (calcified colonies of cyanobacteria)		
Before 3,100	Photosynthesis based on similar photo-chemical processes as today	Porphyrines, phytane sidechains among chemofossils		
Around 3,000	Atmosphere becomes more oxidizing	Oldest banded iron formations, hexavalent Cr and U in certain sediments	Implies contributions to heterotrophs nutrition from processes similar to previous chemical evolution came to an end	

Fig. 1.15 "Late Heavy Bombardment" on Earth. *Left*: An artist's impression of a Ceres-sized asteroid (≈1,000 km diameter) hitting Earth during Precambrian. *Right*: Barringer Meteor Crater in Arizona. Created 50,000 years ago by an impactor only 50 m (160 ft) across, it evidences that the accretion of the Solar System is not over. Image courtesy of (*left*) D. Davis, work commissioned by NASA; (*right*) D. Roddy, U.S. Geological Survey

Fig. 1.16 Earth history mapped to 24 h. An Earth clock showing relationship of duration of the various era/periods of the earth history to 1 day. The Quaternary, comprising the last 2.6 million years, is just 47 s on a clock where 24 h are related to the total age of the earth of 4.5 Billion years. Image courtesy of H. Grobe, Alfred Wegener Institute for Polar and Marine Research, Bremerhaven, Germany



(Hellas Depression) or Mercury (Caloris Basin) does not display truly huge impact craters or lava-filled basins of like origin.

As for details of the process, not too much is known: we now know how to make "interesting" compounds, fairly small molecules, from a set of precursors and energy sources (and catalysts) which are fairly realistic in geochemical terms. But it is open what might have been the pathway from there to polymers capable to do reproduction/replication, metabolism and eventually undergo Darwinian evolution. This also limits the extent of information to be obtained from the existence of e.g. amino acids and sugars in meteorites, of still ill-defined organics on Mars, HCN, HC_2CN on Titan, or biomonomer precursors like glycol aldehyde, aminoacetonitrile, formamide etc. in interstellar gas clouds. This statement also holds for chiral biases detected in meteorites: probably both the compounds and some of their features were "useful" for origins of Life—but we now cannot really tell in how far and to which extent. Figure 1.16 shows how the different events are distributed over history of this planet. While vertebrates and other highly evolved animals, as well as land-dwelling green plants, did exist only during the last about 10 % of this history, one should not conclude that evolution got faster or even approaching some "aim" in the nearer past: simply for the vast majority of both morphological and chemical fossils (including fossil fuels) came from these last 13 % (21:00–24:00 in the mapping), and the animals found there are more related to ourselves, we tend to make more and more detailed distinctions in periods of time close to us than when considering older stages (although there are quite a number of different sub-divisions of old geological periods, defined by biostratigraphy, some of them [e.g. Tommotian, Frasnian, Maastricht, also referred to in this volume). The chemical features of biogenesis, however, remain inaccessible from fossils, e.g. there are no cyanocomplex minerals like Prussian Blue while HCN was an obvious intermediate of chemical evolution.

Meanwhile the results corroborate our laboratory simulation experiments and suggest **biogenesis** was more likely/frequent/abundant to occur than without these building-blocks around. We cannot deduce a meaningful estimate on how likely it actually was on different bodies of this Solar System, on this or that exoplanet/ exomoon or in this region of the Galaxy[28] or much farther out. Generally speaking, chemical evolution creates chemical complexity in some small fraction of organic compounds subjected to a flow of energy while biogenesis, requiring previous chemical evolution is the huge leap from there to self-replicating systems capable of mutation and selection.

The Miller-Urey experiment was truly a seminal one (Fig. 1.17). Even though there were precedents in interpretation of which the respective authors, aware of e.g. the Strecker synthesis pathway for making amino acids, the relationship between autocatalysis and reproduction (Kuzin 1938; Oparin 1947) or of the possibility to prepare sugars from HCHO (Löb 1913; Groth and Suess 1938; Garrison et al. 1951), considered implications for understanding origins of life. However, most of them, including Miller & Urey, used conditions which are rather far from realistic geochemical settings in the early Earth, f.e. applying some high level of photochemically very labile ammonia. Nevertheless it inspired lots of work also considering more realistic conditions and ways of energy input in a very short period of time while the old champion theorists, including Oparin and Haldane, started supervising much of this work in the USSR and United Kingdom, respectively.

1.2.1 Photochemistry Controlling Chemical Evolution

A planet or moon obtains all light, UV radiation and heat from some central star. Now, the radiation flux at some black body increases with the fourth power of absolute temperature (Stefan's and Boltzmann's law of radiation). It takes about 1 W/m^2 on average to maintain the temperature of liquid nitrogen or CO (68 K melting point), for liquid methanol or ammonia (some 190 K) it would be some 60 W/m^2 and for water (273 K) it amounts to 250 W/m^2 if the planet or moon has an atmosphere of just negligible greenhouse effect. An atmosphere will produce a certain greenhouse warming effect, requiring less insolation to keep surface lakes

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[28] The levels of biorelevant elements are higher in the part of the Galactic disc than in either the halo or near its center, however, the "thrilling" molecules were spotted right around the center ("large molecule heimat", near to Sagittarius A2) of the Milky Way or next to old, dying, carbon-emitting ("sooty") stars such as IRC 10216 which means there could be no more productive chemical and biotic evolution; in the best of cases, a supernova might blow most of this matter out into the building-blocks of yet novel stellar systems.

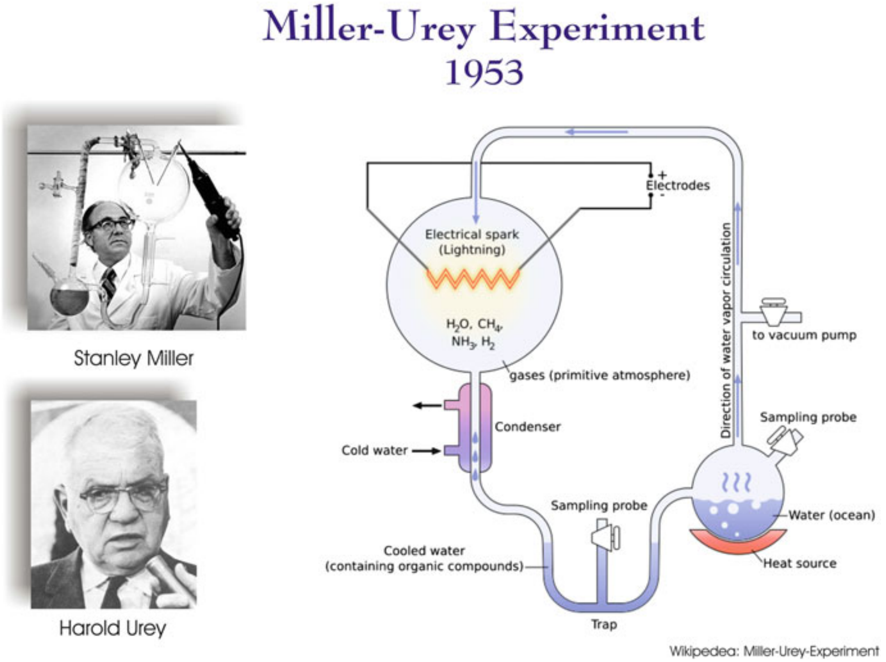

Fig. 1.17 The Miller-Urey Experiment simulated the conditions thought at the time to be present on the early Earth, and tested for the occurrence of chemical origins of life. Specifically, the experiment tested Alexander Oparin's and J. B. S. Haldane's hypothesis that conditions on the primitive Earth favored chemical reactions that synthesized more complex organic compounds from simpler organic precursors. Considered to be the classic experiment concerning experimental steps towards abiogenesis, it was conducted in 1953 by Stanley Miller and Harold Urey. Fotos courtesy of Wikipedia

liquid (liquidospheres which consist of the above compounds). However, a star is a source of approximately blackbody radiation itself, hence the visible and IR radiation needed to keep possible liquidospheres liquid (and keep the atmosphere from collapsing) and sustain possible life evolving there is accompanied by an impact of UV radiation, and the latter spectral fraction will produce photochemical changes in all the media and phases.

Hence the question what now is left over from chemical evolution is related to the timescales this UV radiation needs to thoroughly alter chemical state of atmos- and liquidosphere versus the age of some planet. A liquidosphere will control surface chemistry and mobilize metal ions if it consists of compounds which are both photochemically reasonably stable and capable of solvating ions or form complexes with them, being so polar as to dissolve salts also; if the above conditions are fulfilled **and** temperature (unlikely on Mars, an open question concerning Titan), pressure are such that an extended liquidosphere can persist for long periods of time, it might become the key and main site of chemical evolution on that celestial body. Even for a dense atmosphere and lakes in an outer-solar-system object, CH_4 and other reactive compounds should be removed from surface and atmosphere within a few million years. All the chemical evidence on Earth which is available from the few sites where very ancient sediments and minerals survived from about the origins of life, in Western Australia, South Africa, Greenland, and Minnesota, shows that there were no piles of organics produced[29] from a strongly reducing atmosphere even then. Concerning chemical evolution, there are two possibilities to account for this phenomenon:

1. the organics were produced but mostly consumed thereafter by evolving heterotrophic life-forms (Darwin's 1871 argument), though some are conserved in the Greenland and Australian shales. In addition the Isua and Akilia samples are rather metamorphic, having experienced considerable heat and pressure after deposition which implies organic matter had been fairly soon removed from access and being devoured by whatever organisms. In addition comparatively recently formed oil and brown, black coal deposits give proof of the modest though fair chances of organic carbon to escape consumption even if deposited under a strongly oxidizing atmosphere and with an extant biota.
2. production rate of organics was small from the beginning, implying levels of CH_4 and other hydrocarbons in the atmosphere were at least too low to produce all-organic aerosols, that is, less than about 0.1 %.

Obviously the second line of explanation is the much more likely one. This, however, places some stringent limit on extent of greenhouse warming in the early atmosphere, too.

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[29] The interpretation of (carbon) isotopic data, which are often used to pinpoint biological/biochemical activity, for carbonaceous sediments from Greenland (Isua and Akilia sites, some 3.8 bio. years old, both located next to Greenland's capital Nuuk) still is controversial. While there is ^{12}C enrichment in organics in these shales over the average 1.1 % ^{13}C like that which would be expected analyzing biogenic carbon, one must address the question which isotopic signatures would be produced by (a) photolysis of organics (whether these organics are themselves formed from CH_4 or represent products of some later stage of chemical evolution unrelated to methane or are biogenic) and (b) Fischer-Tropsch-type (FTT) reactions making hydrocarbons from CO and H_2. In case (a), obviously photochemical removal of methyl or methoxy groups is favored by higher vibrational excitation and lower bond energy of ^{12}C containing functional groups with respect to ^{13}C counterparts. As a result, photolysis would produce "light" (that is, ^{13}C-depleted) methane while the solid or liquid residues would be enriched—rather than depleted—in ^{13}C, with the effect most pronounced in longest effective wavelengths which prevailed in the spectrum of young Sun. FTT processes can produce almost any isotopic composition of carbon products, mainly depending on the kind of catalyst used, including minerals, clays or even iron meteorites, So, while Isua and Akilia organic samples may or may not be biogenic, they are obviously not produced by photolysis. Hence the (carbon species of the) atmosphere of that times might have been dominated by either CO (giving rise to FTT reactions) or CO_2 (like today or on both Mars and Venus, also matching the composition of gases exhaled by volcanoes) but not by CH_4 or other (less stable) hydrocarbons.

1.2.2 Catalysis of Reactions in Prebiotic Chemistry

The key intermediates of chemical evolution are generally produced by exposing more or less reducing gas- or gas/liquid- or gas/sorbate systems to energy sources (UV light, ionizing radiation, spark discharges, mechanochemistry) and accordingly contain compounds which are somewhat enriched with energy. Yet, they may or may not represent the least energetic, thermodynamically most stable ones among their isomers while the above energy-input and creation of novel functional groups (aldehyde, carboxylate, carboxamide, phosphonate, alkyne etc.) rendered them capable of more, faster and more different reactions than the molecules they were made from. This does not imply that reactions which provide (in our point of view) "interesting" products now would occur at particularly high rates or even in a selective manner; on the contrary, there are mutual reactions which destroy products already prepared. You are familiar with several of these "obstructive" reactions: just mix and heat some mixture of sugars (saccharose, fructose, starch) and amino acids or peptides (egg yolk, hydrolyzed soy protein, white cheese, etc.), add some source of gases such as CO_2—and you end up with bread or a cake or cookie. Why? This is due to the Maillard polycondensation which leaves behind but few volatile compounds which combine all four elements included in both reaction components, namely, C, N, H and O, as oxazoles (responsible for the tasty smell of fresh bread or cake) and the notorious acryl amide which forms in frying potatoes and other starchy plant samples.

Hence you must find a way to work around reactions which provide polymers which are insoluble and thus protected against dilution but cannot be processed any further during chemical evolution. Simply speaking, you must somehow enhance (speed up) reactions which convert the above components into something "useful" rather than having them react mutually, that is, certain processes must be **catalyzed**. In "advanced" biology, this would be done by enzymes; however, many of these still depend on metal ions in the central units which give rise to their catalytic activities. When enzymes were not yet around (before life originated), the very metal cations or complexes thereof could act as catalysts for the same transformations, their specific modes of catalysis favoring certain chemical reaction pathways among the many open to a larger "energetized" molecule. Thus they are producing more of certain secondary products on expense of side reactions like the Maillard transformation.

This will prompt us to look for catalysis by metal ions or complexes or metalliferous solids in prebiotic reactions, comparing the empirical results on this topic which considerably increased during the last years to the pattern(s) of essential metal elements. There are theoretical reasons associated to features of autocatalytic or even reproducing systems which constrain conditions (Eigen 1971; Eigen and Schuster 1979; Clarke 1980; Wächtershäuser 2007; Orgel 2008; Fränzle 2010); these constraints and specific (selective) catalytic modes produce more information than could be gained from simply comparing the present state of knowledge on "prebiotic catalysis" and the metals used there to inorganic biochemistry.

The common pathways into formation of amino acids and sugars use compounds which are rather high-level in energy, often considerably endothermic with respect to the elements, like HCHO, CH_3CHO, HCN, HC_2CN, and so on. Accordingly, these intermediates have plenty of possible reaction pathways, particularly since they are unsaturated compounds which can add quite different chemical species[30] including mutually each other. Most of these pathways yield products which cannot readily go on into chemical evolution, although there are "positive" exceptions, e.g. the primary product of HCN hydrolysis, formamide HCO–NH_2. Chemical evolution consists of an appreciable number of subsequent reactions on intermediates during which yields (each just a fraction of one [=100 %]) must be multiplied with each other. In the end, the yields would be minute, detection of the respective "prebiotic product" being rather a challenge in ultratrace analytics than depicting a real(-istic) pathway unless one increases selectivity of one or several steps of the reactions. And this is the point about catalysis:

A catalyst, especially an ambient one like clay minerals, will promote (enhance reaction kinetics of) just one or two of the many possible reactions accessible to some intermediate; thus processing the intermediate in presence of a catalyst will "focus" chemistry into this pathways, with increase of yields being dramatic in multistep reactions. Catalysis, however, does not (cannot) shift position of chemical equilibria. Hence, production of "prebiotic" compounds many of which do not represent the minimum energy isomer of the possible compounds of equal composition [e.g. minimum of $C_2H_5NO_2$ hypersurface [stable species only] is not glycine but carbamic acid methyl ester, then glycolic acid amide (Szöri et al. 2011; Lattelais et al. 2010)] from precursors by catalytic (rather than photochemical, photocatalytic [PEC] or radiation-chemical) transformations takes use of rather energy-rich precursors. Sakurai and Yanagawa (1984) studied catalytic ("modified seawater medium", 105 °C) syntheses of glycine, oxalic acid, hydantoin, and carbamoyl glycine, plus several condensates including oligoglycine peptides from $HCHO_{aq}$ and $NH_3OH^+{}_{aq}$, that is by way of formaldoxim $CH_2=N(OH)$. Given thermodynamics of NH_2CH_2COOH, $H_2C_2O_4$, urea etc. and energies of CH_3NO precursor isomers according to $3\ CH_3NO\ \{\text{catal.}\} \rightarrow NH_2CH_2COOH + \text{urea}\ CO(NH_2)_2$, this could not be done using CH_3NO = formamide HCO-NH_2 but only either putting energy to this molecule before (see Table 1.5) or employing more energetic CH_3NO equivalents like aqueous HCN or just formaldoxim. Before and during biogenesis, **crosswise** (A favors formation of while B favors formation of A) and **auto**catalysis additionally attain significance which then permits to stabilize structures and chemical entities which are both hard to make and not too stable in thermodynamic as well as photochemical terms (except for glycine). If one really wants to understand chemical evolution, one must thus consider reasonable, that is, geochemically reasonable catalysts and photocatalysts. That is the purpose of Table 1.5; most of corresponding work was published only during the last 10 years.

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[30] Cp. the comparative study on catalysis of HCN oligomerization and amino acid formation by nitriles formed by additions such as glyconitrile (HCN bound to HCHO), glyceronitrile (HCN bound to HCHO dimer glycol aldehyde), methoxyacetonitrile and aminoacetonitrile (Schwartz et al. 1984).

Table 1.5 Metal ions and -complexes and solid phases (including photoelectrochemical catalysts) involved in promoting or catalyzing reactions of some prebiotic significance or consumed in such reactions

Product (molecule group)	Educts	Metal promoters, *catalysts*, speciation form	Metals and speciation forms used in technical syntheses	Educts of technical syntheses	Energy sources, reaction conditions, possible intermediates	Remarks, quotations
Higher hydrocarbons	$CO + H_2$	Various (clays, iron meteorites)	Transition metal oxides, doped with various materials	Same		
NH_3	NO_x^-	Fe(II)			None, RT, aqueous	exothermic reduction
	N_2	FeS/pyrite	Doped Fe oxides	$N_2 + H_2$		High-pressure, high-T reaction
	$N_2 + (HCHO)_n$	**MoO_3**/HCHO (photochem.)			Light	N gets also included in amino acids (Bahadur et al. 1958), visible light
		Fe(II), Mo salt, aminothiol, reductant			None	Self-organized Fe/Mo complex; aminoethane thiolate works better than cysteine (Schrauzer 1975), ambient temperature and pressure
HCN	$CO + NH_3$	**Al (clays)**				Formamide is also processed
			hot Pt or Bi_2O_3, educts $CH_4 + NH_3$ (+ O_2)			

(continued)

Table 1.5 (continued)

Product (molecule group)	Educts	Metal promoters, *catalysts*, speciation form	Metals and speciation forms used in technical syntheses	Educts of technical syntheses	Energy sources, reaction conditions, possible intermediates	Remarks, quotations
HCOOH	CH_4	Unspecified metal ions (mixture)			Spark discharge, NH_4^+ also present	M carbonyls as intermediates? Kobayashi and Ponnamperuma (1985)
	HCHO	**Al**- or **Zr** salts, OH^-				Cannizzaro disproportionation, by-products methyl formate and sugars
Oxalic acid	Formamide	**Fe-sulfur compounds,** including pyrite, pyrrhotine FeS, bornite Cu_5FeS_4 and CuS			160 °C	Is it stoichiometric reduction or catalytic process?; Saladino et al. (2008)
Pyruvic acid	HCOOH	**Fe thio compounds**			250 °C/2000 bar	HCOOH acts as source of CO and H_2; probably heterogeneous catalysis (FTT)
	Oxaloacetate	**Ni^{2+}, Cu^{2+}**			Decarboxylation	Pedersen (1948)
Lactic acid	Glyoxylate CO_2, SO_3^{2-}	**ZnS**			Photoelectrochemical, sulfite as sacrificial oxidant	By-products formate, oxalate, and little glycolate; Guzman and Martin (2010)
Long-chain carboxylic acids	Glycine	**$MnCO_3 + Al_2O_3$**; 240 °C			Mn^{2+} directs pathway of reactions, for products from neat glycine/Δ see Heyns and Pavel 1957	Ivanov and Slavcheva (1984)
HCHO, higher aldehydes	Alcohols	Fe(III), photo-oxidation				

Aminoacetonitrile	NH_4^+, CN^-	**Fe(II)** (probably being $[Fe(CN)_6]^{4-}$ or $[Fe(CN)_5(NH_3)]^{3-}$; photochem. ($\lambda = 253.7$ nm)			UV light	Absorption maximum of polycyanoferrates (II) about 270 nm; Abelson (1957)
	Cyano-complexes, $NH_3 + HCHO$	All metal ions producing sufficiently stable but photoactive cyano complexes				Complex photolysis releases cyanide to start Strecker synthesis
HCN oligomers		Mo(IV) or **$[Mo(CN)_8]^{4-}$**				Template synthesis of adenine
Sugars	HCHO	$HO\text{-}CH_2CHO$ (addition required), **clays** or **Ba^{2+}** or **Pb^{2+}**				
Amino acids	Cyanogene	**Cu(I)**				Beck et al. (1977)
	$CO + H_2 + NH_3$	**Al (clays), iron** (meteorites)				Hayatsu and Inoue (1971); iron meteorites contain Ni in mixed-metal ("alloy") phases, schreibersite and other components which are known to influence product patterns of FTT processes
	$(HCHO)_n + (NH_4)H_2NCO_2$	**Cu^{2+}**				Photochem., yields Asp, Glu, and Lys; Santamaria and Fleischmann (1966)
	$(HCHO)_n + (NH_4)H_2NCO_2$	**CuS/Na_2S**				Photochem., yields Lys and Asp; Santamaria and Fleischmann (1966)

(continued)

Table 1.5 (continued)

Product (molecule group)	Educts	Metal promoters, *catalysts*, speciation form	Metals and speciation forms used in technical syntheses	Educts of technical syntheses	Energy sources, reaction conditions, possible intermediates	Remarks, quotations
	$(HCHO)_n + (NH_4)$ H_2NCO_2	**Fe^{3+}**				Photochem., yields some Val and Ala; Santamaria and Fleischmann (1966)
	$(HCHO)_n + (NH_4)$ H_2NCO_2	**Co^{2+}**				Photochem., yields much Lys first but then photodecomp. takes over; Santamaria and Fleischmann (1966)
	$(HCHO)_n + (NH_4)$ NO_3	**Cu^{2+}**				Photochem., yields traces of Leu, His and Val first but then photodecomp. takes over; Santamaria and Fleischmann (1966)
	$(HCHO)_n + (NH_4)$ H_2NCO_2	**FeS/Na_2S**				Photochem., yields Lys and Asn; Santamaria and Fleischmann (1966)
	$(HCHO)_n + (NH_4)$ H_2NCO_2	**CoS/Na_2S**				Photochem., yields very much Ala, Asp in the beginning; Santamaria and Fleischmann (1966)
	$(HCHO)_n$ + air (N-source)	**Co^{2+} + Fe^{3+}**				Photochem., yields Gly and Ala; Santamaria and Fleischmann (1966)

	CO + aqueous nitrite	**Fe(III)**				
	$(HCHO)_n$, NO_3^-	**Fe(III)**				Photochemical excitation necessary although net process is exothermic; only prolific synthesis of proline (Bahadur 1954; Bahadur et al. 1958)
	N_2 + $(HCHO)_n$	**MoO_3**/HCHO (photochem.)			light	Process demonstrated to be lightdependent, PEC activation of MoO_3? (Bahadur et al. 1958), visible light
	CH_4, C_2H_6, NH_4Cl, $S_2O_3^{2-}$	**Fe^{2+}** or **FeS suspension**; UV light (253.7 nm)			(Difficult to reproduce; Miller and Urey 1959)	Products include phenylalanine, valine, and methionine; Ellenbogen (1958)
	HCHO, NH_4^+, SCN^-	**Mg^{2+}**			RT	Cell-like hollow structure also form (“sulphobes”), AAs in hydrolysate; Herrera (1942)

(continued)

Table 1.5 (continued)

Product (molecule group)	Educts	Metal promoters, *catalysts*, speciation form	Metals and speciation forms used in technical syntheses	Educts of technical syntheses	Energy sources, reaction conditions, possible intermediates	Remarks, quotations
Aliphatic amino acids	glycine	**$MnCO_3 + Al_2O_3$**; 240 °C				
	H_2O vapor (66 %), CO_2, N_2 (16 % each), NH_3 (g; 1.6 %)	**Ash from Tolbachik volcano** (Russia), eruption in 1975/76, obtained by grinding volcanic bombs			30 g ash; gas mixture passed through solid periodically at 530 °C, spark discharge at Pt electrodes, condensate trap	Traces of aromatic amino acids and purines detected also; mineral composition unknown but probably including “exotic” minerals as well as high levels of olivine. Lavrentiev et al. (1984)
	$CO + NH_3$	**Zeoliths doped with either Ca^{2+} or Fe^{3+}**			275–320 °C	HCN major product, many different AAs; Linde zeoliths X or Y which are similar to natural ones, metal loading required; Fripiat et al. (1972)
	2-keto acids, NH_4^+	**(Zn, Cd)S**				Photoelectrochemical reduction, sacrificial donor usually SO_3^{2-}; pure ZnS will not work
	NH_4^+; CH_4, CH_3OH or ethanol as C sources	**TiO_2 or WO_3**				Photoelectrochemical oxidation; higher yields

						with preformed C–C bonds (EtOH)
	10 % aq. $(NH_4)_2CO_3$	**Mg^{2+} and (better) its oxalatocomplex**			UV, 230–600 nm	Mg^{2+} enhances yields, addition of C_2 acid derivatives multiplies effect (Ser and Asp seen only then); Kihara et al. (1990)
	Glycine, aliphatic aldehyde or alkene	**Co(III) glycinatocomplex**			Thermochemical addition to acidified α-C atom	Abelson (1959)
	Glycine, photolytically produced alkyl radicals	**Glycinato complexes, mainly of Cu(II)**				Products include leucine, valine, and phenylalanine
	HCHO, NH_4^+, CN^-	**Fe mineral mixture** which in addition acts as a redox buffer (fayalite, magnetite and FeS)			150 °C/10 bar (i.e., mixture does not boil)	Main product glycine like in Strecker reaction but 11 times higher yield, besides alanine, serine, glutamic acid and leucine do form, possibly cyanoferrate intermediates; Hennet et al. (1992)
	CH_4, C_2H_2, NH_3, CO_2	**SiO_2** (quartz sand)			Optimum yields and product patterns close to 1,000 °C, $T = 0.1$ s	Narrow T region between minimal turnover and graphitization of CH_4; Harada and Fox (1964)
N-carbamoyl-amino acids, peptides	Formaldoxime	**Mo** or **V salts**, −complexes				Hatanaka and Egami (1977); Sakurai and Yanagawa (1984)

(continued)

Table 1.5 (continued)

Product (molecule group)	Educts	Metal promoters, *catalysts*, speciation form	Metals and speciation forms used in technical syntheses	Educts of technical syntheses	Energy sources, reaction conditions, possible intermediates	Remarks, quotations
Peptides	Amino acids	**Cu^{2+}** and peptide complexes thereof				Le Son et al. (1998); *autocatalytic* process
	Diglycine, trimetaphosphate	**Mg^{2+}**				Tetra- and hexaglycine formed; Yamagata (1997)
	AAN	**Ferric clays**			130 °C	Abelson (1959)
	Decaglutamic acid, glutaminic thioacid, HCO_3^-	**Cyanoferrate(III)**			Chain lengthening to $(Glu)_{15}$	
	Amino acids (mainly glycine)				Up to pentapeptides	Apparently photoelectrochemical oxidation, mainly In-containing semiconductors including In_2O_3 and roquesite $CuInS_2$[c]
Other carboxamides	Nitriles	**Co^{2+}**				Similar to hydrolases in bacteria
Carbamoyl phosphate	Cyanide, HPO_4^{2-}, oxidant[a]	**$[Fe(CN)_6]^{3-}$**; photochemical				
ATP	Carbamoyl phosphate + ADP	**Ca^{2+}**				Saygin and Ellmauerer (1984)
Acetyl phosphate	Carbamoyl phosphate + acetate	**Be^{2+}**				Saygin (1984)
cAMP	AMP, condensating agents diminosuccinonitrile or cyanogene bromide	DISN[b]: **Mn^{2+}, Pb^{2+}**, small effect of **Zn^{2+}; BrCN: Co^{2+}** and **Cu^{2+}**				Applying DISN: inhibition by Fe^{2+} and Ni^{2+} Ferris et al. (1984)

	Adenosine + trimetaphosphate	**Mg^{2+}**			Neutral solution; 140 °C (pressure?)	Byproduct ATP, Yamagata (1997)
Thymidin oligophosphates	Thymidine, $(NH_4)_2C_2O_4$ or cyanogene	**Ca^{2+}** (in hydroxyl- or fluoroapatite)			Activation by Ca^{2+} complexation via oxalate, oxamide	Schwartz et al. (1975)
Nucleoside bases	Formamide	**TiO_2**			Photoelectrochemical process, cooled surface in UHV	Simulating circumstellar gas cloud; guanine, and other NBs formed; Senanayake and Idriss (2006)
	Formamide	**$CaCO_3$**			UV light	$CaCO_3$ is not a PEC catalyst; purine and hypoxanthine yields largely increased by UV irradiation. Barks et al. (2010)
	Formamide	**Zr minerals**				Adenine and isocytosine; Saladino et al. (2010)
	Formamide	**Iron-sulfur minerals**			160 °C	Pyrite, and others; Saladino et al. 2012

Catalytic species are given in bold letters

Remark to the table: This table does **not** include cases with just trace yields or such which employ mixtures of metal ions or –complexes (commonly dubbed “simulated ocean water”) where the role of specific metals can no longer be attributed, e.g. modifications of Miller spark discharge experiment containing five dissolved metals (Kobayashi and Ponnamperuma 1985) or the “golden primordial broth” (Egami 1974) in which $HCHO_{aq} + (NH_3OH)Cl$ are processed by some similar mixture likewise containing Mg, Ca, Fe, Cu, Zn, and MoO_4^{2-} but in other concentrations). Likewise we omit such reactions which include very rare metal catalysts (moreover in highly oxidized states impossible to be formed in prebiotic environments) for producing amino acids, heterocycles or precursors thereof, e.g. synthesis of α-aminonitriles from (mainly cyclic) amines and NaCN by RuO_4/Co-oxidant systems (Petride et al. 2005) or of peptides prepared from polyaziridine by the same oxidant

FTT Fischer-Tropsch-Type

[a] Required to make system catalytic (reoxidation of $[Fe(CN)_6]^{4-}$)

[b] DISN: obtained by oxidation of HCN tetramer DAMN

[c] Roquesite does occur in nature and forms a continuous series with chalkopyrite $CuFeS_2$

1.3 Link in Between Chemical and Biological Evolution

Biology will not go without metabolic exchange of matter with the near environment at least; even cryptoendolithic biota do this beyond degrading carbonate minerals they are embedded in for obtaining CO_2, HCO_3^- for photosynthesis: cryptoendolithic biota were discovered in the 1970s (first in the Antarctic, then almost everywhere in the World) by placing stones collected there into a device measuring gas exchange (O_2, CO_2, CH_4,. . .) exhibited by these stones if exposed to sunlight and darkness; the stones were found to both "breathe" and doing photosynthesis, absorb dinitrogen also, and algae, cyanobacteria and lichens were spotted several mm below the surface upon breaking the stones (Friedmann 1978; Friedmann and Kibler 1980; Friedmann and Ocampo-Friedmann 1984). Accordingly gas exchange can be pinpointed across the surface of stones while sulfate reduction commonly is restricted to the very surface. Formation of minerals beyond biomineralization likewise requires some more or less or at least sustained supply of reaction partners which then undergo precipitation, possibly after some redox reaction took place like with formation of pig iron. During chemical and biological evolution, the original minerals were exposed to changing chemical conditions (sulfate reduction, advent of and secondary attack by atmospheric O_2) which can alter them to develop into many more than existed before ("mineral evolution"; Hazen 2010; Hazen and Ferry 2010).

While circumstellar dust contains about a dozen different minerals, there are some 70 in meteorites already partly subject to (liquid) aqueous alteration, about 500 on Mars[31] but >4,000 so far identified on Earth, processing advanced by both direct and indirect biochemical attack as well as plate tectonics. Besides of gaseous or liquid water or photochemical attack, products of early chemical evolution like oxalate ions would add to the manifold of existing minerals. The chiral ones among them might then turned into a template for synthesis of likewise chiral prebiotic organics. Now biological activity can both improve and reduce access to essential and other metals and non-metals given there was redox speciation in between: while the states of alkali metals would not have changed ever during development of conditions on Earth, excess CO_2 would have precipitated most of Mg, Ca, and all the other (mostly, essential) divalent ions into carbonates becoming unstable once photosynthesis depletes atmospheric CO_2 beyond a certain level. Sulfate reduction likewise decreases metal ion availability in a water-logged soil by sulfide precipitation while air and light attack on sulfides improve it.

Biomineralization products may become the starting-point of mineral formation e.g. teeth or bones around which manganese nodules use to form in the abyss around 5,000 m water depth. Mineral-formation may offer regionally exceptional

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[31] Based on both on-site evidence, mainly by rovers "Opportunity" and "Curiosity", and analysis of meteorites coming from Mars (so-called SNC objects) > 100 of which were retrieved on Earth now even though just five were observed falling. Unlike the very surface, just evidence of ferromagnetic behavior in Martian fines means they are not fully oxidized but contain Fe(II).

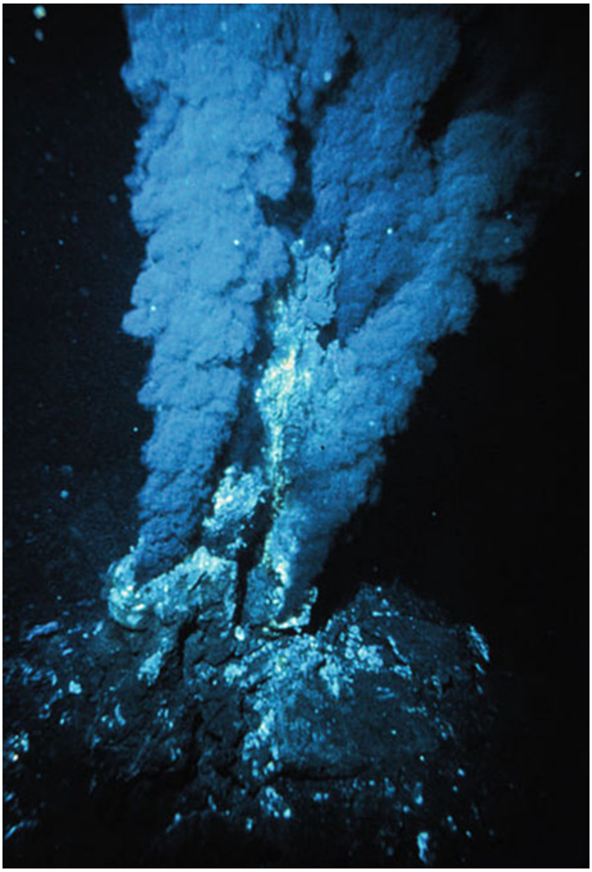

Fig. 1.18 A “black smoker” submarine hot spring in deep ocean. The black suspensions are due to precipitations of metal sulfide. Image courtesy of P. Rona. via Wikipedia

conditions for biology: black smokers (Fig. 1.18) are a well-known example of this while common granite as a block will not provide sufficient access to Mn to permit oxygenic photosynthesis on its surface unless for sites where (blackish) MnO_2 dendrites form (oversaturation). Geology/geobiochemistry (often associated with volcano activity and/or plate tectonics) and geobiochemistry mix up in a way which mobilizes substantial parts of certain essential (Zn, Cu, Mn, P) and non-essential (Be) elements to become locked up in living matter with biochemistry influencing chemical potentials and thus release of elements in either directions. In ternary or more complicated phases, redox speciation of or ligand formation from just one of the elements might influence availability of all the components if some very stable (sometimes insoluble) species is formed in certain conditions: while Mg does never undergo redox speciation and phosphate P is hardly reduced in and by biology, nitrate reduction going beyond N_2 will minimize availability of either (and thus, ATP bioproduction in these precarious conditions) once struvite $Mg(NH_4)PO_4$ does precipitate (which it readily does in e.g. municipal sewage water treatment plants, sometimes producing struvite of remarkably high purity); reduction of N alone, rather than Mg or P, does suffice for this to happen.

Biological agents and biochemical processes will not alter identities of atoms (they do never cause nuclear reactions) in the direct way. But, given the influence of methyl groups, or porphyrine, cyanide etc. ligands already present, the very biological (or bioinorganic) features of elements are well subject to biological impact, sometimes including a change of roles: semi-metals, behaving as inorganic electrophiles capable to form complexes, often may undergo biomethylation to finally afford ligands! Nevertheless the change of roles is something hard to deal with: except for As and Sb (and possibly Tl), biomethylation inevitably brings about a massive increase in toxicity towards quite diverse organisms and target organs. Modification of properties by complexation obviously puts a challenge on evolution:

- organometal chemistry in biology is essentially limited to Co (cobalamine, in vertebrates, and some cyanobacteria) and Ni(-porphyrin, in Archaea and clostridia [Moorella thermoacetica, exerting the Monsanto synthesis of acetate by a Ni oligopeptide complex]), and
- ligand arrangements in metalloproteines are outright monotonous compared to what one could do with amino acids side chains providing eleven different kinds of ligands, let alone co-factors acting as donors, too!

Thus there are two different sets of data on essentiality which probably are linked to each other in some way, one looking forward in time while the other is directed oppositely:

- key compounds of chemical evolution and present biology can be better (i.e. more efficiently) prepared (when) using some catalysts which are more or less likely to have been available in those days on early Earth, suggesting certain of these catalysts then made it into biology;
- some eight metals are omnipresent in contemporary life forms, fulfilling some catalytic or controlling function in metalloenzymes (K, Mg, Ca, Mo, Mn, Fe, Cu, Zn), with a couple of exceptions discussed elsewhere.

The first line of reasoning would mean particularly abundant and almost ubiquitous elements which display demonstrated catalytic or photocatalytic functions will be carried over and maintained into biology once there is inheritance permitting production of proteins which bind and activate/functionalize these very elements. The second relies on either one of two assumptions:

(a) there was a common last universal ancestor (LUCA) of all present living beings, and its set of functional elements (in particular, metal ions) was maintained until today
(b) this basic set of elements is, given abundances in ambient conditions, the optimal one for biocatalysis, just to be supplemented by certain others in metazoans, higher plants, other multicellular organisms or archaeans.

The first argument then would be on history (again), the other on evolution. Interestingly, for many of the said elements there are "exceptions": f.e., many arthropods can do without iron, while in other organisms there are "backup" systems of enzymes to replace (even) zinc (carboanhydrases, phosphatases and several others) or molybdenum (nitrogenase). These backup systems use to be not closely related to genetic/protein sequences and structures of those which they can replace; as a rule, the "substituted" enzyme molecules are considerably bigger. This suggests the present outcome of "natural selection of the chemical elements" (Williams and Frausto Da Silva 1996) represents evolution at work. On the other hand, several very abundant elements are not used by living systems or in enzymes thereof today. This again suggests the original set of "useful" catalysts underwent massive modification, especially given the pronounced stability of Al complexes.

If there was LUCA (last universal ancestor), the link between chemical and biological evolution would consist of a single event and object in time, namely that one which first (and perhaps as the only one) "learnt" how to reproduce while allowing for mutations and thus optimization. At this point in space and time the bouquet of components remained identical just before and after biogenesis or was changed by acquiring something additional which then enabled reproduction or at least replication of some entity hitherto incapable of doing this. While the story of chemical evolution (and simulating it) is much about how to make compounds still being used in biochemistry, the differences can be expected to become the larger the further we get off this point in space and time. Back in time, there were conditions changing rather fast and several 10^8 years of time forward there were changes which were due to biology for a substantial part within almost 4×10^9 years. Thus, "deviations" from the patterns are not expected to be symmetrical around biogenesis now. If there still is a noticeable link, it might be related to preferences in metal ion binding.

From chemical considerations, the crucial addition which turned chemical evolution into biogenesis rather was one of taking up an entire organic species of some complexity rather than happening to meet another (probably not too exotic) metal ion. F.e., endoribonucleases or other ribozymes (if you "believe" in the RNA world) are distinguished in certain catalytically active sequences which they use for restriction of themselves or of other RNA molecules although all of them require Zn^{2+} ions. Obviously, zinc was around before but these specific sequences came later in evolution (if at all). Chemical elements in biology may guide the way on which things can be done but protein sequences do matter also, and it is the latter which are modified by mutations in genetics. Sometimes, "exotic" enzyme functions can result from small modifications on enzymes which processed a chemically related element in quite another way, see the switch from phosphatases to As (V) oxidoreductases.[32]

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[32] Possibly in this case the change was most easy to accomplish, assuming starting with mixed P (V)-O-As (V) chains which then would have orthophosphate as a well-established biochemical leaving group for removing excess oxygen atoms during reduction (sulfate reductases work similarly via mixed O-bridged S (VI; IV)/P(V) acids or anions thereof).

The link we look for probably is a historical one while it is most difficult to tell or even guess the entire story. It is multidimensional insofar as both factors in space and time are covered, and necessarily so making use of rather different, unlike chemical entities (rather than a single kind of polymer or just one metal ion activating them).

These authors believe that the moment assemblies of polymers started to use an array of metals to catalyze crucial transformations by peptide or NA assemblies in some feedback mode is the very moment of biogenesis; from then on the conditions were rather constrained, even with respect to chances to introduce yet more chemical elements into the procedures of life.

Chapter 2
The Biological System of the Elements

Abstract Starting (in the 1990s) with abundance correlations among pairs of chemical elements in different kinds of plants which grow at a common site (a drying bog in Lower Saxony), the Biological System of Elements (BSE) was advanced by Bernd Markert striving to understand reasons why these—and no other—elements are used in biology to accomplish certain chemical transformations and how fractionation of elements from surrounding water or soil does take place in quantitative terms. For metals, essentiality apparently is related to coordination chemistry while it turns out that entire plant organs behave like homogeneous (single or equifunctional) ligands with respect to fractionation of elements after uptake from the environment. The BSE is arranged as a triangular picture in which the axes refer to the capability to form highly aggregated (e.g., polymeric) chemical species, the relative role in biological matter, and the response to (changing) salinity. It now is a double-layer body of knowledge, combining statistical statements on analytical bioinorganic chemistry and embracing quantitative chemical pieces of information to account for roles of most chemical elements with Z <84.

The position and classification of the chemical elements in the Periodic System of the Elements (PSE) does not permit any statement to be made about their functional essentiality or their acute or chronic toxicity for living organisms. This is due to the fact that the PSE is based on purely physicochemical aspects. The attempt has therefore been made, based on previously published papers of Markert (1987, 1988, 1993a,b, 1994b), to develop a Biological System of the Elements (BSE), which primarily considers aspects of basic biochemical and physiological research.

Especially B&B (Bioindication & Biomonitoring)-Technologies and modern instrumental techniques of chemical analysis have produced interesting results in the past decades:

– *related to B&B*: i.a. Arndt 1992; Herzig 1993; Markert and Weckert 1993; Herpin et al. 1997; Bargagli 1998; Carreras et al. 1998; Markert et al. 1997, 1999; Garty 1998; Freitas et al. 1999; Franzering and Van der Erden 2000; Klumpp et al. 2000; Loppi and Bonini 2000; Genßler et al. 2001; Bleise and Smodiš 2001; Herpin et al. 2001; Kostka-Rick et al. 2001; Vutchkov 2001;

B. Markert et al., *Chemical Evolution*, DOI 10.1007/978-3-319-14355-2_2

Altenburger and Schmitt 2003; Kettrup 2003; Markert et al. 2003b; Smodis 2003; Tabors et al. 2004; Fränzle et al. 2005; Herzig 2005; Elias et al. 2006; Reimann et al. 2006; Markert 2007; Araújo et al. 2008; Markert et al. 2008a,b; Markert 2008; Otte and Jacob (2008); De Bruyn et al. 2009; Wolterbeek et al. 2010; Catharino et al. 2011; Suchara et al. 2011; Kirschbaum et al. 2012; Kłos et al. 2012; Rodriguez et al. 2012; Amoozadeh et al. 2014;

- *related to the instrumental techniques of B&B:* i.a. Berlin et al. 1979; Stoeppler et al. 1982; Jeran et al. 1993; Wittig 1993; Wolterbeek et al. 1995; Saiki et al. 1997; Breulmann et al. 1998; Rutgers et al. 1998; Siewers and Herpin 1998; Quevauviller and Maier 1999; Bode et al. 2000; Siewers et al. 2000; Figueiredo et al. 2001; Prange 2001; Wolterbeek 2002; Pacheco et al. 2003; Freitas et al. 2006; Sucharová and Suchara 2006; Suchara et al. 2007; Zechmeister et al. 2007; Quevauviller et al. 2008; Algreen et al. 2012; Feldmann et al. 2013; Michalke 2014; Michalke and Witte 2014;
- *related to experimental applied investigations of B&B:* i.a. Keith 1988; Schroeder et al. 1996; Schwarz and Jonas 1997; Fargašová and Beinrohr 1998; Rasemann and Markert 1998; Fomin et al. 2003; Lux et al. 2004; Fränzle et al. 2005, 2007; Mench et al. 2006; Lepp and Madejon 2007; Broadley et al. 2007, 2008; Schroeder et al. 2007, 2008a, b; Cakmak 2008; Chaney et al. 2008; Irtelli and Navari-Izzo 2008; Hartley and Lepp 2008; Li et al. 2008; Schroeder et al. 2008; Smeets et al. 2008; Szárazová et al. 2008; Verkleij 2008; Fränzle 2011; Jacob et al. 2011; Wang et al. 2011; Diatta et al. 2015.

From the resulting configuration of the chemical elements in the BSE it can be expected that in the future, elements such as Br, Sr, Cs, Ge, and Te will be classified as physiologically essential, whereas elements such as Tl, Pb, Ga, Sb, In, Bi, Hg, and Cd will continue to exercise an exclusively toxic function on living systems in elevated concentrations and certain forms of bonding.

2.1 Occurrence, Distribution and Contamination of Chemical Elements in the Environment[1]

An overview of the occurrence, distribution and contamination of inorganic chemical substances in various environmental compartments and the rates of flow between these will be given. In an ecosystem the pathways and location of elements can be influenced in a specific manner by the organisms, e.g. by selective uptake and enrichment of the inorganic substances. Special emphasis is placed on the distribution and activity of chemical elements in plants in relation to their occurrence in the earth crust, their beneficial effects to living organisms and their acute or chronic toxicity to living systems. From here a so called "reference plant" (Sect. 2.2) could be developed, which allows for a direct comparison of individual plant species by

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[1] Markert (1994a, b, 1996).

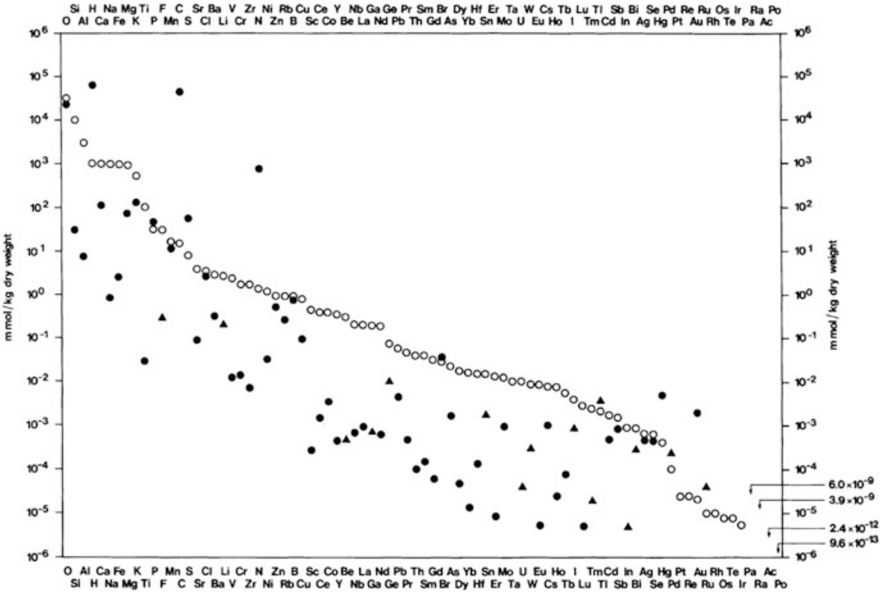

Fig. 2.1 Concentration of 82 naturally occurring elements (excluding the noble gases) in plants in the earth's crust (from Markert 1992d). The elements are listed in decreasing order based on their presence in the earth's crust. *Open circles*: concentration in the earth's crust (from Bowen 1979); *filled circles*: concentration in plants according to Markert (1986); *filled triangles*: concentration in plant material according to Bowen (1979)

standardizing them against the reference plant. A Biological System of the Elements (BSE) has been established (Sect. 2.4), which takes interelemental correlations, the biological function and the uptake form of individual elements into consideration. If the relationship in between these functions of elements is out of balance the inorganic contamination might have a toxicological effect.

Studies in the global circulation of carbon, sulphur, and phosphorus and studies on trace gases show how important knowledge is of the global circulation of these substances between the atmosphere, the biosphere, hydrosphere, and the geosphere. The earth's crust can be viewed as a natural reservoir for all of the chemical elements of the biosphere. More than 99 % of the total mass of the earth's crust consists of only 8 of 82 naturally occurring elements. It is made up to 46.4 % oxygen, 28.15 % silicon, 8.23 % aluminium, 5.63 % iron, 4.15 % calcium, 2.36 % sodium, 2.33 % magnesium, and 2.09 % potassium. Of the eight most common elements in the earth's crust, oxygen and silicon are the only non-metals. The other 80 elements of the periodic table make up less than 1 % of the total (Fig. 2.1).

The largest portion of the fresh weight of living plant organs (those showing active metabolism) consists of 85–90 % water on average. The dried matter of the plant is made up mostly of the following elements: carbon (44.5 %), oxygen (42.5 %), hydrogen (6.5 %), nitrogen (2.5 %), phosphorus (0.2 %), sulphur (0.3 %), and the alkali or alkaline earth metals: potassium (1.9 %), calcium (1.0 %), and magnesium (0.2 %).

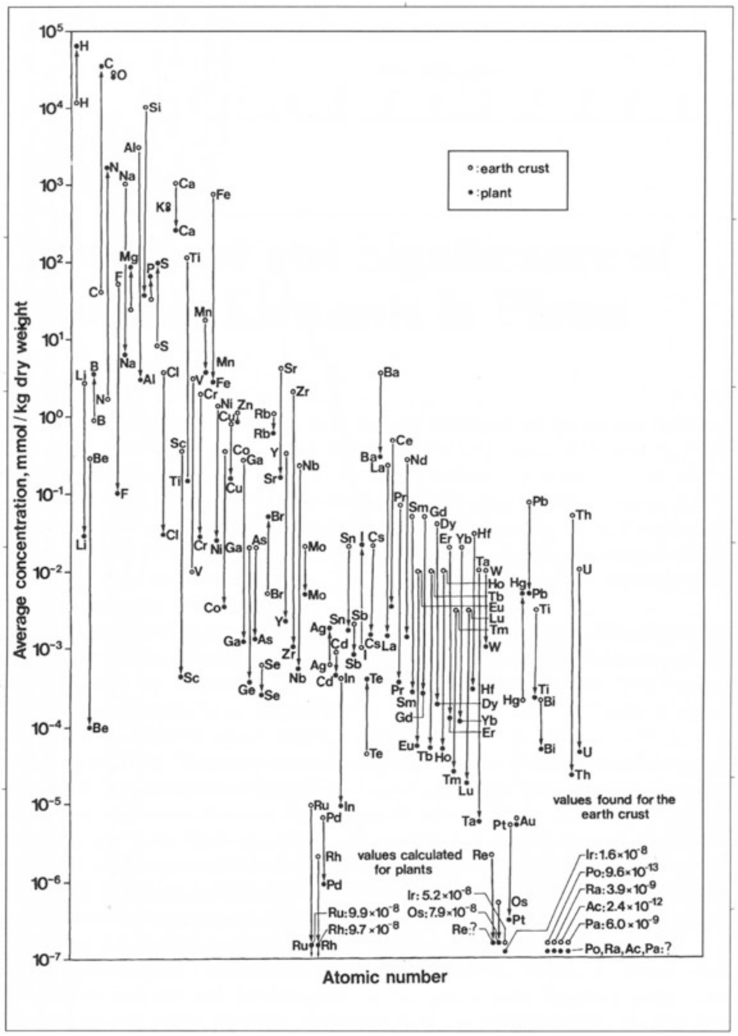

Fig. 2.2 Average concentration of 82 naturally occurring elements in plants and in the earth's crust as a function of their atomic mass (Markert 1996)

Thus, in contrast to the earth's crust, the main mass of organic life consists largely of non-metals (Fig. 2.2). The nine elements listed are also called macroelements because they occur in vegetation in increased amounts. There are also microelements, which are present in plants in reduced concentrations and which are vital for most plants. The microelements are chlorine (2,000 mg/kg of dry material), silicon (1,000 mg/kg), manganese (200 mg/kg), sodium (150 mg/kg), iron (150 mg/kg), zinc (50 mg/kg), boron (40 mg/kg), copper (10 mg/kg), chromium (1.5 mg/kg), molybdenum (0.5 mg/kg), and cobalt (0.2 mg/kg).

Macroelements and microelements are plant nutrients which are necessary for the growth and normal development of the plant (i.a. Danserau 1971; Likens et al.

1977; Pacyna 1985; Ellenberg et al. 1986; Sheppard 1991; Adriano 1992; Roots 1992, 1996; Fränzle 1993; Farago 1994; Schüürmann and Markert 1998; Markert and Friese 2000; Vtorova et al. 2001; Clemens et al. 2002; Heim et al. 2002; Markert et al. 2002; Reimann et al. 2003; Golan-Goldhirsh et al. 2004; Marquard and Schaefer 2004; Salt 2004; Hodson et al. 2005; Fränzle et al. 2007; Reimann et al. 2007; Watanabe et al. 2007; Fränzle et al. 2008; Hanikenne et al. 2008; Greger 2008; Marmiroli and Maestri 2008; Murakami et al. 2007, 2008; Prasad 2008; Trapp et al. 2008; Verbruggen et al. 2008; Dickinson et al. 2009; Fränzle 2009; White and Broadley 2009; Höllriegl et al. 2010; Hooda 2010; McGrath et al. 2010; Zhao et al. 2010; Hermans et al. 2011; Kissoon et al. 2011; Monaci et al. 2011; Poschenrieder et al. 2013; Vijgen et al. 2011; Ent et al. 2012; Enti-Brown et al. 2012; McGrath et al. 2012; Nriagu et al. 2012; Salazar et al. 2012; Serbula et al. 2012; White et al. 2012; Feng et al. 2013; Jacob et al. 2013a, b; Lombi et al. 2013; Pacyna et al. 2013; Zhao et al. 2013; Michalke and Fernsebner 2014); their function cannot be replaced by any other element. Therefore they are essential (Fig. 2.3). For this reason, macroelements and microelements are also called macronutrients and

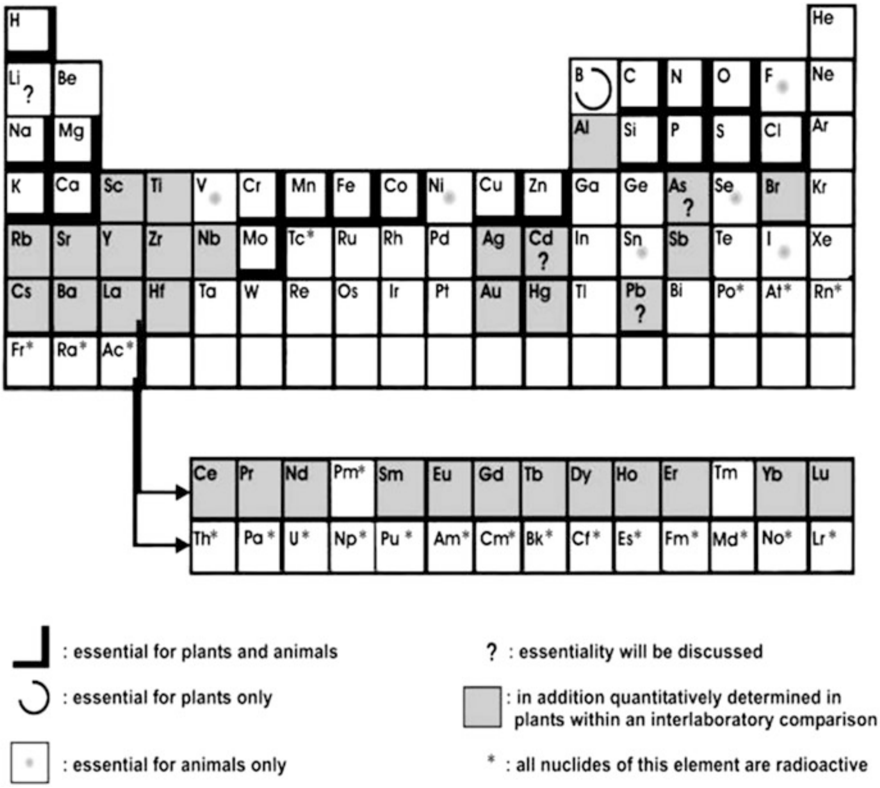

Fig. 2.3 The periodic table of the elements with indicators on elements that are essential and that have been quantitatively determined (Markert 1996)

micronutrients, respectively. The division of the periodic table into essential and non-essential elements does not always seem to be useful, because there are numerous exceptions in the plant kingdom, especially when one compares higher plants with lower ones. For example, calcium, boron, and chlorine are not considered essential in some bacteria and fungi, nor are sodium and silicon in higher plants.

In addition to the macronutrients and micronutrients just discussed, another series of chemical elements is also present in plants. For speculations of a possible physiological function during evolution of these inorganic substances (Fig. 2.4) which shows the molar concentration of element concentrations in a plant compared with the molar masses of the average concentrations of individual elements in the earth's crust.

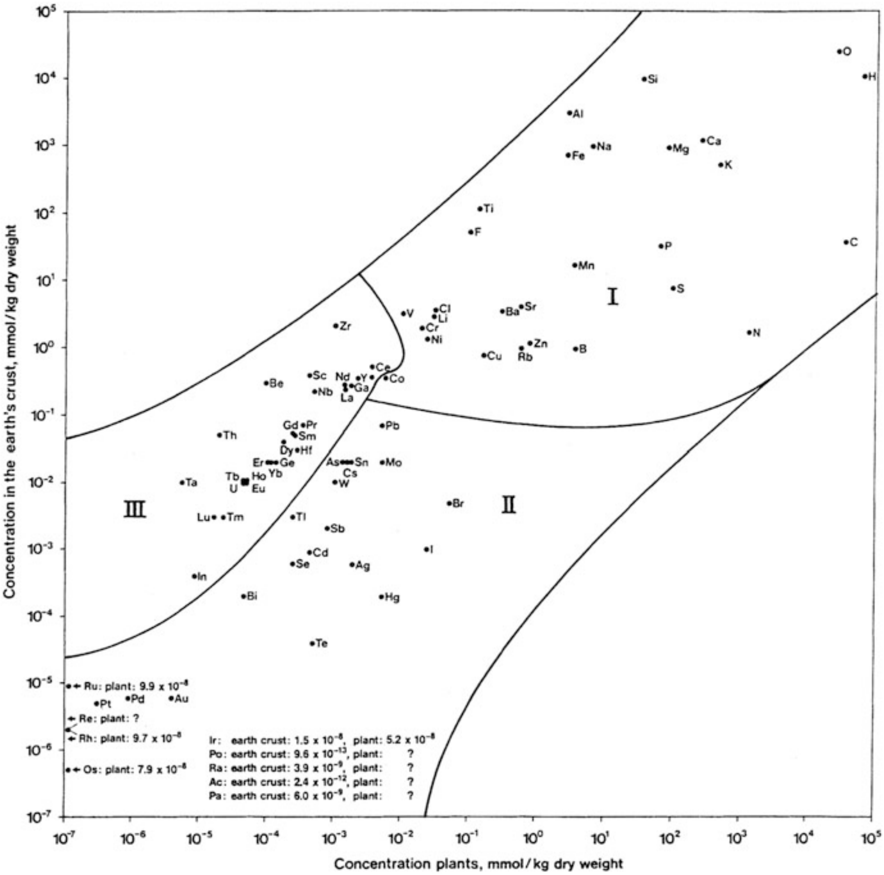

Fig. 2.4 Average concentration of chemical elements in plants in relation to the average concentration of elements in the earth's crust. All data are in mmol/kg dry weight (Markert 1996)

Most of the element concentrations are arranged along the median line of these two components of the concentration. On the one hand, this shows that the extra-terrestrial genesis of the elements is reflected in the earth's crust as well as in living biomass. On the other hand, it shows that individual elements have attained particular significance during the evolution of the earth and especially in modern biological life. These are the elements in Group I in Fig. 2.4, namely C, H, O, K, Ca, Si, Na, Fe, P, S, N, Mn, B, Zn, Cu, Ni, Cr, Co, Cl, V, F, Rb, Sr, Ba, Ti, and Al. All but the last five have a vital (essential or beneficial) function in at least some groups of organisms. Even the last five elements, Rb, Sr, Ba, Ti, and Al, are assumed to have an essential/beneficial function, although this cannot be described in any more detail currently. Group II includes those elements which, although some of them do have known essential functions (I, Mo, Se, and Sn), are characterized by their high toxicity, usually even at low concentrations. This is particularly true for the heavy metals Pb, Cd, As, Tl, Hg, etc. Group III includes elements which did not get beyond a passive role in the earth's crust in the course of evolution, nor integrated themselves into an active component of living organisms. Group III consists of the lanthanides and the platinum metals in particular. This evolutionary concept of a selection of chemical elements for the generation of living organisms led to the creation of a first Biological System of the Elements (BSE), which will be described later.

Just like the division into essential and non-essential elements, the classic division into microelements and macroelements described above, which strictly refers to the physical mass of an element within the organism, has undergone considerable modification in modern plant, animal, and human physiology. The list of the macroelements had to be expanded for certain groups of organisms. For example, the element silicon is considered to be a macroelement for horse-rails and diatoms. Also, element-specific and organism-specific accumulation processes frequently occurs due to their specific habitat: sodium, bromine, and chlorine are enriched by many halophytes; copper, nickel, zinc, lead, cadmium, and other heavy metals are taken up in increased measure by metallophytes.

2.1.1 Functional and Toxicological Aspects of Chemical Substances[2]

It is certainly true that accumulation is not the same as an increased physiological use of the element for the organism; often it might merely involve an adaptation to the particular habitat. In spite of this, the examples above help point out problems that develop with a systematic classification of the chemical elements based on their physical mass. Not infrequently one finds that a macronutrient and a micronutrient behave physiologically much more similarly than do two micronutrients or two

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[2] Markert (1994a, b).

Table 2.1 Division of the chemical elements according to physiological function (derived from Sansoni and Iyengar 1978)

Structural elements:	C, H, O, N, P, S, Si, Ca
Electrolytic elements:	K, Na, Ca, Cl, Mg
Enzymatic elements:	V*, Cr, Mo, Mn, Fe, Co, Ni, Cu, Zn, B**, Sn*, Se*, F*, I*, Mg
Up to now without biological function:	
1st main group: Li, Rb, Cs, (Fr)	2nd main group: Be, Sr, Ba, Ra
3rd main group: Al, Ga, In, T1	4th main group: Ge, Pb
5th main group: As, Sb, Bi	6th main group: Te, Po
7th main group: Br, (At)	
8th main group: He, Ne, Ar, Kr, Xe, Rn	
1st subgroup: Sc, Y	2nd subgroup: Ti, Zr, Hf
3rd subgroup: Tb, Ta	4th subgroup: W
5th subgroup: (Tc), Re	6th subgroup: Ru, Os
7th subgroup: Rh, Ir	8th subgroup: Pd, Pt
9th subgroup: Ag, Au	10th subgroup: Cd, Hg
Lanthanides: La, Ce, Pr, Nd, (Pm), Sm, Eu, Gd, Tb, Dy, Ho, Er, Tm, Yb, Lu	
Actinides: Ac, Th, Pa, U, (Np), (Pu), (Am), (Cm), (Bk), (Cf), (Es), (Fm), (Md), (No), (Lr)	

( ): Not naturally occurring elements (according to Hofmann and Rühdorf 1973)
*: So far essentially proven only for animals
**: So far essentially proven only for plants

macronutrients. Since the significance of an element to the plant is not determined by its proportional volume of the plant material, it would seem that a systematic division according to physiological and biochemical considerations would make more sense. Table 2.1 shows an attempt to do so. Structural elements here are those elements which participate in the construction of functional molecular components of the cell's metabolism (proteins, lipids, carbohydrates, nucleic acids, etc.) or which provide direct support or firmness (calcium, silicon).

Nitrogen and sulphur are integrated into the carbon chain biochemically, which means that after reduction of their usually high oxidation state (nitrate and sulfate), they bind tightly to the organic substance. Phosphorus, boron, and silicon, however, are present in their highest oxidation state and are not reduced; rather, they tend towards the formation of esters with OH groups on a wide variety of molecules, especially sugars.

The electrolyte elements are required for the construction of specific physiological potentials, and they are important in the maintenance of defined osmolytic ratios in cell metabolism. Thus, the element calcium can appear as a structural element and as an electrolyte at the same time. A number of chemical elements, especially metal ions, have catalytic functions in cell metabolism in the form of metal complexes. These elements are described as enzymatic elements in Table 2.1.

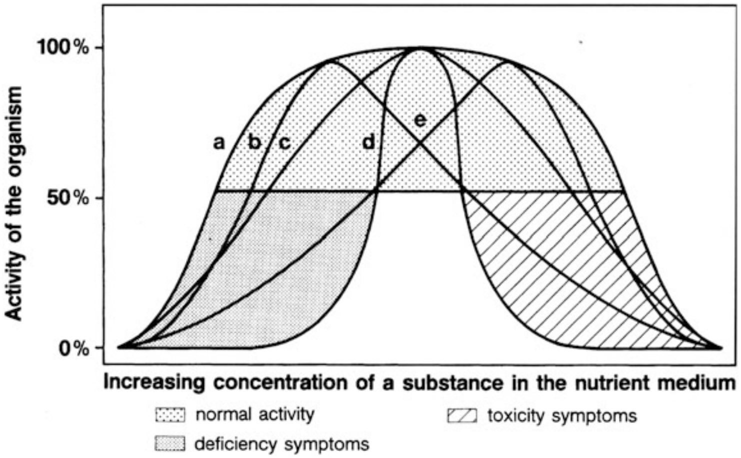

Fig. 2.5 Idealized dose-effect relations between substrate concentrations and activity of the organism (Markert 1996)

The physiology of these elements in metabolism is described in detail in textbooks dealing with plant, animal, and human biology.

The relationship between the nutrient supply in the substrate (soil, nutrient solution, atmosphere) and the plant's activity is not linear in broad ranges. Rather, it describes an optimum curve, which can take either a symmetrical (Fig. 2.5a,c,d) or an asymmetrical course (Fig. 2.5b,e) and have narrow (Fig. 2.5b,d,e) or broad (Fig. 2.5a,c) limits of tolerance.

The course of this kind of dose-effect relationship depends on the type of plant, the element species, and the conditions of the location. In general if an essential nutrient element is completely absent, the activity is equal to zero: the organism is not viable. Up to now, the usual test to determine whether an element was essential for photoautotrophic plants was to culture them on media with a defined composition, like nutrient solutions. In recent years it has been found that in the trace range and especially in the ultratrace range it is difficult to determine experimentally whether an element really has no influence on the growth of a plant, because often even the slightest amounts of the element are sufficient to prevent symptoms of deficiency from appearing in the organism. These minimal amounts can be present as pollutants in the nutrient solution, in the outside air, or in the vessel, and often they are present in such small amounts that it is very difficult to detect the elements analytically. For this reason, test plants are kept in an environment which should largely prevent contamination with trace elements. Today insulators made of different plastics are used because they release the trace elements contained in them less readily than glass or metals do. Trace elements in dust varied in the air are removed using strong air filters. The animals are given nutrients consisting of chemically pure amino acids (instead of proteins, which are often tightly bound to microelements) and other substances. The trace element considered to be essential is withheld. If this element is vital, observable and/or measurable metabolic disorders will appear, which usually subside with the administration of normal nutrients. Similar to the problems with contamination which are introduced when working in the ultra-trace range in an analytical chemistry laboratory, with these experiments one cannot exclude the possibility that the absence of any physiological metabolic disorder only simulates a non-essential condition because the element in question is already present in sufficient concentrations as a contaminant in the substrate or in the air in the laboratory.

The inadequate addition of an element from the culture medium often leads to the presentation of symptoms of deficiency. Theses symptoms can be prevented by adding a smaller (Fig. 2.5a,b) or larger (Fig. 2.5c,d,e) amount of nutrient. With sufficient nutrients, the organism's activity will reach its maximum.

At first, an increased administration of nutrients does not lead to an increase in activity. The activity remains constant over a broader (Fig. 2.5a) or narrower (Fig. 2.5b,c,d,e) concentration range for the substrate (nutrient saturation). Additional administration of substrate leads to evidence of toxicity and then finally to the organism's death. What Paracelsus said some 500 years ago is true for all chemical materials, regardless of whether they are toxic, essential, or indifferent:

> What Is There, that Is Not Poison? All Things Are Poison; Only the Dose Makes a Thing Not a Poison.

A clear description of the activity of a certain element is made difficult due to the presence of other materials which often have similar ionic radii and the same charge. This is because usually it is not the concentration of a given element or of given element species which is responsible for the healthy growth and normal development of an organism; more important is a well-balanced relationship between the individual elements or element species. Interelement interactions in the sense of competitive inhibition or enhancement can have a decisive influence on the physiology of individual organisms.

Quantitatively, the uptake of substances is adequately characterized by the intensity and scale of the uptake up to a particular point in time. For a defined nutrient, the uptake by the plant is dependent on the amount of the nutrient in the medium taken up and its availability. As a rule, the plant has no positive influence on the supply, but it does have an effect on the material and spatial availability of the nutrients. For example, from a material aspect, the nutrient availability can be changed by modifying the pH of the soil solution (elimination of H_3O^+ or HCO_3^- ions by the root), by the liberation of organic acids with chelating-ligand activity from the root, or via the participation of micro-organisms (mycorrhiza) as well as by the effect on the redox potential in the soil due to the release of H_3O^+ and O_2 at the root surface. The most readily available elements are present in the soil solution as ions or as soluble organic complexes. The least readily available ones are tightly bound to the soil structure, for example as a secondary component of the crystal structure of primary minerals. The most important source between these two extremes are small particles loaded with metals and having a large surface, such as clay, sludge, and organic material. All of this together can be labelled as an

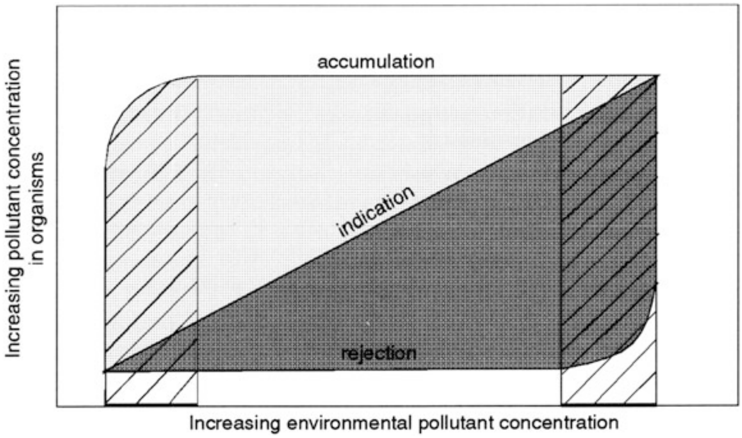

Fig. 2.6 Differing uptake activities in living organisms as a function of the substrate concentration (Markert 1996, modified after Baker 1981)

'exchange complex'. At the surface, ions can exchange between one another, such as calcium with magnesium, potassium, or hydrogen.

Thus, the intensity and the range of the uptake both influence the actual amount of an element in the plant. Depending on the type of plant being studied, the element species, and the specific location, one can differentiate between roughly three kinds of uptake (Fig. 2.6). In the ideal situation, there is a direct proportionality between the amount of nutrients available and the amount taken up by the plant. In this case the specific element contents of the plant reflect the concentration ratios in the nutrient substrate. Thus, the chemical composition of the plant has an indicative character. This association, which has been observed in a series of plants and for a wide variety of elements, both in experiments and in the field, is being taken into account more and more in practical applications, such as in prospecting for ore or when using (usually low-level) plants for biomonitoring. Because of unfavourable location of growth, many plants have developed the ability to enrich high concentrations of individual elements, often regardless of whether these elements are physiologically useful or not. These plants are called accumulators. With respect to biomonitoring there should be a correlation between the environmental concentration of a pollutant to be observed and the content in the organism proper. A linear, indicative interrelation of both parameters has not been found so far for any organism. The concentration ranges which might be interesting for bioindication and biomonitoring showed very small 'measuring ranges' (black bars) in accumulator and excluder organisms (Fig. 2.6).

For example, regardless of the amount of element in the soil, some Ericaceae have a high concentration of manganese, and beeches have a high amount of zinc. The accumulative behaviour, which may have genetically predetermined origins rather than ones determined by locations, makes it possible to chemically

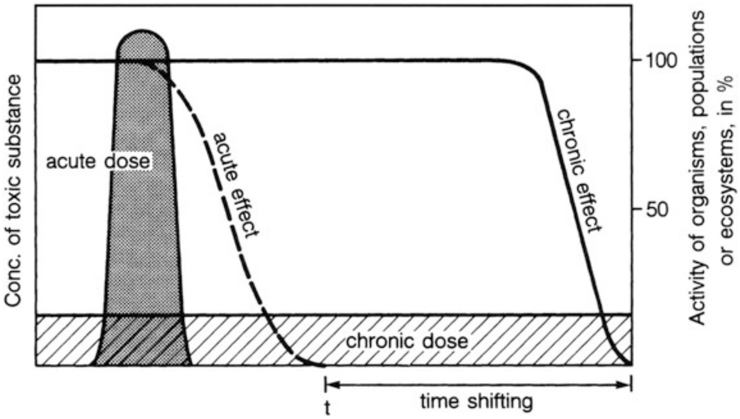

Fig. 2.7 Comparison of effect of acute and chronic doses of toxic substances on living systems (Markert 1996)

fingerprint a very wide variety of types of plant. In the future, this might lead to the chemical characterization, and therefore to the systematization, of individual plant types, which could provide information about evolutionary connections on a phytosociological level. A rejection, or reduced uptake of individual elements, occurs less frequently than does an accumulation of elements, but rejection behaviour has been demonstrated for numerous plant species. The reduction in concentration of an element in an organism can be the result of a complete or a partial exclusion. For example, bacteria, algae, and higher plants contain populations which are resistant to heavy metals and which can reduce considerably the uptake of heavy metals by excreting mucilagenous substances or by changing their cell walls.

In the context of activity studies, and especially in toxicity monitoring, one generally must distinguish between acute and chronic effect models. As is shown in Fig. 2.7, the acute delivery of a substance is usually followed by a direct, short-term effect on the organism or the population. These types of toxic effects are relatively easy to generate experimentally in the laboratory by adding different substances to the test organisms. However, it is more difficult to investigate chronic effects of a substance, meaning the subthreshold, long-term application of a substance which only shows an effect (usually a toxic one) after lengthy constant uptake. These mechanisms of chronic activities are considerably more difficult to study because all other values and parameters which could influence the test organism have to be kept constant over a considerable period of time. Often the chronic effect of substance differs from an acute effect only by its chronologically displaced occurrence. Thus, the chronic effect usually only creeps along, and so in reality it is often recognized too late.

The explanations given above point out the difficulties as well as the enormous possibilities associated with more intense multi-element research especially with environmental samples. In subsequent chapters we will present new findings

Table 2.2 Total element content in the world plant biomass in t

Ac	?	Hf	9.2×10^4	Rb	9.2×10^7
Ag	3.682×10^5	Hg	1.841×10^5	Re	?
Al	1.47×10^8	Ho	1.472×10^4	Rh	1.84×10^1
As	1.841×10^5	I	5.523×10^6	Ru	1.84×10^1
Au	1.841×10^3	In	1.841×10^3	S	5.523×10^{10}
B	7.3640×10^7	Ir	1.841×10^2	Sb	1.841×10^5
Ba	7.3640×10^7	K	3.497×10^{10}	Sc	3.682×10^4
Be	1.841×10^3	La	3.682×10^5	Se	3.682×10^4
Bi	1.841×10^4	Li	3.682×10^5	Si	1.841×10^9
Br	7.364×10^6	Lu	5.523×10^3	Sm	7.364×10^4
C	8.19×10^{11}	Mg	3.682×10^5	Sn	3.682×10^5
Ca	1.841×10^{10}	Mn	3.682×10^8	Sr	9.2×10^7
Cd	9.2×10^4	Mo	9.2×10^5	Ta	1.841×10^3
Ce	9.2×10^5	N	4.602×10^{10}	Tb	1.472×10^4
Cl	3.682×10^9	Na	2.76×10^8	Te	9.2×10^4
Co	3.682×10^5	Nb	9.2×10^4	Th	9.2×10^3
Cr	2.7615×10^6	Nd	3.682×10^5	Tl	9.2×10^4
Cs	3.682×10^5	Ni	2.76×10^6	Ti	9.2×10^6
Cu	1.841×10^7	O	7.824×10^{11}	Tm	7.364×10^3
Dy	5.523×10^4	Os	2.7615×10^1	U	1.841×10^4
Er	3.682×10^4	P	3.682×10^{10}	V	9.2×10^3
Eu	1.472×10^4	Pa	?	W	3.682×10^5
F	3.682×10^6	Pb	1.841×10^6	Y	3.682×10^4
Fe	2.76×10^8	Pd	1.841×10^2	Yb	3.682×10^4
Ga	1.841×10^5	Po	?	Zn	9.2×10^7
Gd	7.364×10^4	Pr	9.2×10^4	Zr	1.841×10^5
Ge	1.841×10^4	Pt	9.2×10^1		
H	1.196×10^{11}	Ra	?		

The data were calculated by using net primary productivity data of the world plant multiplied by data of element contents in green (photosynthetically active) parts in plants of the northern hemisphere. For this, the standard reference plant of Table 2.3, were aggregated (Markert 1996)

obtained from multi-element research. These findings have close ties to the terms concentration, correlation, accumulation, indication, and rejection. A preliminary estimate of the total content of individual elements in the earth's plant biomass is listed in Table 2.2. The data of the total element content in the world plant biomass were calculated by using net primary productivity data of the world plant multiplied by data of element contents in green (photosynthetic active) parts in plants of the northern hemisphere.

2.2 Establishing of ‘Reference Plant’ for Inorganic Characterization of Different Plant Species by Chemical Fingerprinting[3]

Inorganic environmental chemistry is far from having a detailed understanding of interdependence and possible synergistic interactions among chemical elements (Adriano 1986; Bowen 1979; Hamilton 1980; Horovitz 1988; Zeisler et al. 1988). Two thirds of naturally occurring chemical elements in ecosystems are normally not investigated although there is no proof of their inessentiality or nontoxic behavior (Kabata-Pendias and Pendias 1984; Lieth and Markert 1985, 1988, 1990; Iyengar 1988, 1989; McKenzie and Smythe 1988; Nriagu and Pacyna 1988; Tölg 1989; Markert 1991a, b). More efforts must be undertaken to overcome this lack of knowledge. In view of the important role played by plants in most ecological systems an inorganic chemical characterization using different instrumental multi-element techniques seems of the highest interest (Sansoni 1985, 1987). The establishment of ‘Reference Plant’, comparable with ‘Reference Man’ by ICRP, can be a successful tool for inorganic chemical fingerprinting (Markert 1991a).

Beginning in the fifties the International Commission on Radiological protection (1975) started by establishing a so-called ‘Reference Man’. This kind of ‘Reference Man’ was used to make an estimate of the human body radiation dose, whether received from external or internal sources. ‘Reference Man’ was defined in the fifties as being between 20 and 30 year of age, weighing 70 kg, 170 cm in height, and living in a climate with an average temperature from 10 to 20 °C. He is a Caucasian and is a Western European or North American in habitat and custom. Beside characteristics and data of different organs, water balance, respiration etc. are included. Especially the chemical composition of the total body and various tissues were given. Up to 1959 data on 46 naturally occurring elements found in the adult body and in body tissues have been reported. In later years ‘Reference Man’ was extensively modified and additional characteristics were included. Up to now ‘Reference Man’ has been a valuable tool to compare data produced by different analysts in various human tissues of different origin (Markert 1992b).

With respect to ‘Reference Man’ the idea of establishing a ‘Reference Plant’ was born (Markert 1992b). Of course, such an undertaking seems to be much more complicated because the plant kingdom is characterized by different types of plants, different plant families and by different plant species and not as in the case of ‘Reference Man’ only characterized by different “races” of only one species: man. But according to earlier works carried out by Duvigneaud and Denaeyer-de Smet (1970), and Kinzl (1982), who established a ‘reference values’ for macronutrients in plants, and bearing in mind the goal to obtain a data base system for comparing different analytical data from plant analysis with each other, it seems for a first

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[3] Markert (1992a, b, c, d).

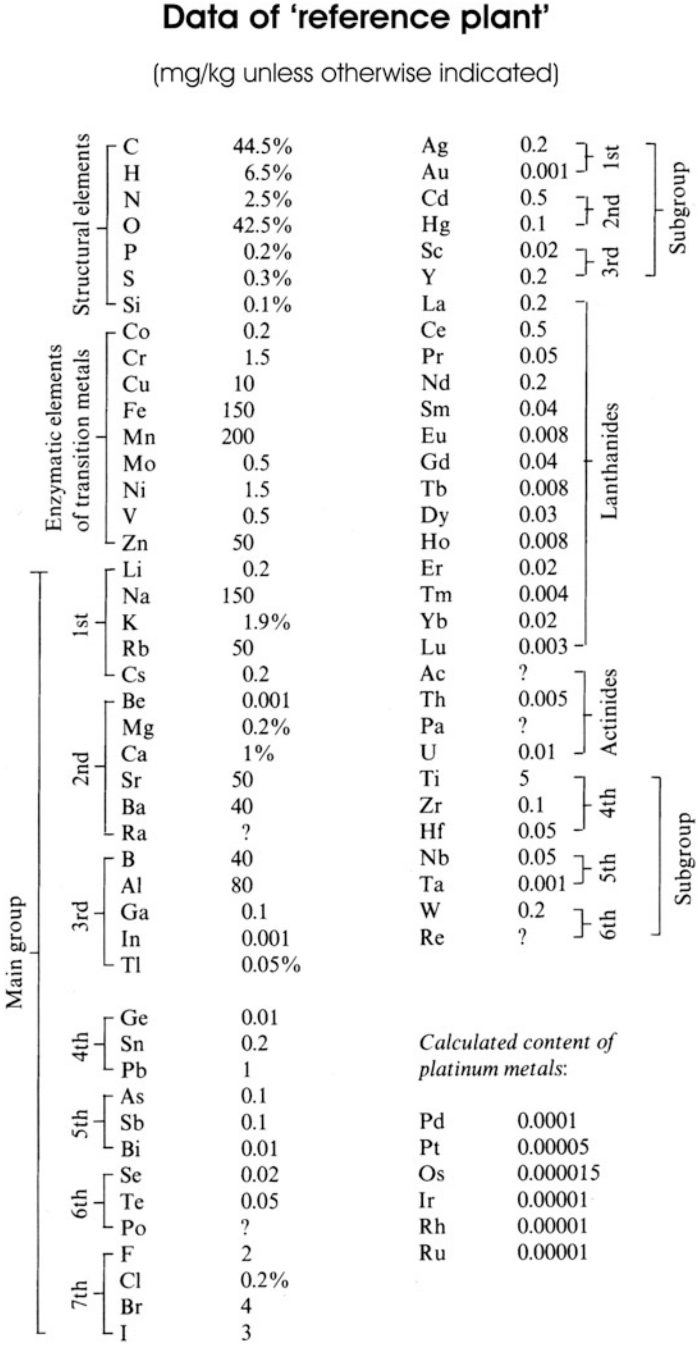
approximation unimportant whether 'Reference Plant' is a moss, a fern or a higher plant. In Table 2.3 the first values of 'Reference Plant' for different chemical elements are given. The data were mainly extracted from our own analysis (Markert 1986, 1991b), and when no data were available they were collected from Bowen (1979) or Kabata-Pendias and Pendias (1984). In Table 2.3 no data of accumulator plants or plants with abnormal contents of elements like halophytes were included. Because no data of natural Pt contents are available at the moment, calculated Pt values given by Markert (1991b) were included.

For the fingerprints of different plants species in Fig. 2.8 the values of 'Reference Plant' were set to zero (normalization) and the data of the element concentration of the plant species under consideration given as deviations from the values of 'Reference Plant'. Some fingerprints will be discussed in more detail in the following. E.g. Vaccinium vitis-idaea (Fig. 2.8a), growing on a podsolized flysand dune in the Grasmoor bog near Osnabrück, Germany, is characterized by the accumulation of following elements: Mn (674 mg kg^{-1}), Sn (2.9 mg kg^{-1}), Cs (0.371 mg kg^{-1}), and Hf (0.276 mg kg^{-1}); the enzymatic elements (Co, Cr, Fe, Mo, Ni, V and Zn) appear in lower concentrations compared to 'Reference Plant'. In addition the alkaline (with exception of Cs) and the alkaline earth elements and B are decreased.

Low concentrations are also observable for the halogens Cl (100 mg kg^{-1}) and Br (0.91 mg kg^{-1}). The lanthanide elements appear in almost the same order of magnitude like in 'Reference Plant'. In the same ecosystem under similar soil conditions Sphagnum grows as typical character plant in large amounts. The fingerprint of Sphagnum (Fig. 2.8b) represents accumulations of Co, Cr, and Mo. Mn appears in lower concentration as in 'Reference Plant'. An enrichment of concentration is observable for the alkali elements Li, Na, and Cs with decreasing concentrations of K and Rb. All alkaline earth elements and B appear in lower concentrations than in 'Reference Plant'. The elements Al (482 mg kg^{-1}), As (0.23 mg kg^{-1}), Hg (0.417 mg kg^{-1}), Pb (7.25 mg kg^{-1}) and the lanthanides were accumulated by Sphagnum mosses. Therefore Sphagnum can be characterized as typical accumulator plant with a completely other element distribution pattern compared with Vaccinium vitis-idaea. The different composition of Sphagnum and Vaccinium is explainable by fully different uptake mechanisms of elements, either mainly by air (Sphagnum) or by roots (Vaccinium).

As one can see from the examples above plant species can be characterized by their different distribution patterns of the inorganic composition. In the past 30 years we have analyzed a lot of different plant species under different edaphic and climatic conditions; results cannot be reported here in detail here, but we have seen the use of inorganic chemical fingerprinting for characterization of different plant species. E.g. of interest is the comparison of different fingerprint graphs of plant species belonging to the same plant family and growing in the same ecosystem with each other. Vaccinium vitis-idaea (red whortleberry) and Vaccinium myrtillus (blueberry) are both Ericaceae. With reference to Fig. 2.9, a high degree of agreement between both fingerprint graphs is observable, especially to the elements P, Si, Co, Cr, Cu, Mn, Na, K, Rb, Cs, Mg, Ca, Sr, Ba, B, Hg, Sc, most of the lanthanide elements and Hf. Different element distributions are only

Table 2.3 Contents of elements in 'reference plant'



Data of 'reference plant'

(mg/kg unless otherwise indicated)

	Structural elements	C	44.5%	Ag	0.2	1st	Subgroup
		H	6.5%	Au	0.001		
		N	2.5%	Cd	0.5	2nd	
		O	42.5%	Hg	0.1		
		P	0.2%	Sc	0.02	3rd	
		S	0.3%	Y	0.2		
		Si	0.1%	La	0.2	Lanthanides	
	Enzymatic elements of transition metals	Co	0.2	Ce	0.5		
		Cr	1.5	Pr	0.05		
		Cu	10	Nd	0.2		
		Fe	150	Sm	0.04		
		Mn	200	Eu	0.008		
		Mo	0.5	Gd	0.04		
		Ni	1.5	Tb	0.008		
		V	0.5	Dy	0.03		
		Zn	50	Ho	0.008		
Main group	1st	Li	0.2	Er	0.02		
		Na	150	Tm	0.004		
		K	1.9%	Yb	0.02		
		Rb	50	Lu	0.003		
		Cs	0.2	Ac	?	Actinides	
	2nd	Be	0.001	Th	0.005		
		Mg	0.2%	Pa	?		
		Ca	1%	U	0.01		
		Sr	50	Ti	5	4th	Subgroup
		Ba	40	Zr	0.1		
		Ra	?	Hf	0.05		
	3rd	B	40	Nb	0.05	5th	
		Al	80	Ta	0.001		
		Ga	0.1	W	0.2	6th	
		In	0.001	Re	?		
		Tl	0.05%				
	4th	Ge	0.01				
		Sn	0.2				
		Pb	1				
	5th	As	0.1				
		Sb	0.1				
		Bi	0.01				
	6th	Se	0.02				
		Te	0.05				
		Po	?				
	7th	F	2				
		Cl	0.2%				
		Br	4				
		I	3				

Calculated content of platinum metals:

Pd	0.0001
Pt	0.00005
Os	0.000015
Ir	0.00001
Rh	0.00001
Ru	0.00001

No data of typical accumulator or rejector plants were used. Data were mainly extracted from the analytical work by Markert (1986, 1992a). If data for single elements were not available they were collected from Bowen (1979) or Kabata-Pendias and Pendias (1984)

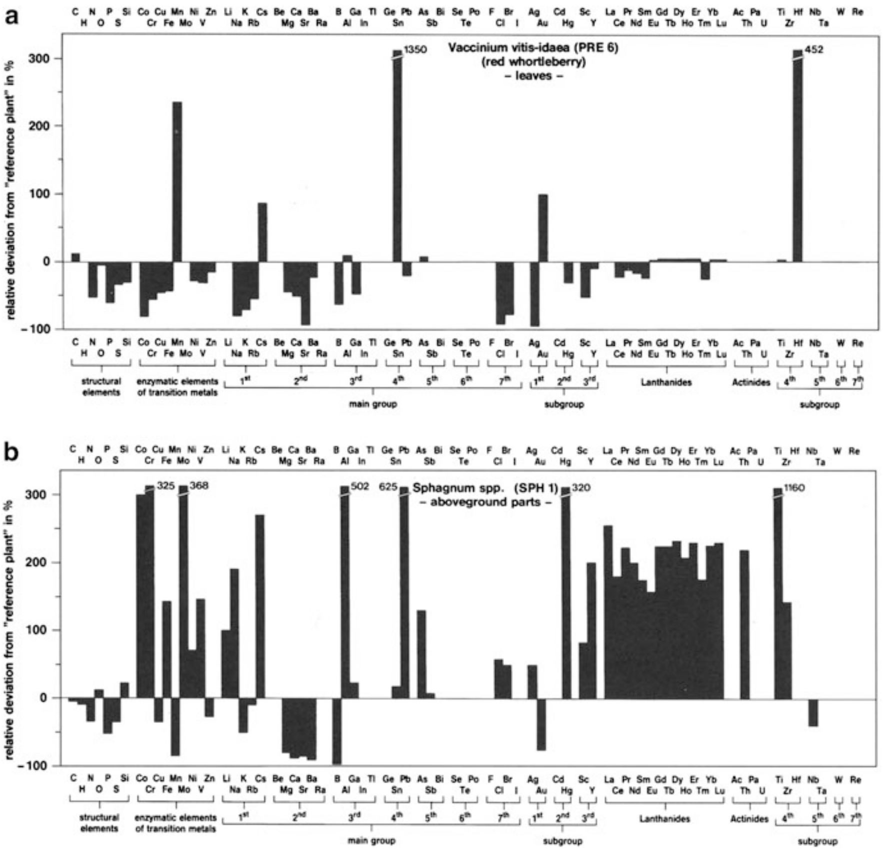


Fig. 2.8 Chemical fingerprints of (**a**) Vaccinium vitis-idaea (red Whortleberry, leaves) grown on a podsolized sanddune in the Grasmoor near Osnabrück after normalization against 'Reference Plant' and (**b**) different Sphagnum species (mosses, aboveground parts) grown in the Grasmoor near Osnabrück after normalization against 'Reference Plant' (Markert 1996)

observable for a few elements such as Ga and Pb. This example demonstrates that the close relationship of the two plant species can also be observed in a similar distribution pattern of the chemical elements.

With respect to the examples mentioned above fingerprint graphs after normalization against 'Reference Plant' have various properties. Each plant species can be characterized by a specific element distribution pattern in accumulation or rejection of elements compared to 'Reference Plant'. Related plant species seems to develop similar distribution patterns of single elements. Further multielement analysis may give more comprehensive explanations of flows and pools, temporal dynamics of storages, and concentration gradients for different biogeochemical models. Today we have analytical tools available to undertake this type of study which were unavailable a few years ago. Most importantly, today's analytical methods can precisely determine elemental abundances in tissues even when they occur at very

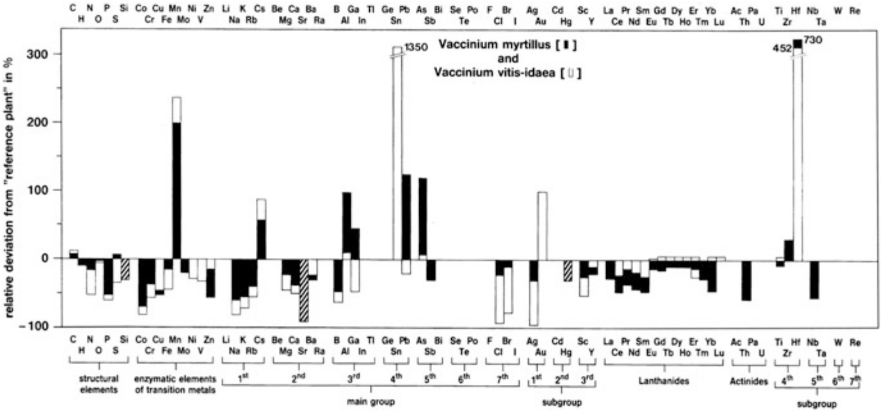


Fig. 2.9 Comparison of single fingerprints of Vaccinium vitis-idaea and Vaccinium myrtillus both grown in the Grasmoor near Osnabrück on sanddunes (Markert 1996)

low concentrations. Advances in geobotanical prospecting have led to a better understanding of plant substrate relationships which in turn provide a firm basis for the study of global and regional patterns. However, beyond the value of establishing the parameters of elemental abundance in ecosystems and species, the study can provide the basis to determine the influence of the abundance of one element on another, and on the chemical interrelationships among the biota and its substrate and of plants and consumers.

2.3 Interpretation and Explanation of Functional (Abundance) Correlations in Biological Processes[4]

Biological processes on the molecular level are frequently based on physical and chemical conditions whose fundamental chemical systematics in the Periodic System of the Elements (PSE) were already determined by Mendeleyev & Meyer in 1869. However, these physical and chemical regularities are frequently modified in biological systems. The reason for this is the adaptation of all organismic life to the aqueous environment. For example, in many biochemical processes, ions have to pass through cell membranes. It is remarkable that because of their positions in the PSE, the larger K^+ ion (ϕ : 0.133 nm) passes through the cell membrane more easily than the smaller Na^+ ion (ϕ : 0.95 nm). The explanation for this is to be found in the reversal of the size ratio of the two ions in the hydrated state (ϕ : K^+_{hydr}: 0.340 nm; ϕ : Na^+_{hydr}: 0.480 nm). Even if transport phenomena of this nature can be explained relatively easily by classic tools of chemical knowledge, the demands on chemico-physical interpretation become increasingly difficult to satisfy with the

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[4] Markert (1994a, b).

growing degree of complexity of physiological processes. The demands made on the chemico-physical approach to physiological processes become more taxing if, for example, a biochemically substantiated explanation of the effects of individual substances or groups of organisms is involved. Effect research of this type includes both issues of the essentiality and also the toxicity of individual substances or groups of substances (Epstein 1972; Mertz 1981; Grill et al. 1985; Marschner 1986; Bodek et al. 1988; Verkleij 1993). The PSE does not permit any approach which would enable the functional essentiality or the chronic or acute toxicity of individual elements or their compounds to be derived from their position in the PSE.

2.3.1 Existing Regularities in the Periodic System of the Elements to Explain Biological Functions of Chemical Elements

This becomes particularly clear whenever we search for common physiological features among elements within one group of the Periodic System of the Elements. What, for example, have the elements of the fourth main group, carbon, (C), silicon (Si), germanium (Ge), tin (Sn), and lead (Pb) in common from a physiological point of view? Carbon (C) largely occurs in living systems as a structural element in macromolecules, silicon (Si) is considered to be a ‘strengthening’ element in a few special groups of organisms (diatoms, grasses and some others), Ge has as yet no known physiological function, although in the from of spiro-germanium (4.4-dialkyl-4-germacyclohexanon and 8.8-dialkyl-8-germaazaspiro(4.5)decan) it is used medically as an antitumor agent. Tin is an important component of various enzyme systems for all vertebrates and at present lead appears only to have a toxic effect on the systems of all living organisms.

Even in a consideration of diagonal relationships within the periodic system, similarities and relations between individual elements are only apparent on a superficial level. It is thus, for instance, striking for the elements of the 4th–7th main group (C, P, Se and I) that all these elements have an essential significance. A consideration of the elements of the 3rd–6th main group (B, Si, As, Te) reveals that these elements only have an essential physiological function for special groups of organisms. In the case of boron (B) this is true of plants, with silicon (Si), as already mentioned above, this holds for some specific groups of organisms, while arsenic (As) is regarded as a growth promoter for domestic animals (e.g. As deficiency leads to cardiac death in the third generation of goats), and tellurium (Te) has no recognized physiological function as yet. As far as we know, the elements arranged in the 3rd-6 h main group (Al, Ge, Sb, Po) do not have any essential function at all. On the contrary, it is assumed that these elements already have a toxic effect on living organisms at low concentrations. That is to say, in biological and medical research, the arrangement of the elements in the chemical periodic system does not provide any clear answers to questions of the toxicity and essentiality of individual elements or their forms of bonds.

2.3.2 Criticism on the Classical Periodic System of the Elements

The Periodical System of the Elements has long been criticised by chemists since it displays a wide range of confusing irregularities and only appears periodic upon superficial consideration. Allen (1992) recently put the question what the common chemico-physical features between carbon, silicon, tin and lead could be since they are shown to be related with element group 4, or between boron (B) and aluminium (Al) in element group 3, whereas, for example, boron and silicon, on the one hand, and aluminium and beryllium, on the other, have many common features. Allen comes to the conclusion that something fundamental is missing from the PSE as our basic instrument for organizing chemical phenomena. It contains no information on the energetic states of the atoms, without which no satisfactory description of the structure of matter can be given. Even if all the graphical tricks of the trade are applied, it is only possible to represent the PSE in two dimensions. To this end, Allen defines the concept of configurational energy, a mean function of the electron energy of an atom. Such energies can be determined by spectroscopic methods from the ionization potentials of the valency electrons. Allen conjectures that the configuration energy is the long sought after, missing third dimension of the PSE. Its suitability for predicting the properties of as yet unknown chemical compounds can be applied as a touchstone.

2.4 Milestones of Multielement Research and Applications Related to the Scientific Development of the Biological System of the Elements[5]

The development of knowledge concerning functions and roles of chemical elements (in biology) was always closely linked to progress in multielement (and later on speciation) analytics of biological samples. In the following a rough synthesis on milestones in Biological Trace Elements Research is given in Table 2.4 reflecting the personal European point of view by the authors. Multielement analytics in turn depend on the quality of data with respect to both precision and—which is even more important—to accuracy. In the beginning for geochemical purposes first larger sets of data and comprehensive papers were produced as far back as the 1950s and 1960s (Bowen 1966, 1979; Vernadsky 1967; Wedepohl 1969). Already then it became obvious that there are mainly two different ways to improve quality and reliability of analytic data, i.e. either by analyzing the same sample several times by mutually independent methods or in different laboratories or else by using standard reference materials with a well-defined chemical composition for

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[5] Markert (1994a, b) and Fränzle and Markert (2002a).

Table 2.4 Milestones of multielement research and applications related to the scientific development of the Biological System of the Elements (BSE)

Author	Year	Results and publications on
Vernadsky	1951	Geochemical data mainly from Russia; development of the concept of increasing specific element transfer into the biosphere with ongoing evolution
Bowen	1966 and 1979	Geochemical and biochemical data (worldwide)
Wedepohl	1969–1974	Geochemical data
Bowen	<1965, 1965–1975	"in-house" reference materials produced by geochemists Production and use of BOWEN's kale as first biological reference material for **quality control** of analytical data
EU and other International Societies, Nations or Institutes	1972	Foundation of the Bureau Community of Reference in Brussels for the professional development of standard reference materials (Similar Quality Control Centers grow up worldwide f.e. NIST in USA, BCR and IAEA in Europe)
Duvigneaud and Denaeyer de Smet	1965–1975	First systematic publications on element fluxes through forest ecosystems in Belgium (ecosystem research)
Garten (USA)	1976	Stated **"stable" correlations** of elements in plants
Kabata-Pendias and Pendias	1984	First more general textbook on trace element distribution in plants and soil
Adriano (USA)	1986	International conferences series directly related to trace element research
Sansoni	1985	First textbook on use and development of instrumental multielement techniques for environmental samples
Nriagu and Pacyna (USA, Canada)	1988	Worldwide estimation of contamination by heavy metals in the atmosphere, soils and water
Lieth and Markert	1988	Determined quantitatively by various instrumental methods more than 60 elements in different plant species in Europe
Lieth and Markert Rossbach* Jayaserera Zeisler et al.*USA Kovacs Djingova	1985 1986 1987 1988 1993 2000	Application and use of instrumental multielement methods on environmental samples in terms of highest quality from analytical point of view. * ESB: Environmental Specimen Bank-Development in Germany and the US Developing of instrumental multielement-techniques for environmental purposes
Markert	1988/1993	Interelement correlations found in different standard reference materials and highly representative research samples

(continued)

Table 2.4 (continued)

Author	Year	Results and publications on
IUBS	1991	The IUBS co-sponsors, with its Section for Ecology (INTECOL) a worldwide project titled "Element Concentration Cadasters in Ecosystems" (details in Markert 1996)
Allen	1992	Proposed an extension and completion of the periodic table of elements
Markert	1992	Establishing of a "**reference plant**" for inorganic characterization of different plant species by **chemical fingerprinting**
Markert	1994	First publication for a "**Biological System of the Elements**" (BSE) Analytical and biochemical aspects based on: – Accurate and precise multielement data including representative sampling procedures – Interelement relationships – Physiological function of elements – Uptake mechanisms and bioavailability – Evolutionary aspects
Farago Bargagli	1994 1998	Further textbooks on trace elements in plants
Fränzle and Markert	2000 a, b,c	Theoretical considerations and applications of Stoichiometric Network Analysis on the BSE
Markert and Fränzle in Markert	2001	The Biological System of the Elements as a platform for technical and general application – Generation of Biochips – Creation of 'designer molecules' – Novel routes for and refinement of Bionics – Terrestrial colonization of green plants from freshwater – From single hypotheses to multiple theories – New paths in 'vision design'
Fränzle	2010	Chemical Elements in Plants and Soil: Parameters controlling Essentiality
Markert and Fränzle	2014	BSE modified

comparison (Markert 1996). Starting with so-called in-house standards, standard reference materials were developed, both non-biological and biological ones. The first of the latter was conceived and developed by Bowen (1979) and thus now is known as "Bowen's kale". These "**first-generation**" reference materials meant to be used in chemical analytics solely then were replaced with "**second-generation**" ones produced by national and international organizations—materials which are closely similar to the original material but made suitable for standardization by methods applied in their preparation for avoiding contamination—and eventually with "**third-generation**" ones (integral standard reference materials to be used also with respect to an interdisciplinary extension of analytical procedures and of problem-related application fields). The corresponding organizations include f.e. the Bureau Community of Reference (BCR) at Brussels, the International Atomic Energy Commission (IAEA) at Vienna and the American National Institute of Standards and Technology (NIST) at Gaithersburg, MD.

Taking an ecosystems point of view distributions of elements and trace elements were first investigated in Belgium. Duvigneaud and Denaeyer-De Smet (1973) first attempted to systematically classify the differences between plant species relative to their inorganic chemical composition. Garten (1976) discovered high interelemental correlations for the elements P, N, K, Ca and Mg for 54 species growing in the field, resulting independently of the site of the respective plant species studied. The results of multi-element analyses first done in the 1980s permitted the element spectrum to be extended for correlation analyses of this type (f.e. Lieth and Markert 1985, 1988; Rossbach 1986; Jayasekera 1987; Zeisler et al. 1988; Kovacs et al. 1990, 1993; Djingova and Kuleff 2000). In addition the publication of more general textbooks on trace element distributions and effects in the plant/soil/atmosphere/biosphere context has brought new insights into the complex dynamic of this field (f.e. Kabata-Pendias and Pendias 1984; Sansoni 1985; Adriano 1986) including atmospheric and anthropogenic impact mechanisms (Nriagu and Pacyna 1988). The organization of conference series [f.e. the “Adriano” conferences in Orlando (1990), Taipeh (1993), Paris (1995), Berkeley (1997), Vienna (1999) and Guelph (2001)] especially in the interdisciplinary field of Biogeochemistry brought scientists together in regular intervals to strengthen exchange of latest information.

The interelement correlation found by Garten (1976) could be extended first with accurate data from standard reference materials (Markert 1988) and 5 years later with data from highly accurate research investigations (Markert 1993b). Using these data it appeared highly probable that besides the extent of supply of trace elements and parameters which influence bioavailability (solubility etc.) aspects from genetics and molecular biology have to be considered additionally, possibly even are more important than the former factors. Moreover, instead of the total abundance of some element the corresponding speciation forms must be taken into account. To systematize the “element behaviour” in form of a table leads first to the attempt of using the (chemical) Periodic System of Elements, but the (chemical) Periodic System of Elements itself has been long criticized by chemists since it displays a wide range of confusing irregularities and the PSE basically only appears periodic upon superficial consideration (see in detail with Markert 1996). Allen (1992) comes to the conclusion that something fundamental is missing from the PSE as our basic instrument for organizing chemical phenomena.

To handle the large set of analytical data for f.e. plants and to produce a common comparability first a so called “reference plant” comparable to reference man (International Commission on Radiological Protection 1975) has been established, so that different chemical fingerprints of different plant species could be derived (Markert 1994b). Here the genetic influence on heavy metal distribution in living organisms becomes clear: Related plant species show similar distribution patterns! F.e. the Ericaceae Vaccinium vitis idea (red whortleberry) and Vaccinium myrtillus (blue whortleberry) show similar element distributions, f.e. extreme accumulation of Mn, independent of the bioavailability!

On the 24th General Assembly of the International Union of Biological Sciences in Amsterdam IUBS co-sponsors, with its International Section for Ecology (INTECOL), initiated a project titled “Element Concentration Cadasters in Ecosystems” which deals with a new area of ecological chemistry, emphasizing the methods for the evaluation and assessment of element concentrations in the environment (International Union of Biological Sciences 1992; for details see Markert 1996).

Due to the inadequate chemical description of biological and medical relationships in the PSE, from the above mentioned findings a first Biological System of the Elements (BSE) was established in 1994 (Fig. 2.10). The main factors for establishing this first “intuitive” system have been accurate and precise multielement data including representative sampling procedures, interelement relationships, physiological function of elements, uptake mechanisms and evolutionary aspects (Markert 1994a).

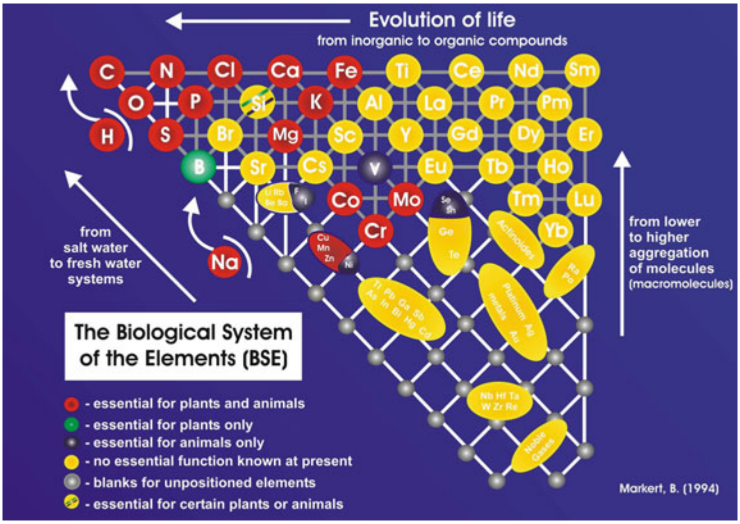

Fig. 2.10 The Biological System of the Elements (BSE) for terrestrial plants (glycophytes) (Markert 1994a). The diagram shows relationships among the elements together with their corresponding essential functions (*colours)*, extent of biochemical functions and the corresponding capacity to form macromolecules by condensation reactions (*vertical arrow at right side of diagram*). Whereas in “pure” geochemistry oxophilic metals produce the most complicated condensation products, i.e., clay minerals, there was a shift towards non-metal-based structures during chemical and biological evolution which afforded polymeric structures based on the latter (C, N, O) (*horizontal arrow to the left*). The diagonal arrow refers to changes of concentration from ocean- to freshwater. There is substantial decrease of concentrations in some elements (Mg, Sr, Cl, Br) from ocean to freshwater requiring them to be enriched by biomasses if their biochemical use is to be continued. Such kinds of enrichment can only be accomplished by means of certain biochemical features which involve properties and/or components of the corresponding biogenic materials—many of which are specific for one species at least in their particular combination

The complication of this system of the elements is based on considerations arising in particular from data on the multielement analysis of terrestrial plants. The data were compiled from standard reference materials from the National Institute of Standards and Technology (NIDT, Gaithersburg, U.S.) and highly accurate research samples. The data pool for plant reference materials is composed of certified element contents for citrus leaves (NIST SRM 1572), tomato leaves (NIST SRM 1573), pine needles (NIST SRM 1575) and Bowen's kale. The data pool was supplemented by multielement data spectra from the following plants: leaves of *Betula pendula*, needles of *Pinus sylvestris*, leaves of *Vaccinium vitis-idaea*, leaves of *Vaccinium myrtillus*, the aboveground parts of *Deschampsia flexuosa*, *Molinia caerulea*, *Polytrichum formosum* and different *Sphagnum* species. All the plants were gathered during the 1987 vegetation period on Grasmoor near Osnabrück (Markert 1993a, b). Only data from terrestrial plants of freshwater systems (glycophytes) were used; no results of typical accumulator plants or halophytes did enter the data base (Bowen 1979; Nierboer and Richardson 1980; Horovitz 1988; Pais 1991; Markert 1992a; Streit and Stumm 1993).

Since BSE was first conceived in 1994, support and discussion by many colleagues from abroad brought about translations of BSE diagrams published in the respective countries and languages, including French, Spanish, Chinese, Persian (Farsi), Latvian, Lithuanian, Polish (Markert et al. 2010, 2012a, b, 2013a, b, c, 2014) with Russian, Arabic, Hindi versions and others soon to come. Two examples (Polish and Persian) are given in Fig. 2.11.

Meanwhile further research has shown that there are exceptions of the role of certain elements to specific animals/plants. Therefore the original BSE was extended into a modified BSE (Fig. 2.12) where Cr, Ba, Rb, Sr and Li take probably following role[6]:

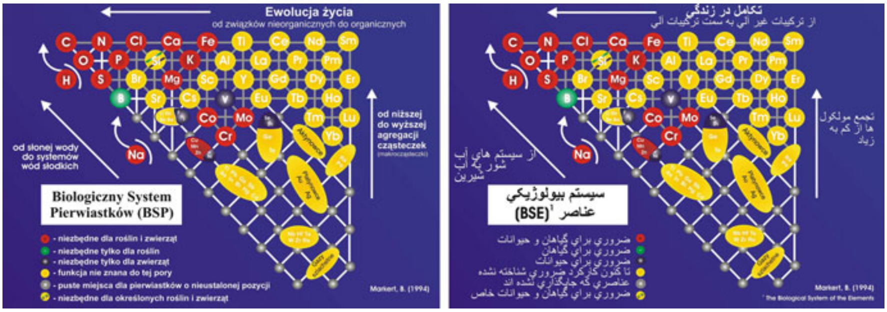

Fig. 2.11 The Biological System of the Elements (BSE) after Markert (1994a, b) was already published in several languages like in French, Spanish, Chinese, Persian (Farsi), Latvian, Lithuanian, Polish (Markert et al. 2010, 2012a, b, 2013a, b, c, 2014) with Russian, Arabic, Hindi versions and others soon to come. Two examples (Polish and Persian) are given in the figure

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[6] Extended and more detailed information on the functionality of each chemical element are given in Appendix.

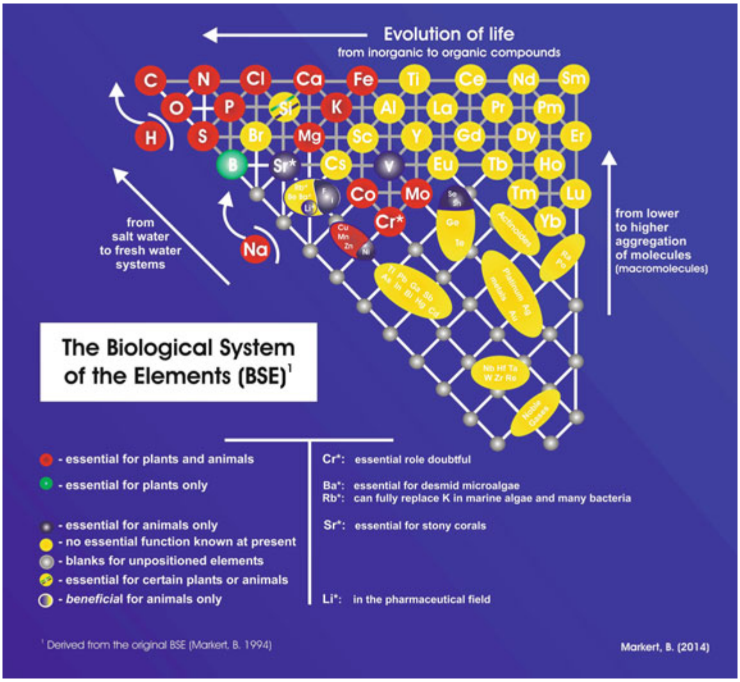


Fig. 2.12 Extended Biological System of the Elements after Markert (1994a, b) showing exceptions of the role of certain elements to specific animals/plants

- The essential role of Chromium is doubtful for plants and animals;
- Barium is essential for desmid microalgae;
- Rubidium can fully replace K in marine algae and many bacteria;
- Strontium is essential for stony corals;
- Lithium has a beneficial effect to animals (humans) in the pharmaceutical field (see Sect. 3.1).

The BSE after Markert (1994a, b) was derived and constructed according to the following criteria outlined in the next Sects. (2.4.1–2.4.3) of the book.

2.4.1 *Interelemental Correlations*

Garten (1976) discovered high interelemental correlations for the elements P, N, K, Ca and Mg for 54 species growing in the field, independent of the site of the respective plant species studied, and expressed a highly positive correlation according to the linear correlation of the individual-species measured content values. The high correlation coefficients for N and P were attributed to the high association of the two elements, especially during protein biosynthesis, while for

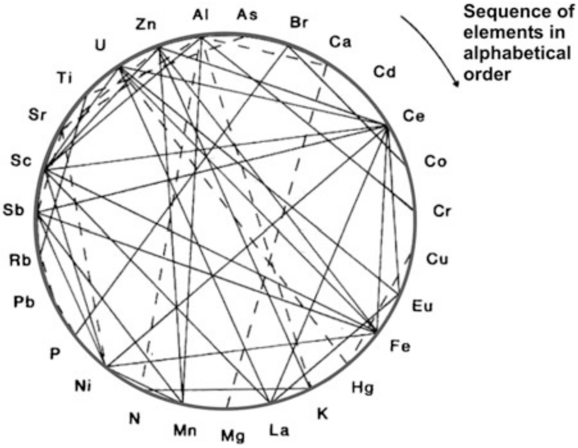


Fig. 2.13 Highly positive (*straight connection lines*) and highly negative (*broken connection lines*) abundance correlations among pairs of chemical elements in 13 species of plants (Markert 1996)

Ca and Mg they were explained on the basis of common enzyme activators during various metabolic processes (Garten 1976).

The results of multielement analyses in the 1980s permitted the element spectrum to extended using correlations analyse of this type. The result of these correlations is shown in Fig. 2.13. The individual results of the correlation analysis cannot be discussed in detail here (see Markert (1993a, b) for an exhaustive discussion).

However, the correlation data represented an important criterion in compiling the BSE (Fig. 2.14). It was thus striking that, of the alkaline metals in particular, the element potassium (K) and the alkaline-earth metals Ca and Mg, and to a certain extent also Sr, display both high correlations to each other and also to the macronutrients N and P. It is interesting to note that the correlation tendency drops considerably in the sequence Ca, Mg, Sr, and Ba although the ionic radii of the hydrated elements do not display any great differences (Ca^{2+} : 0.6 nm; Mg^{2+} : 0.8 nm; Sr^{2+} : 0.5 nm; Ba^{2+} : 0.5 nm). Potassium displaying highly positive correlations with almost all macroelements (K/Ca: 0.7545; K/N: 0.8370; K/Mg: 0.7928; K/P: 0.7768) and with the halogens (K/Br: 0.88684; K/Cl: 0.6904) is most probably an indication of its outstanding role as an electrolytic element in plant metabolism. If metals are involved then the biochemical function of the electrolytes is largely determined by their tendency towards complexation. The alkaline metals have hardly any tendency towards complex formation, the alkaline-earth metals a moderate tendency and the transition metals a strong tendency. This property also determines the form in which these elements are transported in the plant organism. With regard to their function, sodium and potassium ions mainly function as transporters of charges, magnesium and calcium as stabilizers of organic structures and information transmitters, and the transition metals, in combination with

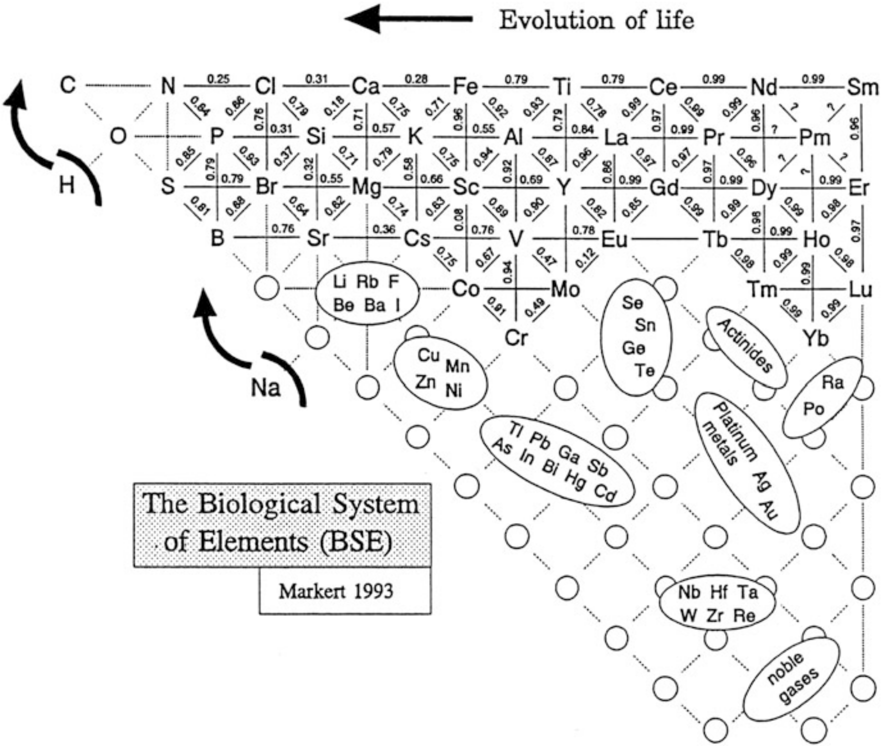


Fig. 2.14 The Biological System of the Elements (BSE) with correlation data from linear regression analysis (Markert 1996)

proteins, as catalysts. Together with large organic anions, chloride ions ensure the maintenance of electroneutrality in the case of the intercompartmental displacement of charge carriers. Highly positive interactions were established for the two halogens, Br and Cl, both with each other (r = 0.7587) as well as with K, N and P. In this connection, the tendency of Br to from positive correlations was even greater than that of Cl: Br/K (0.8684), Cl/K (0.6904); Br/P (0.9276), Cl/P (0.6572); Br/N (0.8981), Cl/N (0.2540). The high correlations of the halogens with K could involve a typical charge antagonism between K^+ ions and halogenide ions.

The high correlation tendency of the elements Al, Fe, Sc and La, which as a rule is greater than r = +0.9, can be attributed to the trivalent charge state of the cations of these elements and the very similar radius of the hydrated ions Al^{3+}, Fe^{3+} and La^{3+} of 0.9 nm. This must also be the reason for the correlations between the lanthanide elements or with Al, Fe and Sc. The high correlations of boron with P (r = +0.7917) and N (r = +0.88121) confirm that boron can be regarded as an essential element for plants. The high correlation of P and N at r = +0.8352 confirms the high correlation coefficient reported by Garten (1976) (r = +0.84) and the high degree of association which the two elements display, especially during protein biosynthesis.

2.4.2 Physiological Function of Elements

Since the significance of an element in the living organism does not depend on the amount contained in the organism, a systematic division according to physiological and biochemical aspects seems meaningful (Hoagland and Arnon 1950; Bowen 1979; Nierboer and Richardson 1980; Woolhouse 1983; Pais 1991). Those elements (C, H, O, N, P, S, Si and Ca) which participate in the constitution of the functional molecular structural element of the cell metabolism (proteins, lipids, carbohydrates, nucleic acids, etc.) or display a direct supporting or strengthening character (potassium, silicon) are termed structural elements. Nitrogen and sulphur are biochemically integrated into the carbon chain, i.e. after reduction of their generally high oxidation stage (nitrate or sulphate) they are firmly bound to the organic substance. In contrast, phosphorus, boron, and silicon are present in their highest oxidation stage and are not reduced; indeed they rather tend towards ester formation with OH groups of the most varied molecules, particularly the sugars. All structural elements are in the top left of the BSE. They seem to be the elements which during evolution have developed via the photochemical process from a silicon dioxide matrix towards the basic organic matrix as the ‘building blocks’ of life. As the former structure-forming element on Earth, silicon is now only present as a structural element totally (e.g. diatoms) or partially (e.g. Sphenopsida) in lower plants.

The hydrogen atom represents an exception within the structural elements and also in the chemical system of the elements. Although it is contained in almost all structure-forming macromolecules, it additionally has three further decisive functions to fulfil in living organism. It provides the reduction equivalents in many redox processes [usually via the system of nicotinamide adenine dinucleotide or nicotinamide adenine dinucleotide phosphate (NAD/NADP) or flavin adenine dinucleotide (FAD)] and in the form of the H_3O^+ ion, it is also responsible fo the pH value conditions in the cell body. Hydrogen was therefore not rigidly fixed in the BSE in Fig. 2.14, but its special position was rather accommodated in a more or less dynamic manner.

In contrast, the so-called electrolytic elements (K, Na, Ca, Cl and Mg) are required for the constitution of specific physiological potentials and are important for maintaining defined osmolytic conditions in cell metabolism. The element calcium may thus occur simultaneously as a structural element and an electrolytic element. In the BSE, the electrolytic elements are positioned directly adjacent to the structural elements since a compartmentalization in the cell environment was only possible by the formation of membrane systems due to the constitution of structure-forming units, and a constitution of potential differences was only able to result due to this type of compartmentalization of the cell environment. On the basis of the high correlation coefficients with their directly adjacent elements in the BSE, Br, Cs and Sr can probably also be included among the essential electrolytic elements. Sodium is an exception here and can probably be regarded as the ‘information’ element, at least in rapidly progressing reactions (for example, in the conduction of excitation at neurons), since potential reversals frequently occur by changing the permeability for Na^+ ions at the cell membranes, thus making the information flow possible at all. The high affinity of Na for organic structures is clearly expressed in the high correlation coefficients with the individual non-metal (Na/B: 0.72; Na/Br: 0.78; Na/N: 0.76; Na/P: 0.81; Na/S: 0.97).

A number of chemical elements, above all metallic ions, exercise a catalytic function in the cell metabolism as metal complex compounds. These elements are termed enzymatic elements. They include, for example, V, Cr, Mo, Mn, Fe, Co, Ni, Cu, Zn, Sn and Se. Due to the present imprecise nature of the data, it has not yet been possible to offer a satisfactory solution to the conclusive position of these elements in the BSE, so that the physiologically related elements in Fig. 2.14 still have to be combined into groups.

2.4.3 Uptake Mechanisms and Evolutionary Aspects

The relationship between the nutrient supply in the substrate (soil, nutrient solution, atmosphere) and the activity in the plant is not linear over a wide range, but rather describes an optimum curve. Ingestion is adequately quantitatively described by the intensity and extent of uptake up to a certain point in time. In the case of defined nutrient, uptake by the plant depends on the supply of the nutrient in the uptake medium and on its availability. The plant does not generally have any positive influence on the supply, although it does on the material and spatial availability of the nutrients. Nutrient availability may thus be altered in a material sense, for example by influencing the pH value of the soil solution (excretion of H_3O^+ or HCO_3^- ions by the root), by the release of organic acids with a chelating effect by the root, by the participation of microorganisms (mycorrhiza), and also by influencing the redox potential in the soils by H_3O^+ and CO_2 excretion at the root surface.

The most readily available elements are present in the form of ions or as a soluble organic complex in the soil solution. The most poorly available elements are those which are firmly bound to the soil structure, e.g. as secondary constituents in the crystal structure of primary minerals. In the BSE in Fig. 2.14, those elements primarily taken up in the form of neutral molecules are arranged at the top left. They include carbon and oxygen (uptake form mainly CO_2) and hydrogen (uptake in the form of H_2O). However, sulphur and nitrogen can also be taken up as neutral molecules in the form of gaseous SO_2 and NO_2, particularly if they occur as deficiency elements in the primary nutrient medium, the soil. Otherwise in the BSE in Fig. 2.14, nitrogen and sulphur form a transition to those elements which are primarily available to the plant organism in an anionic form. They occur here as a function of the pH value and redox conditions mainly in the form of HSO_4^-, SO_4^{2-} or NO_3^-. The elements chlorine (as Cl^-), bromine (as Br^-) and boron (as $B(OH)_4^-$) are similarly taken up anionically. All other elements, if they do not occur in a chelated from as a complex, are mainly incorporated cationically and are therefore located on the right side of the BSE in Fig. 2.14. This includes, in particular, the alkaline and alkaline-earth elements, as well as most of the heavy metals.

2.5 The "Systems" of Chemical Elements and Their Distinctive Features

2.5.1 *The Periodic Table of the Elements: Historical Origins and Development in Response to Ongoing Discoveries of Chemical Elements*

Early in nineteenth century it was discovered that there are groups (triplets) of chemical elements with similar chemical properties among which the molar masses increase rather regularly:

- phosphorus, arsenic and antimony (roughly 31, 75 and 122),
- lithium, sodium and kalium (7, 23, and 39),
- beryllium, magnesium, and calcium (9, 24, and 40) or
- calcium, strontium, and barium (about 40, 87, and 138),

meaning the "middle" value is close to the arithmetic mean of the other two (Doebereiner's triads, Fig. 2.15).

Now we know that there are electrons orbiting and "wrapping" a nucleus (which latter was unknown to exist till 1911), electrons which can be bound weaker or much stronger to the latter. Weak bonding causes cations to form easily (metals) while strong binding of also additional electrons translates into ready formation of both covalent bonds and anions (non-metals). Doebereiner's rule of triads (Döbereiner 1819) thus lets us to assume that

- there are similar effects in both electron shells and nucleus (being constructed of similar shells of both protons and neutrons) causing utmost stability, and that

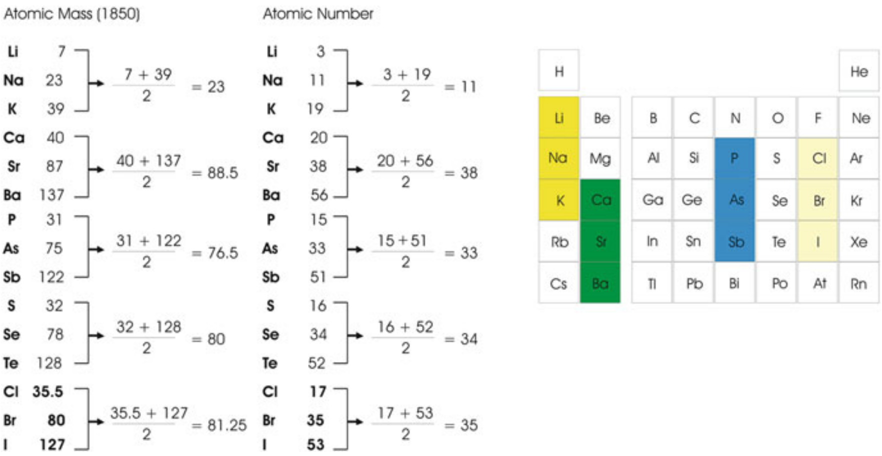
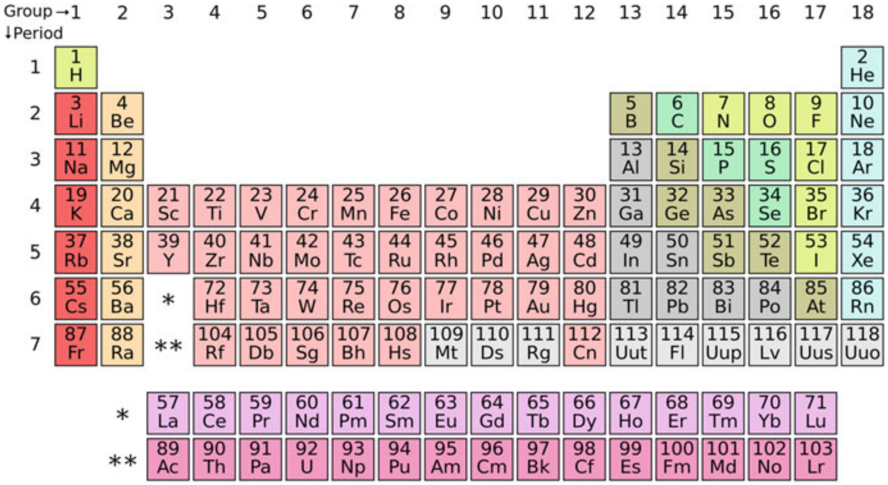


Fig. 2.15 Doebereiner's triads (Döbereiner 1819) as corresponding to modern PSE representations



Group→ ↓Period	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
1	1 H																	2 He
2	3 Li	4 Be											5 B	6 C	7 N	8 O	9 F	10 Ne
3	11 Na	12 Mg											13 Al	14 Si	15 P	16 S	17 Cl	18 Ar
4	19 K	20 Ca	21 Sc	22 Ti	23 V	24 Cr	25 Mn	26 Fe	27 Co	28 Ni	29 Cu	30 Zn	31 Ga	32 Ge	33 As	34 Se	35 Br	36 Kr
5	37 Rb	38 Sr	39 Y	40 Zr	41 Nb	42 Mo	43 Tc	44 Ru	45 Rh	46 Pd	47 Ag	48 Cd	49 In	50 Sn	51 Sb	52 Te	53 I	54 Xe
6	55 Cs	56 Ba	*	72 Hf	73 Ta	74 W	75 Re	76 Os	77 Ir	78 Pt	79 Au	80 Hg	81 Tl	82 Pb	83 Bi	84 Po	85 At	86 Rn
7	87 Fr	88 Ra	**	104 Rf	105 Db	106 Sg	107 Bh	108 Hs	109 Mt	110 Ds	111 Rg	112 Cn	113 Uut	114 Fl	115 Uup	116 Lv	117 Uus	118 Uuo
		*	57 La	58 Ce	59 Pr	60 Nd	61 Pm	62 Sm	63 Eu	64 Gd	65 Tb	66 Dy	67 Ho	68 Er	69 Tm	70 Yb	71 Lu	
		**	89 Ac	90 Th	91 Pa	92 U	93 Np	94 Pu	95 Am	96 Cm	97 Bk	98 Cf	99 Es	100 Fm	101 Md	102 No	103 Lr	

Fig. 2.16 The present state of the PSE (2014) includes superheavy Platinum Group Metals (PGMs: Hs, Mt, Ds), coinage metals (Rg), carbon-group (eka-lead flerovium Fl) member and chalcogenes (dwi-tellurium livermorium Lv) although even few-atom chemistry experiments until now are limited to $Z < 109$

– similar electron configurations and binding properties repeat regularly among the chemical elements (here, $\Delta Z = 8$ or $\Delta' Z = 18$, respectively).

Dimitry I Mendeleyev and Lothar Meier (in the late 1860s) extended Doebereiner's finding to many more elements, thus constructing the periodical system of elements independent of each other. Yet the periodical system of elements had to be accommodated once again (Seaborg in late 1940s): With discovery in nature, the continuous fractionation of rare earth oxides (achieved 1843–1907) followed by preparation by nuclear reactions two more large groups of elements had to be "accommodated" to the PSE. Thus the subgroups of lanthanoids ($Z = 58$ [Ce]–71 [Lu]) and actinoids[7] [$Z = 90$ [Th]–103 [Lr]) were inserted into the periodic system. Ongoing synthetic efforts ($Z > 103$ up to 118, i.e. Rf, Db, Sg. . .) were added by superheavy representatives of the common transition-, platinum group-, coinage- and main group elements [$Z > 112$ up to 120] so, that now the system is almost complete[8] (Fig. 2.16).

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[7] While for the actinoids similarity with lanthanoids was driven so far as to name analogs according to similar rules ($Z = 63$: europium, $Z = 95$: americium; $Z = 65$: terbium (alluding to a village in Sweden where it was found first), $Z = 97$: berkelium) the lighter actinoids (protactinium to americium) differ from their REE analogs in stabilizing oxidation states + V to + VII which the latter will never reach in condensed matter while the heavy ones ($Z > 100$, Md [mendelevium], No, and Lr) turned out to be commonly much more stable in divalent states than corresponding REEs Tm, Yb, let alone Lu.

[8] To our present knowledge it will be almost impossible to prepare atoms with $Z > 123$ of sufficient half-lives (>0.2 μs) even to identify them (otherwise, nuclei formed in a target would decay during mass separation and hence before reaching the detector device), let alone doing any chemistry.

The present (2014) “record” of making very large atomic nuclei is $Z = 118$ ($^{294}118$), a still-unnamed noble gas (working name “moscovium”), whilst the heaviest element which already was given an official name by IUPAC is the chalcogene (homolog of Te and Pb) livermorium (Lv, $Z = 116$). Except for neutron stars and their gravitational disruption by close access before mergers, there are no hints that nature does any better; on the contrary, it is unlikely every of the processes of stellar nucleosynthesis would produce anything with $Z > 101$.

Generally speaking, the PSE organizes the manifold of chemical elements according to periodicities brought about by the number of electrons orbiting some atomic nucleus vs. the aufbau principle. It is related to Pauli’s law and electrons having half-integer spin, which means not even two of them can occupy the same site or state within some connected structure. The organization of atom structures can be accounted for by Pauli’s principle mainly, and oxidation states, stability and even physical properties of certain compounds can be predicted by this reasoning (which already Mendeleyev did much before any knowledge of electrons, atomic nuclei, let alone quantum mechanics). Small (about 1/1,800 of a proton or neutron) mass, half-integer spin, and mutual electrical repulsion of electrons unbalanced by anything else than spin-pairing[9] cause electrons to produce fairly extended assemblies. They follow hierarchical rules which were found long before one got the theoretical means to understand their reasons.

By the way, if the electron spin value was different, there was no way either to distribute electrons across a network of positively charged nuclei arranged somehow in space; in fact, rather than forming any molecules electrons would accommodate very close to one of the nuclei (that is, the more positively charged one). So there could be salts[10] in such a world but no molecules other than homoatomic diatomic ones, of course excluding formation of any polymers required to construct living beings. Moreover, the lightest elements, particularly hydrogen, would anyway give away their electrons to any heavier ones: H_2 could exist but there would be only very strong acids instead of any compounds with covalent element-hydrogen bonds other than H_2. The redox behavior would be right the other way round than it actually is: antimony, tellurium, iodine (and xenon, caesium, barium!) attracting electrons much more strongly than nitrogen, oxygen or fluorine, do! Accordingly, there would be only metal ions with Ahrland B-type behavior.

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[9] On the opposite, protons and neutrons in nuclei attract both each and the other kind of nucleon due to the strong nuclear force, partially compensating mutual repulsion of protons even though they are tightly packed. Thus the “magic” numbers producing closed, most stable nuclear orbitals (8, 20, 28, 50, 82, 126, plus 14, 34, 62, 108 for non-spherical arrangements) differ from the Z values of noble gases (10, 18, 36, 54, 86, and 118) and fairly inert metal ions (28, 46, 78) which are caused by electron properties alone.

[10] Both one-dimensional ones, ylides, and three-dimensional assemblies of charged atoms.

2.5.2 The Biological System of the Elements

The BSE, originally being a statistical abundance correlation among a couple of plant species (Lieth and Markert 1990; Markert 1994a, b, 1996), is outlined detailed in Sect. 2.4. On this basis the authors Fränzle and Markert tried in the further course to investigate the relationship between some chemical feature of metal ions, namely the tendency to form complexes of a certain variation width and hydrolytic stability and biological function (Fränzle and Markert 2000a, b; Markert et al. 2004; Fränzle 2010). For one reason or another, this goes along with their presence and positive life-supporting function in proteins, be it restricted to some organisms living in strange environmental conditions or be it (close to) universal in life as we know it. The biological properties of chemical elements do not follow periodicity, on the contrary: Zn is essential to all living beings, Cd functional in just a couple of enzymes, Hg a notorious and universal poison, the same in the 2nd main group, comparing Mg and Ca to Ba and Be (Sr is both abundant and essential to certain organisms, such as stony corals).

Thus a "Biological System of the Elements" cannot be derived by direct extrapolation from the Periodic System of Elements as the latter is focused on valence while the formation of any polymer having side-chains for some function of course takes covalently-bound backbones which include at least trivalent elements. Empirically, there is a bias in favor of divalent cations in biocatalysis as well. The backbone must be reversibly formed from monomers while the former must be reasonably stable towards both liquid water and heat. That is, these covalent frameworks undergo neither thermal decay nor violent solvolysis unless much above the melting point of water. Nature uses polyphosphates (in nucleic acids), polyamides (peptides, proteins) and acetals (cellulose, chitin, lignocellulose) for this task. But hardly any polyesters or other structural motifs for which appropriate monomers are at hand likewise while ion pair structures and disulfides are only used to bridge some parts of a polymer chain. May polyamide linkage by simple inorganic or monomer-metal ion complex catalysts be more straightforward than that of polyesters? Probably not: in prebiotic simulation experiments, as a rule glycolic, lactic, malic acids are formed in yields which are at least as high as those of the most readily forming amino acids including glycine. Polyesters withstand water as well as proteins do (textiles woven from polyesters can be washed repeatedly without dissolving or hydrolyzing quite like those made from wool or nylon). Branches in polyester monomers rather tend to be introduced into some (then duroplastic) network than be used for retaining metal ions or forming hydrogen bonds which they tend to do in a polyamide framework.

As pointed out in Sect. 2.1, thus

- biological function is not directly related to the position in the PSE. This does hold for other than the 2nd and 12th group of PSE, also. E.g. pnictogenes and halogens but (among metals) rather to complex formation properties (which within some group obviously change continuously with atom size and thus with Z), and

- elements now almost generally essential to life on Earth, whatever it may look like, bear a kind of history, namely the history summarized by the term of evolution ("nothing in biology makes any sense except in the light of evolution" [T. Dobhzhansky]).

To put it bluntly, this latter history—the "natural selection of the chemical elements" (Williams & Frausto daSilva 1996)—may be either a static or a dynamic phenomenon concerning its origins: when putting energy suitable to cause chemical transformations to some inorganic mixture containing C, H, N, O (and S, P) which is not fully oxidizing in character (or given some reductant like Fe(II) is present), ligands become present in this "primordial soup". They are rather weak except for CO, and cyanide will be converted into much more effective, but likewise selectively binding ligands such as amino acids or oligocarboxylic acids and eventually polymers (probably attached to some interface by adsorption). These latter will extract metal ions from seawater, underlying sediment or even compact minerals and do so according to their local abundances and chemical potentials. Roughly speaking, the difference between mineral solubility or dissolved ion concentration on one hand and complex stabilities on the other: Thus some array of complexes (cp. Beck and Ling 1977; Beck et al. 1977) is produced from minerals among which certain ones will act as catalysts, that is, protoenzymes. The "dynamic" assumption starts with catalytic transformations producing some of the very intermediates of chemical evolution accomplished by minerals or dissolved ions. E.g., formation of sugars from $HCHO/HOCH_2–CHO$ is promoted by Ba^{2+} or Pb^{2+} or clays or there are various transformations of formamide. The minerals or dissolved ions causing catalysis are to be "trapped" by the forming organics. In this latter scenario the now essential elements are just testimony of previous catalytic transformations. In either case endosymbiosis—in first formation of eucaryota which apparently happened only once little more than 2 bio. years ago—added some more elements to the "joint" essentiality list. That means that all recent eucaryota have broader arrays of essential elements than both eubacteria and archaea while certain metalloenzymes are almost restricted to certain organelles. These containing and using Mn are limited to mitochondria (Mn in malate enzyme [cp. Tipton et al. 1996]) of bacteria, animals, and fungi alike (in oxygenic photosynthesis of higher plants, algae, and cyanobacteria Mn is also located in photosystem II which accomplishes water oxidation).

A theoretical fundament of abundance distributions and their causal analysis was achieved by using the so-called Stoichiometric Network Analysis (SNA; Clarke 1975, 1980; Fränzle and Markert 2000a; Fränzle and Markert 2000a,b; Fränzle 2010) for the purpose of analyzing the biological roles of some species (see Sect. 4.2.1). This approach showed that deep-lying biochemical reasons and factors which give rise to the correlations among abundances of chemical elements in biological samples can be worked out. Chapter 4 gives examples how SNA considerations and empirical correlations allow for probable conclusions whether some chemical element can be essential or toxic at all. A further consideration would be to look in which speciation or binding form there will be biological activities, including pH and redox potential effects on speciation and biological activity (Sect. 4.2.1).

Very often, the same chemical reaction can happen in different conditions, e.g. it might run spontaneously[11] in ambient conditions or be caused by some abiotic catalyst or brought about by (some members of) the biota. The above difference is not just about kinetics but needs a more detailed scrutiny: while abiotic catalysts, say, mineral or clay interfaces or element oxides are there at levels which keep fairly constant with time and thus effect a rather constant turnover of substrates into products, organisms might grow and even reproduce. This happens while doing the same chemistry: reduction of sulfate or oxidation of Fe^{2+} (by air) or of H_2S (by nitrate, in deeper layers of euxinic or mesomictic water basins like Black Sea or Lake Alat [Bavaria]). If elements like C (say, in photosynthesis), N (e.g. nitrate reduction), S, metals such as Fe or Mn are involved in such a biochemical transformation, it is most likely that some part of the substrate processed into a product will be retained by the biota for purposes of growth and reproduction. Then, the average concentration of the catalyst—and thus the turnover rate—will steadily increase with time. The same can happen without biology, too:

- MnO_2 (pyrolusite) behaves as a both powerful and versatile oxidation catalyst towards a multitude of organic (e.g. phenols, malonate ion, but also amino acids) and inorganic species; at neutral or alkalinic pH it does form upon reduction of permanganate MnO_4^- readily. Hence in these conditions ($pH > 6$) oxidations by permanganate become **autocatalytic** and exhibit strange, sometimes even oscillating[12] kinetics.
- another common autocatalyst is the solvated proton; oxidations of hydrogenated compounds having CH-, NH-, or PH-bonds (for example) produce protons, thereby increasing reaction speeds until either the substrate was completely consumed, an explosion occurs or some competing entity intercepts the acid.

There are few uncontested and unequivocal examples for autocatalysis in chemical evolution (Orgel 2004) while "ordinary" catalysis is quite frequently observed and often crucial in making substantial amounts of key intermediates or biorelevant compounds. That is why the cases of autocatalysis related to chemical evolution were specifically marked in the Table 2.5. Thus it would appear biogenesis was a real game-changer in processing those high-energy intermediates afforded by

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[11] There are significantly exergonic reactions which literally will not take place, not even allowing for geological periods of time, like hydrogenations of N_2 or of nitriles unless there are efficient specific catalysts, either homogeneous (dissolved) V-, Mo, W- or Re complexes or iron (or Os) chalcogenide particles. Another hard-to-activate reaction (at least if $T < 250$ °C) which, unlike nitrogenase activity, almost every living being can induce is **reduction of sulfate**; activation (oxidation) of aliphatic CH bonds without additional functional groups (Hal, OH, $-OPO_3^{2-}$, -COOR, -COSR) is less far-spread in biota.

[12] Oscillations in permanganate-based systems (like others) require addition of orthophosphate **plus** two reductants to be present besides each other, like nitrite and formate, or NH_3OH^+ and an organic compound like malonate.

chemical evolution. Accordingly the first structures capable of reproduction would soon deplete the "pool" of organics around due to this autocatalytic feature, and the "invention" of photo- or chemosynthesis some 3.5 bio. years ago came just in time to avoid a major crisis. But this is not a case of the remote past only: planets or large moons where there are living beings (some of which do photosynthesis) are distinguished by a larger extent of chemical non-equilibrium next to the surface. Especially in astrobiology, three questions arise from this fact:

(a) Does extant biota effectively compete for these resources with non-biological chemical reactions?
(b) Can kinetics be used to tell what happens (predominantly) over extended periods of time?
(c) Are there any experiments to tell apart biology (or autocatalysis at least) from common reactions which fall short of isolating organisms invoked to be involved?

Assuming in each case that possible local organisms can make more than a very modest sustaining of their existence in local or experimental conditions, not lacking anything crucial (vital) to reproduction. Time will tell whether they dominate the corresponding chemical pathway. This does imply the same experiment which is possibly related to some indigenous metabolism must be repeated on the same sample several times to look for either declining, fairly linear or increasing reaction rates, going to sigmoid kinetics once resources are depleted. Since autocatalysis including biological reproduction is distinguished by "non-linear" kinetics, a mathematical method which "carves out" autocatalytic vs. "normal" pathways of one (identical) kind of chemical reaction can be used to identify

- biological contributions
- the likelihood that biota will take over majority of resource depletion in given circumstances

As well as any kind of feedback (autocatalysis does mean feedback as it increases the level of a catalyst promoting the studied reaction). The refutation of vitalism means that you cannot identify biology just by observing that reactions on simple substrates go strange ways: non-biotic reactions are not kept from doing the same. One classical though not very frequently used mathematical method to make the above distinctions and identify autocatalysts—be they alive or not, like in the above cases of manganese dioxide, oxonium ions, or others like OH radicals, bromine oxides—is **Stoichiometric Network Analysis** (SNA) (Chap 4). As it was designed for identifying autocatalysis (mainly associated with chemical oscillators), it can be used probably to do the above. But there is more to it: stabilities of foodwebs may be investigated, too (Fränzle 2000), as are common features of biochemistry (Clarke 1975, 1980).

We know the eventual result of (at least) one of Nature's experiments to create an assembly of autocatalysts processing (or even producing) organic matter in an autocatalytic feedback mode: it actually did work, hence we are here, besides of lots of other hetero- and autotrophs among which most went extinct sooner or later. The game-changer of biogenesis accordingly altered kinetics but did so in a way which left a reasonably large chance to escape resource depletion problems with many creatures, from heterotrophic bacteria to ourselves, still relying on consuming organics from outer sources mainly.[13] Perhaps one can understand or at least formally constrain the "bottleneck" associated with biogenesis in a setting when C^{red} production rates can be estimated now sooner or later by SNA arguments also but this is not our focus yet.

2.5.3 Geochemical System of the Elements

'The Earth Scientist's Periodic Table of the Elements and their Ions' after Railsback (2003) alias Geochemical System of the Elements (GSE) tries to demonstrate an integrated view of geochemistry applicable from the mantle to soil to seawater. Railsback states that as a result of this new table trends, patterns, interrelationships in mineralogy, soil and sediment geochemistry, igneous petrology, aqueous geochemistry, isotope geochemistry, and nutrient chemistry become apparent (Fig. 2.17). Generelly spoken, it deals with mineral stability and conditions of their formation (ion radii, electronegativity). These control the tendency of elements to form salts, minerals while the presence of biological agents and biogenic compounds later-on can modify the original minerals (minerals for this purpose including neat elements of reasonable chemical stability, both metals [Cu, Ag, Au, Bi etc.} and non-metals [C, S, As, Sb] in their solid states[14]).

The GSE is thus closely linked to the Periodic System of the Elements (PSE) while its relationship to the Biological System of the Elements (BSE) is rather remote.

Soil is a most heterogeneous multiphase medium, and the same holds for minerals (one of its principal phases!) even though the latter are chemically

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[13] There are some exceptions: even humans can make glycine from CO_2 and NH_4 cations by C (IV) reduction via the folate reduction pathway, and glycine itself is linked to other organics via oxidative desamination affording glyoxylate (in malate synthase glyoxylate is linked to acetyl CoA producing C_4 compound malate). Though this process falls far short from C autotrophy, it is an interesting question in how far these "exceptions" can and will influence general dynamics of essential elements.

[14] In terms of interplanetary comparison, this means what is a mineral depends on local environmental conditions: in the atmospheres of Earth, Venus, Mars, and Titan, N_2 of course is gaseous and not a mineral, but on Triton and possibly Pluto solid nitrogen which is known to be partly crystallized from spectra can well be considered one; conversely solid sulphur (S_8) deposited here on Earth around volcano fumaroles or black smokers doubtlessly is a mineral (even forming large crystals) but on Venus elemental sulphur is a gas (mainly forming species S_4 to S_7) and thus not a mineral!

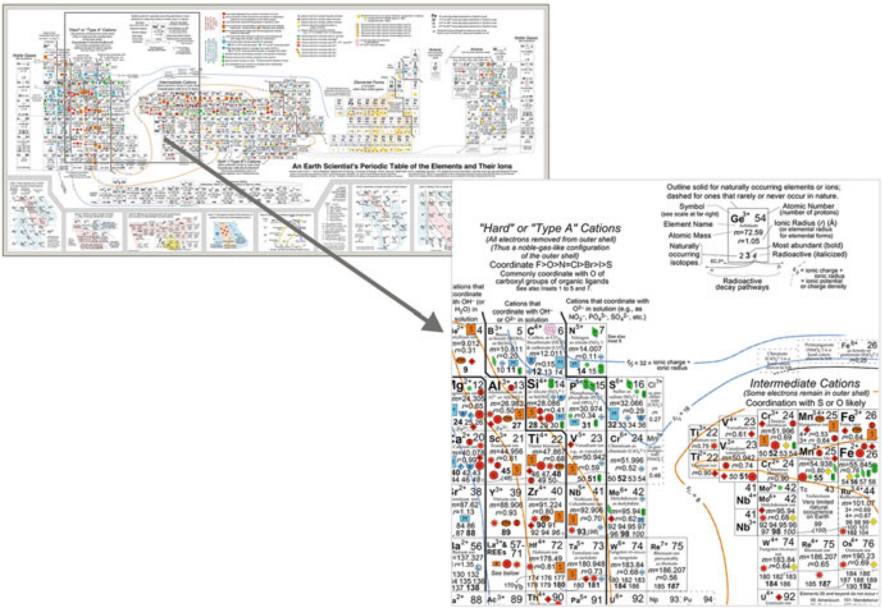

Fig. 2.17 Railsback’s ‘*Earth Scientist’s Periodic Table of the Elements and Their Ions*’ alias ‘Geochemical System of the Elements’ (GSE) shows physical properties and abundances of elements and their ions and isotopes of importance to Earth scientists (Railsback 2003). These trends in mineralogy, aqueous geochemistry, igneous petrology, mantle geochemistry, soil and sediment chemistry, and nutrient chemistry are largely controlled by coordination of cations with O^{2-}. Railsback (2003) states that this synthesis of geochemistry from mantle to soil to seawater provides a framework for understanding Earth systems and predicting geochemical relationships not recognizable with a conventional, elementally constructed, periodic table. The GSE is focused on the key measure of electrostatic attraction, that is, the Z^2/r values where Z is the effective electrical charge (in elementary units $= 1.602 \times 10^{-19}$ C or 0.16 attoCoulomb) and r is a crystallographic (unsolvated) ionic radius (in Å = 0.1 nm = 100 pm). Because of the very large map you can see an extract on the right side. To have a look on the whole map and description please visit f.e. the homepage of Railsback (www.gly.uga.edu/railsback/PT.html)

homogeneous at least to the extent larger single crystals can be produced by ions of similar size.

Formation of minerals depends on charges (and thus relative numbers) of cat- and anions, and—of course—they must be stable towards local environment conditions to have them arrange to form some solid. For anions, there may be either oxidation or protonation (oxides, carbonates, silicates) destroying them, while cations might undergo hydrolysis or likewise redox reactions. The presence of certain minerals or even coexistence of minerals then tells the stability conditions for a couple of specific cat- and anions are met simultaneously.

Once conditions change, e.g. upon contact to air oxygen (e.g. during mining or erosion) some minerals will be destroyed while others now can form. Empirically, this does increase the number of existing minerals considerably. If there are intermediate redox states of either a cat- or anion, precipitation of some mineral phase will often entail disproportionation of the said cat- or anion: even though air oxidation will produce just traces of Mn(III) in neutral aqueous solution, MnO_2 is so little soluble that Mn^{3+} or $[Mn^{III}(OH)]^{2+}$ will straightforwardly decompose into dissolved Mn^{2+} and solid MnO_2, producing one more mineral (birnessite). Of course, redox processes can be afflicted to minerals by the biota as well, and thus living beings serve to modify the patterns of minerals which are present somewhere also. However, in doing (chemolithoautotrophic) metabolism, they will mainly enhance rates of exothermic reactions (others cannot be catalyzed, not even by enzymes, except "investing" ATP), bringing the system closer to thermodynamic equilibrium. Hence the now large manifold of minerals on Earth is due to the fact that there are both unprocessed and oxidized ones, as not all parts of crust or upper mantle saw exposition to dioxygen even though biochemical activity might go far deeper than previously assumed. Organic products of direct or indirect biological origins rarely form minerals. Biomineralization produces a couple of minerals which, however, are fairly common also without involving animals (calcite, apatite, coelestin) or plants (cristobalite) in their formation.

Hazen's notion (2009) hence is related to some non-equilibrium state across the matter column where there is an obvious redox potential gradient like in most soils. This non-equilibrium, plus similar effects from photochemistry and photosynthesis, is a precondition for sustained life, too. Once equilibrium would be reached, life would go extinct, and most of the minerals now to be found here or there would vanish also. Nevertheless, anion/cation interactions giving rise to minerals is not directly related to changes of conditions: there are minerals, sometimes condensing from gaseous phases directly, also on celestial bodies far too small to undergo any differentiation or production, evaporation/photoloss of liquid water. The PSE "offers" elements which form anions gaining almost as much energy as it takes to convert others into cations. Hence salts will form from halogens and chalcogenes O, S, Se plus alkali metals quite readily even when electrostatic interactions were much weaker.

2.5.4 Link in Between the Three Systems of Chemical Elements

The Geochemical and Biological System of Elements are linked to each other by all of

- chemolithoautotrophy (some of the respective organisms, including hyperthermophilic archaeans, produce ZnS and other minerals),
- biomineralization in reef-forming organisms and last not least by weathering of minerals during metal supply of bacteria, fungi, lichens etc. or

- redox-, photoredox (Fe(II)-using photosynthesis in certain bacteria) processes precipitating Fe(III) aquoxides.

While phototrophic organisms, depending on light energy, are obviously limited to the surface of solid Earth and, say, the top 100 m of the ocean water column, chemolithoautotrophs can exist deep into the ground (several km as long as $T < 110$ °C). They even make use of non-equilibrium species directly obtained from the upper mantle (which is fairly reducing) in both fumaroles and black smokers, or even consuming radiogenic chemicals like Desulforudis audaxviator does. Hence their possible effect on mineralogy on Earth is more profound (the average thickness of vegetation C layer on Earth including the oceans is just a few mm) while the consequences of this are still poorly understood. The BSE as is now moreover deals with (terrestrial) plants mainly, implying its implications to be restricted more or less to the very (and illuminated) surface of this planet. Notwithstanding this, aquatic organisms may sequester substantial shares of certain elements as compared to all of the biosphere.

The link among the different “systems” thus is connected to topography, and may be even more so on other celestial bodies where life can persist only far from the surface for presence of aggressive oxidants (Mars), extreme cold (Europa, Titan, Enceladus) or/and strong ionizing radiation (Jovian moons). Statements on minerals are not that strongly restricted in terms of vertical distribution than those dealing with green plants or algae. In turn, some of the latter may be part of the aerosol (seaspray etc.) where formation of minerals, except for NaCl or ammonium salts in polluted rural areas, is uncommon at least.

In terms of hierarchy, one might distinguish among the “systems” PSE, BSE, and GSE in terms of all age, scope, and amount of matter involved. As can be seen from spectra of larger molecules (namely CH_3OH) in gas clouds at cosmological distances the PSE and pertinent parameters do hold almost throughout the observable universe, and cover tremendous amounts of matter over a timeframe of >7 bio. years. The BSE by definition is restricted to biomass, in effect, even to multicellular eukaryotes. The latter do exist for less than 1.3 bio. years now and represent little more than 10^8 metric tons of C located in a thin layer. Minerals did very soon form from interstellar gas once some first supernova had added precursors of hardly volatile solids to the mixture, including perovskite (Ca, Ti), silicon carbide, disthen (Al, Si) and probably only later the most refractory 5d metal grains (Re, Os). Of course, the quantity and vertical extension of the realm of minerals right on Earth also is much larger than those of biomass when going downward until all minerals melt (>200 km depth). First Earth-borne minerals (zircon $ZrSiO_4$ crystals) are 4.40 bio years old, substantially predating biogenesis. In the resulting hierarchy one can link the BSE to both PSE and GSE but not the other way round even though certain minerals are directly related to biochemical weathering and plants, fungi, lichens derive their elements from soil, sometimes even right out of minerals. The increase in complexity, with respect to both number of involved chemical elements and average molecule size, corresponds to an increase in time required to form

Table 2.5 Mutual relationship and key features of PSE, BSE, and GSE

Key structure	Complexity/size	Element uptake described by	Element uptake depending on	First formed [bio. years after "Big Bang"]
Molecule	Two up to many atoms	PSE, rules of valence and coordination chemistry	Relative energy gain upon rearrangement of chemical bonds, valence rules (Monovalent atoms or functional groups can only replace each other at terminal bonds (e.g. H, F, CN), divalent ones (O, S) can form or extend chains while trivalent and more binding ones can give rise to branched chains and interchain-linkages.)	Less than 7 (methanol in remote gas clouds), but probably <1
Mineral	Periodically repeating crystal structure	GSE	Relative ion sizes	Some 9.4 on Earth ($ZrSiO_4$)
Biomass	Assemblies of different polymers which exert different functions	BSE	Biomass sample behaving as a ligand and/or capable of reacting with electrophiles $\neq$ metal ions	≥ 10 on Earth

corresponding species which then take up metals for structure or (catalyzing) certain functions. Mutual relationships and key features of PSE, BSE, and GSE are shown in Table 2.5.

Chapter 3
Analysing the Biological Roles of Chemical Species

Abstract Depending on all element contents, speciation, and dose, chemical elements and their compounds, including molecular ions and complexes, might exert quite diverse effects on (given, it does matter which one is concerned) living beings. Apart from the rather trivial fact 'that overdoses of almost everything are toxic to fatal, roles of elements are closely related to their specific chemical features (which permit to identify and distinguish them). Concerning the set of metals involved in biocatalysis, it was shown that, while appearing to be very diverse and different in their properties, these metals actually do share certain quantitative features in their interactions with potential ligands, such as both amino acid side chains in the proteins to which they belong, and possible substrates of biochemical transformations. The two dimensions—one belonging to "intrinsic" strength of binding between metal ions and ligands of different kinds and the other describing effects of (ex-)changing ligands with one another—do both influence chance and range (also taxonomical range) of positive element-biomass interactions.

3.1 Essentiality of Elements for Living Organisms, Taxonomy and the Environment

No living being can exist, no form of life even be sustained without the presence, catalytic and other use of a couple of metals (about eight of them, normally: K, Mg, Ca, Mo, Mn, Fe, Cu and Zn, as a minimum). They are absorbed as ions or humble complexes and then get integrated into proteins. Those bound to enzymes can take part in catalyzed biochemical transformations; this holds for most of the total amount disregarding insoluble metal salts which form supporting structures such as skeletons or outer hulls (e.g. $CaCO_3$, apatite, or $SrSO_4$). Related to metal ions attached to the outer side of proteins, they are changing their shape as to activate or "switch off" catalytic activity (usually, this is done by Ca^{2+}). While these eight kinds of metal ions are required by almost all living beings, certain taxonomic groups need certain additional elements, and most of the differences are among the three large groups of eukaryotic metazoans. *Essential elements* were defined by Arnon and Stout (1939) as such without which a given living being either would not

B. Markert et al., *Chemical Evolution*, DOI 10.1007/978-3-319-14355-2_3

be able to complete its life cycle in a normal way or might not reproduce. In "less advanced" organisms, certain of these elements may be replaced by (similar) others (V or W instead of Mo, Rb for K, Sr for Ca) but as a rule they are indispensible. *Beneficial elements* just enhance vitality or reproduction rates short of being essential, e.g. light (Y/Ce group) REEs in seed germination, growing and fruit production of scrubs and trees.

Yet, in more specific cases essentiality must be demonstrated in experiments where the special element is excluded from the diet of some living being. Effects can be observed such as inhibited growth, impaired responses to the environment, deficiencies of energy conversion (muscle weakness, -atrophy in animals; chlorosis in plants) or infertility. This test can, however, be extremely difficult for either ultratrace demands or when there are volatile, nanodust speciation forms of the said element. These impurities will get accessible to animals by mechanical attack (biting dogs or rats, playing cats, snail radulae, etc.) whereas fungi and some plants can even accomplish partial extraction by chemical dissolution.

In other living systems, including marine algae (*Ulva lactuca*) or diverse strains of bacteria K can be fully and reversibly replaced by Rb (even several times) without compromising vitality, metabolism or reproduction (Scott and DeVoe 1954); accordingly for those organisms K is not an essential element but just one member of some collective of very similar ions (K^+ and Rb^+) which can fully replace each other. Such cases are not covered by the present notion and concept of essentiality up to this day even though they hold for other metals too, particularly in marine algae also.

Besides of the general features of essentiality issues, i.e. those which apply to large taxa or even entire kingdoms, some chemical peculiarities concerning essentiality should be noted as they refer to heavier elements ($Z > 30$). That is, the rarer ones (see below) which form rather exceptional to fairly far-spread cases. These are given in order of increasing Z (34–74):

- **selenium**, Se, is involved in redox metabolism of many species (animals [glutathione reductase], eubacteria, archaea) owing to the weakness[1] and thus pronounced reducing power of H–Se bonds. Or, considering physiological pH and the acidity of selenols (Pka ≈ 4.5, similar to R-COOH), rather of selenolates $R\text{–}Se^-$;
- **strontium** is necessary to make stony corals grow and reproduce (cause release of eggs and semen from the individual polyps); though its biochemical function is unknown it thus has a substantial ecochemical role. Considering the Sr^{2+} level in the oceans, it is unlikely ever to become critical in "outdoor ecology" but Sr originally was not included in seawater salt mixture recipes designed for seawater aquarium fish tanks. Moreover, some big unicellular organisms make protective shells from $SrSO_4$;

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[1] Compared to both S–Se- and Se–Se bonds; the latter are insignificant here as they cannot form inside proteins because there is only a single selenocystein residue at most in any protein so far investigated.

- **cadmium** can be used as an alternative active ion (replacing Zn or Co) in carboanhydrases which catalyze the CO_2/HCO_3^- equilibration; carboanhydrases with specifically depend on Cd rather than substituting in a Zn-based enzyme are known for *Thalassiosira weissflogii* (Strasdeit 2001);
- **iodine** is required to produce some organoiodine aromatic compounds which act as hormones[2] in vertebrates, causing e.g. metamorphosis in amphibia, like thyroxine, which is a iodinated phenoxyphenyl amino acid;
- **barium** is required by certain algae which thrive in extremely nutrient-poor bogs, the desmids; the biochemical function of Ba is unknown;
- **tungsten**, W, the heaviest essential element so far established ($Z = 74$), is common in oxidoreductase enzymes of archaea and clostridia (Kaim and Schwederski 1993; Johnson et al. 1996), replacing Mo for operation at much lower local redox potentials (where Mo would remain in a reduced state, probably + III), high temperatures (living at about 100 °C) or/and extreme pH levels.

Lead und **uranium** were identified to be located in the centers in some bacterial and archaea enzymes (Cvetkovic et al. 2010), but are not yet known to fulfill any "positive" function there, in full accord with the Biological System of Elements.

Arsenic is a more difficult case: it is readily bioalkylated and undergoes processing in biochemical cycles after substantial enrichment by marine organisms including crustaceans. American lobsters would be highly toxic if the levels of As detected therein were bound in some inorganic forms rather than exist as quaternary arsonium ions (arsenobetaine [= trimethylarsonioacetate]) or arsane oxides [cp. Irgolic 1986]), but there are no lack symptoms associated to As in deprivation experiments.

Several other elements keep to be invoked to be at least beneficial for humans or other species although either there is no idea concerning their possible mode of action or effects, or their chronic toxicity is well established (e.g., Cr, Pb). Though discernible in epidemiological studies covering larger areas, if not entire biogeochemical provinces in Vernadsky's sense of this term—are very special and indirectly linked to biochemistry: f.e., there are epidemiological hints that fewer people commit suicide or suffer from any kind of depressive diseases (from burnout to bipolar depression) where drinking water levels of Li^+ are above-common (Kapusta et al. 2011). This conforms to the known use of **lithium** in treating depression (where much higher doses are used) yet does not give proof whatsoever that the human brain (let alone any other organ of whatever species!) actually does need Li for proper functioning! After Ekmekcioglu (2006) and Quiroz et al. (2004, 2010) there is no exactly known physiological function of lithium in any living being;

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[2] Experiments on hormone activity of thyroxine derivatives showed that this function depends just on bulky substituents at the phenoxyphenyl group and lacks relationship to chemical properties of iodobenzenes; actually, the big iodine substituents can be replaced by even more sterically demanding yet halogen-free alkyl groups like isopropyl or neopentyl (Kaim and Schwederski 1993)!

accordingly Li cannot be taken as an essential element. Notwithstanding its supply will have a beneficial effect in certain circumstances: according to Anke et al. (1990) lithium depletion—induced in either rats or goats by corresponding food composition—will bring about problems concerning both metabolism and reproduction which suggests there are conditions in which Li might be important to humans also. In particular, Li is well-known to be beneficial in bipolar depression (see below) suggesting it might be regularly involved in neurophysiology or CNS (Central Nervous System), brain function. In both whole-animal and tissue experiments pharmacological doses of Li were shown to be active in biochemistry.

In the following there are given some effects of Li and Li compounds in animals and various cell lineages after Ekmekcioglu (2006):

- Stimulation of hematopoiesis
- Altering activity of secondary messengers (adenyl cyclase ↓, phospholipase ↑)
- Effect on inositol metabolism
- Effect on prostaglandin metabolism
- Suppression of Na^+/K^+-ATPase
- Change of circadian rhythms
- Effect on neurotransmitter metabolism[3]
- Antibacterial and antiviral activities
- Effects on ion-[4] and water transport channels
- Neuroprotective effects
- Suppression of some enzymes involved metabolism, like phosphoglucomutase in glycogenolysis

It is unknown whether these effects also apply to humans exposed to levels of Li which are common in and from nutrition (Ekmekcioglu 2006).

The first to report positive effects on manic illness was Cade already in 1949. This prompted numerous researchers to investigate activity of lithium in bipolar affective disorders (then called maniac depression). They could show that continued Li administration would inhibit further maniac or depressive episodes among most of the patients. This made Li salts the medication of choice in treating bipolar affective disorders for quite a period of time already (Schou 1997). More recent reports and studies showed lithium therapy to be more efficient in precluding maniac recursions than in treating the depressive components/phases. Up to now, it is not completely clear how Li does work in bipolar disorders. Anyway, Li does influence the activity of secondary messengers. According to Quiroz et al. (2004, 2010) the effect of Li on inositol metabolism seems to be pertinent (Fig. 3.1).

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[3] It should be noted that Li administration is highly dangerous if combined with antipsychotic drugs like haloperidol or fluphenazine (causing toxic encephalopathy and sometimes irreversible brain damage Gille et al. 1997; Colvard et al. 2013), that is, compounds interacting with the dopamin (rather than serotonin) system.

[4] Due to extreme hydratation and displaying some lipophily as well, Li^+ is even much bigger in aqueous media than either Na or Cs cations.

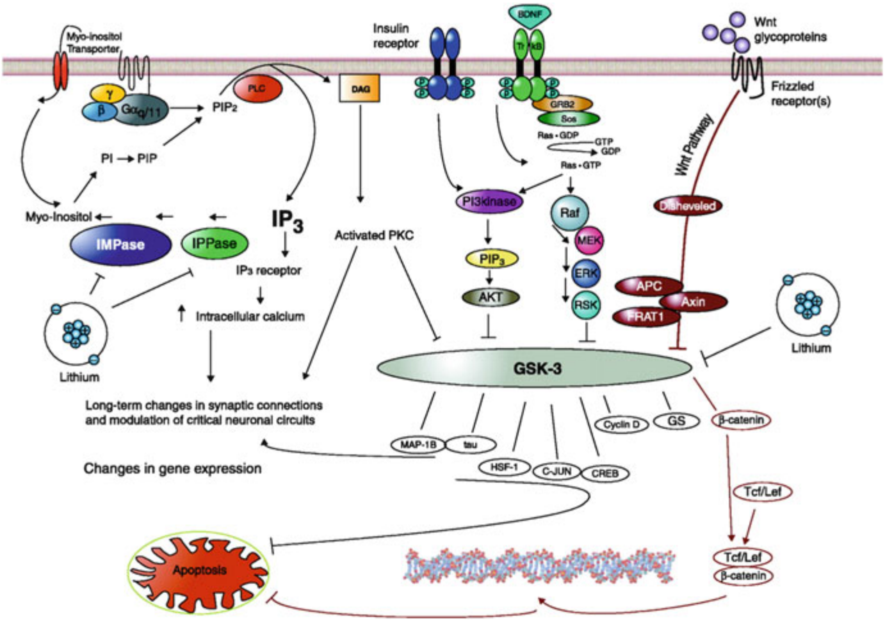

Fig. 3.1 Glycogen synthase kinase-3 (GSK-3) and inositol monophosphatase (IMPase) are direct targets of lithium. This simplified figure highlights relevant interactions among intracellular pathways related to lithium's action. GSK-3 functions as an intermediary in a number of signaling pathways including neurotrophic signaling pathways, the insulin–phosphatidylinositol 3 kinase (PI3K) pathway and the Wnt pathway—activation of these pathways inhibits GSK-3. The *upper left* portion of the figure depicts lithium's actions on the PI signaling pathway. Activation of some G proteins induces phospholipase C hydrolysis of phosphoinositide-4,5-bisphosphate (PIP_2) to diacylglycerol (DAG) and inositol-1,4,5-triphosphate (IP_3). DAG activates protein kinase C (PKC). IP_3 binds to the IP3 receptor that also functions as a calcium channel in the cell. IP_3 is recycled back to PIP_2 by IMPase and inositol polyphosphat phosphatase (IPPase); both of which are inhibited by lithium (Majerus 1992). The inositol depletion hypothesis suggests that lithium exerts its therapeutic actions by depleting free inositol and thus dampening the activation of downstream signaling pathways in neurons (Berridge et al. 1989). Figure and text are reproduced with permission from H Manji (one of the authors of Gould et al. 2004)

Inositol phospholipids are involved in various processes of information processing in the brain (Fisher et al. 1992), e.g. being important for receptor-mediated signal transduction. After G proteins and phospholipase C had been activated, 1,4,5-inositol triphosphate and diacylglycerols do form which in turn initiate different kinds of intracellular reactions. These include Ca^{2+} ion release and, partly linked to this, regulation of ion channels as well as that of enzymes. An increased activity of this signal transduction system is likely to produce increased intra-CNS release of neurotransmitters like serotonin or dopamine.

Lithium does occur as a natural trace element in ground- and drinking waters[5] after being leached from rock and soil. Yet, notwithstanding substantial differences

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[5] In fact, it even was discovered in a sample of mineral water.

with site, these levels are considerably lower than those applied in psychotherapy. Nevertheless Kapusta et al. (2011) could confirm for Austria that there is negative correlation between suicide incidence levels and Li concentrations in drinking waters which, moreover, had been noticed before on other continents. Yet there are no viable conclusions concerning a causal relationship between the values, and thus there are no implications for doing suicide prevention by adding low amounts of Li to food or water.

The terms biomethylation and "organoelement biochemistry" just serve to distinguish between metals and non-metals: although often dubbed so, arsenic is not a metal, let alone a "heavy metal"! In addition, As and Hg (besides Co) can accept organic groups other than CH_3 in biochemistry also, and alkylations of non-metals and metals use to be accomplished in different ways: while non-metals are reduced first to produce intermediates which have one or more vacant electron pair(s) at the centre which then can react with electrophilic organics such as alkyl halides, sulfonium salts (i.e., S-adenosyl methionine) or phosphate esters to create C–E bonds, the cations of metals will only accept and bind carb**anions**. Except for some highly stabilized ones some of which are also present in biochemistry, like malonate esters (malonyl coenzyme A), such carbanions would not persist in aqueous media unless transferred from some other organometal compound. In vertebrates and many aerobic bacteria and cyanobacteria, this other metal is cobalt, while in archaea, especially methanogenic ones, it will be Ni (via methylated nickel porphyrin). So other methyl compounds are formed some of which (like $(CH_3)_2Tl^+$) are extremely stable but not processed any further by living organisms. But they pile up in lipids, the nervous system or at best become readily excreted (such as selenium in speciation form $(CH_3)_3Se^+$). Volatile neutral element polymethyls may also be exhaled ("garlic breath" after uptake of Te and some other elements).

In **quantitative** terms, dominant metals in biomass are

- **Mg**, **Zn** with their broad ranges of biocatalytic functions,
- **Ca** not just for making skeletons or mollusk shells but also controlling cell budding,
- **Fe** in vertebrates and aerobic bacteria, most of it involved in dioxygen resorption, transport and –activation, and
- **Cu**.

Mn levels depend on relative intensity of metabolic activity in animals (it is mainly confined to mitochondria there). It (Mn) is crucial in photosystem II accomplishing water photooxidation in green plants, algae, and cyanobacteria (chloroplasts are/were probably derived from ancient cyanobacteria by endosymbiosis).

In many cases, functions of some element remain an enigma even though the element was shown to be indispensible at least for reproduction or healthy growth of offspring. Nevertheless, certain general rules can be inferred from considerations concerning autocatalytic systems which tend to limit the number of different elements used in biocatalysis.

Fungi are peculiar in their abilities and chemical strategies to attack polymeric organic matter, like wood lignin, lignite and even similar synthetic polymers such as bakelite (which all share a phenol backbone[6] structure), by oxidation enzymes. This ability was developed apparently just once in all of evolution and terminated production of black coal deposits from soft-stem plants, trees and large ferns some 298 mio. years ago. Mainly, wood degradation is effected by exocytic enzymes containing haem and producing aqueous Mn^{3+} which effects the polymer breakdown. Besides, some fungi, especially marine ones, apply vanadium in haloperoxidases or enrich it to remarkable levels in speciation forms which are simple yet versatile catalysts, e.g. with *Amanita muscaria*.

Extremely low levels of essential metal ions are observed in certain black-water rivers in NW South America (Surinam, F Guyana, the Tepui Region in southern Venezuela), combined with pH values near 4, or in bogs all over the world. Figure 3.2 shows the contrast of a black- and whitewater river in Serbia, Europe.

Only fishes adapted to these conditions can survive there, and crustaceans,[7] clams will not cope with them: it is simply too acidic for either to survive, and moreover those amounts of Ca needed for making an aragonite shell are not available to mussels. Interestingly, though there are cartilagenous fishes in freshwaters, including very big ones such as sturgeons (*Acipenser*), large rays and some sharks, these rarely inhabit such black-water biota, except for a couple of freshwater stingray species (*Potamotrygon* spp.) in South America. Apparently there are other problems which keep them from fully using their anticipated biochemical advantage with respect to bony fishes in such waters. At other sites, adapted fishes which no longer create a "complete" Ca mineral skeleton live in bogs, among them the smallest of all known vertebrates (<8 mm total length), namely, *Paedocypris* fishes living in bogs in Indonesia (Fig. 3.3).

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[6] Lignin is a CC-linked network of alkyl benzene and phenol groups while Bakelite was prepared from phenol and aqueous HCHO, making CH_2 bridges among the phenols to produce either rings (cyclodextrines) or a polymeric resin which was the first popular and widely applied synthetic polymer in the 1920s (invented in 1911).

[7] Accordingly the local food chain does considerably differ from that in both marine and other limnetic biocoenoses: while small crustacean zooplankton is key in the latter, providing food to an entire guild of fishes as well as to young larvae of bigger fishes, here fishes try to make food from insects and fruits falling into water, or consuming algae or even wood (submerged roots). All of these provide just a modest supply of trace metals, while loss of them via gill membranes or renal excretion would be critical, limiting the length of food chains.

Fig. 3.2 Contrast of black- and whitewater in Serbia, Europe. Looking down at the confluence of the blackwater Morava River (flowing from *right* to *upper left*) into the whitewater Danube (in *upper left*). Image courtesy of Stanislav Doronenko via Wikipedia

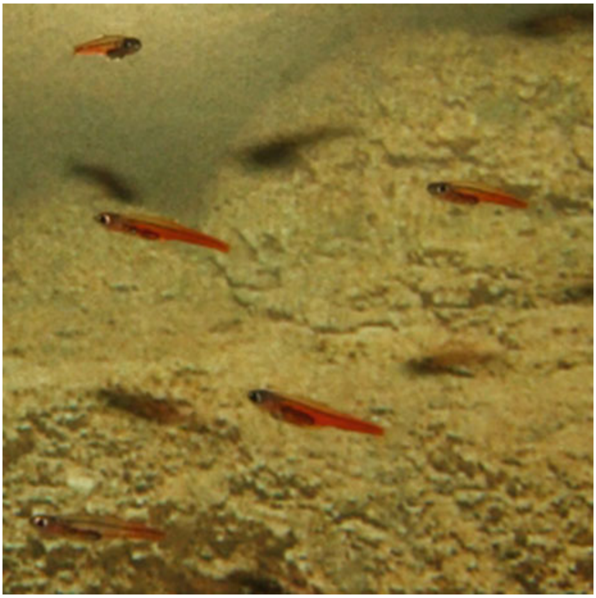

Fig. 3.3 Paedocypris *progenetica* are tiny fishes from Indonesian peat bogs. They are the smallest known fishes in the world. Except for spine, the bony (Ca-rich) skeleton is considerably reduced; note that e.g. the skull just consists of some narrow links around the brain, and there is little left from jaws although these fishes are "genuine" fishes (teleostei) rather than agnatha. Image courtesy of Aquaristikhaus via Wikipedia

3.1.1 Distribution Patterns of Chemical Elements in Plants[8]

As a rule, differences in (elemental) chemical compositions which exist among different species of (e.g.) plants should be caused by some unlike behaviour/ differing processes in uptake or transport. For instance, there may be either active or passive transport of metal ions or other speciation forms of elements, producing

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[8] Fränzle (2010).

different rates and/or equilibria of uptake. In turn abundance correlations among these very plant species appear which are at odds with chemical intuition. That is, a very low, virtually nonexistent abundance correlation in pairs of closely elements one of which is resorbed and shuttled onward to leaves/needles and fruits/seeds in a constant manner. The other is transported by ways/carriers which depend on the corresponding species while conversely chemically apparently unrelated elements may follow similar paths. Geochemistry, including pH and wetness of soil substrate, thus provides very different patterns of elemental abundances for metals as well as certain non-metals. There are both synergistic and antagonistic relationships between uptake or use of different elements by plants. Of course these latter interactions, which partially represent the response of the plant to local geochemical conditions, in turn change the distribution patterns by mainly antagonistic interactions among essential elements (Kaim and Schwederski 1993); also consider Fig. 3.4: Negative abundance correlations (e.g., Ca/Mg) may indicate a direct competition for the same binding centers owing to some chemical similarity among the pair of metals.

Thus, chemical similarity can bring about both highly positive and highly negative abundance correlations depending on dynamic features: if retention to biomass dominates in the end, similar coordination properties will result in positive abundance correlation. Controlled by transport mechanisms, including competition for low concentration carriers, rather gives a negative correlation. However, it is unlikely that both effects will cancel, producing no discernible abundance

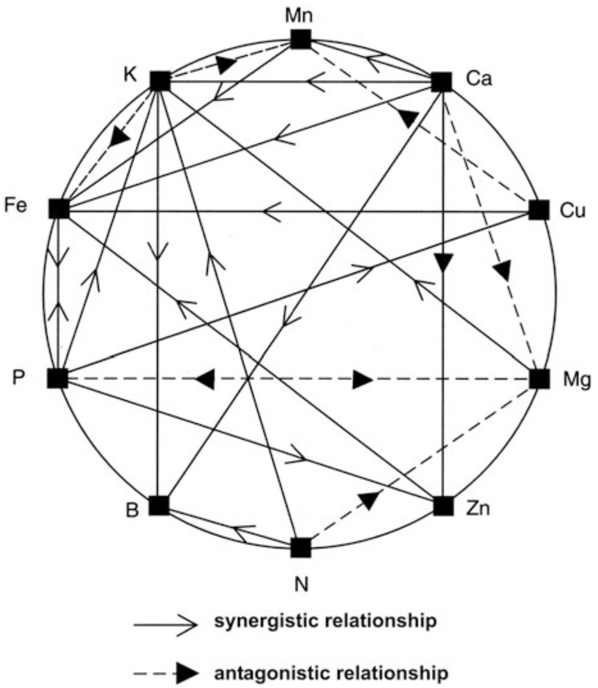

Fig. 3.4 Network of interactions/influences among some essential chemical elements in plants (Kaim and Schwederski 1993). The parameter used for attribution of either synergy or antagonisms to an interelement relationship is rate of plant growth

relationship across various plant species whatsoever. Local enrichment of certain elements within some plant may be due to both complexation with polymeric components of biomass and to precipitation of solid, insoluble, sometimes even crystallinic phases. Before an element may be enriched or separated in any of these kinds, three other factors contribute to the series of events, besides the conditions of uptake, namely:

- Speciation of elements next to its rhizosphere, respectively;
- Mechanisms and kinetics of uptake by roots (or fungal mycelia) or leaves (especially in aquatic plants);
- Mobility inside the plant, controlled, e.g., by phosphate in the xylem.

For example, the relatively large amounts of Rb present in plants may be involved in chemical signalling much like Na or K and will obviously contribute to osmoregulation, but the latter effect does not render Rb essential because it can be replaced by other ions (or even by organic compounds such as glycerol) for this purpose, and other, (more) specific uses are not obvious from analysis alone. Although some chemical details of paleobiochemistry may be inferred from appropriate fossils samples such as chitin in amber inclusions, analytical data most likely will never reveal what element actually was required by some extinct organism.

Though differences in essentiality patterns among protists, animals, plants or fungi are well-known for now, and "genetic clocking" allows for temporal reconstruction of the separations of their common ancestors (Feng et al. 1997), the corresponding changes among essentiality patterns upon evolutionary radiation are not accessible. This holds the more for results of thorough geochemical changes during evolution or for such extinct organisms which apparently do not fit into patterns and categories of recent-time taxonomy at all (e.g., Venda organisms ["venda-biota"] from the uppermost Precambrian).

Once, however, biocatalytic essentiality or chemical signalling with no chance to replace the components by other elements have been identified, matters change radically. Now, life is about reproducing some very complicated chemical gear—including accumulation and appropriate speciation of all the elements which are essential to that species—in an autocatalytic manner. From this point of view, a green plant is a device which produces and employs carbon compounds to obtain more C and increase its throughput/fixation rates of C (and all other essential elements) by (usually) identical reproduction of first the corresponding reactants (rubisco, chlorophyll and all the other proteins involved) and then that of metastructures (cells, entire organisms). Growth and reproduction thus correspond to *autocatalysis*.

The further line of argument is focussed on land plants for reasons of comprehensive data sets available here, yet there also are data for limnetic plants, as well as bacteria and animals. In terrestrial plants, there is a well-defined pathway for uptake and transport of metal ions rather than the chance to establish an equilibrium of element concentrations between water and biomass making use of almost the entire interface like in aquatic plants: for terrestrial plants, few, mainly epiphytes (Strasburger and Sitte 1991), are capable of taking up salts by leaves, otherwise it takes place by way of roots only. Although some (essential) non-metals such as sulfur (as SO_2) and nitrogen (both [either] as NH_3 or various nitrogen oxides) can be absorbed, used and metabolically transformed within the leaves, this pathway can be neglected for metals and so-called semimetals in higher plants and geochemically realistic conditions. In mosses, there are "colloquial" amounts of essential metals, say 35 μg/g DM of Zn and 3 μg/g DM of Cu even if there is no atmospheric deposition (extrapolation to zero AD (atmospheric deposition)-rate). This points to a similar way of uptake to meet essential demands between mosses and vascular plants even though there are no roots in the former. Mosses give away amino acids and peptides when exposed to drought stress, causing weathering of underlying material with the apparent result of complexes to be resorbed by the mosses quite efficiently. Speciation, uptake and transport alike depend on chemical properties and possible chemical and biochemical transformations of the corresponding element. Most of the essential non-metals (N, B, P, S, in addition Mo) are absorbed as oxoanions in their highest oxidation states whereas Cl is taken up as an elemental anion, that is, as Cl^-.

Yet, it must be noted that some 40–50 % of absorbed nitrate N are converted into amino acids in the microroots already, as are—sometimes even larger—shares of other metal or non-metal oxoanions such as CrO_4^{2-}. In higher plants, substantial uptake of metals or semimetals *by leaves* would occur only if there are fairly persistent volatile forms which could be admitted to the stomata, except or particles within hydrometeors small enough to pass the stomata (or soluble in water, e.g., sea salt spray). However, permethyl compounds of Hg, As or Se have tropospheric lifetimes of minutes rather than hours given their reactivities towards OH radicals, much like peralkyls of Sn, Pb or Mo, W hexacarbonyls which are released from anaerobic layers of domestic dump pits (Feldmann 1999).

3.1.2 Pattern of Elements Changes During Evolution

Radiation of metazoans took place quite a period of time (about 1.55 to 1.25 bio. years ago according to molecular dating [Feng et al. 1997]) after both eukaryotic organisms evolved and cell colonies became arranged in a more stable way starting to recognize particular cells.[9] This radiation was during a period of time during which no substantial changes in atmospheric or geochemistry could be detected so far. Radiation among multicellular organisms and diversification of patterns of

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[9] As for "primitive" animals having just three or four different kinds of cells, sponges can be dispersed down to the cellular level. Of course, one can then mix suspensions of cells of different species of sponges. When such a mixture is left alone for a few days, the unlike cells will unmix again to reconstruct little sponges each of which consists of cells taken from just one of these species. Obviously the cells already bear an immunological signature which here causes them to separate (and gather with their closest relatives, reconstituting the individual organs and species) rather than to agglutinate. Both trace metal (e.g. accumulation of Ti [outside the SiO_2 needles fortifying the entire structure]) and organic biochemistry (formation of terpenoid isocyanides, -isothiocyanates, -formamides etc.) of marine sponges are noteworthy and peculiar. Probably isocyanides R-NC (R = terpene residue) do not just produce a disagreeable smell but also peculiar heavy metal ion enrichments in marine sponges.

essential elements probably were not brought about by some thorough change of environmental conditions to which organisms would respond in different manners, with their metabolic modes become increasingly unlike to each other.

The argument that patterns of essential elements may be influenced by environmental conditions as well as adaptive radiation can be traced back further from phylogeny to ontogeny: ontogeny in biology uses to reproduce earlier stages of evolution: very young human embryos first strongly resemble coelenterates (the blastocyst), then fish larvae, to become typical monkey embryos, or rather, fetuses only much later (even in advanced fetal stages, fetuses of man and chimpanzee are still very similar). In the following the terms ontogeny and phylogeny (the biogenetic law) will be more detailed described.

Ontogeny—literally „the way to become (old Greek genein) a being"—refers to the development from a fertilized or otherwise activated (in case of parthenogenesis) egg cell into an adult, fully differentiated multicellular organism; commonly the term is used with (early development phases of) animals, humans rather than that of either plants or fungi while it does apply there also to some extent. In late nineteenth century, eggs of viviparous animals had been identified beyond doubt (in 1875) and certain mammals (monotremes, like *Platypus*) became known to lay down small (<2 cm long) eggs very similar to those of reptiles (1884). Then, Ernst Haeckel (1834–1919) noted that such larval stages (blastocysts, embryos, fetuses) resemble "older" stages of evolution: this was called "biogenetic law". F.e., the internal organization of the blastocyst is most similar to that of a coelenterate while young larvae of primates, other higher vertebrates (including birds) still cannot be distinguished by **shape**[10] from those of either bony or cartilagenous fishes if size is similar. Even much later, even after sexes became obvious in the fetus, human fetuses might be taken to be as such of chimps or bonobos (pygmy chimps) or vice versa, including an almost complete cover by body hair [lanugo]. Intermediate stages (late embryos, young fetuses) were allowing for a broad range of misinterpretation among more remote taxa also. For example, take those coelacanth- or tadpole-like "paddles" of a human embryo of about seven weeks after conception which still have to undergo shaping by apoptosis which carves out either fingers, toes or the typical structures of bird- or bat wings. Here, apoptosis is incomplete leaving behind a skin extending among the entire finger bones whereas in pterosaurs and certain birds parts of hand, arm skeletons were "set free" in much the same way as in land-dwelling vertebrates.

The "biogenetic law" does hold for interior organs also: e.g., the human heart starts as a simple S-curved artery with flip-back valves which closely resembles that simple hearts of fishes, tunicates and lampreys to reshape into a sophisticated device divided into four chambers only later. Often the foramen ovale, the hole between both main parts of the heart which is typical of amphibians and reptiles

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[10] The entire argument relies on morphology and histology exclusively: DNA, of course, is unique from the very moment of conception while kind and series of gene activation will differ (or not) in different animal larvae producing the above results.

keeps open even after birth in humans, deteriorating cardiovascular performance of the individual (it uses to be closed in mammals, birds, and crocodiles). In fetuses, lungs start as simple hollow bags (like those of frogs or air-breathing fishes) only later to form alveoles, etc.

Thus, observation of ontogeny, taking weeks to two years (elephants, whales) in total (from egg fertilization to delivery) at most, provides a kind of “fast-forward movie” version of (higher animal) evolution. While there were arguments that “ontogeny does create phylogeny rather than recapitulate it” (Garstang 1922), the biogenetic law is quite useful for our purposes:

- The processes to shape organs, by differentiated cell growth as well as apoptosis, are **chemical** processes from the beginnings to the very end. They are controlled by a DNA some 70 % of which is identical, and hence produce identical results up to a certain point of ontogeny among all animals;
- among animals, certain enzymes, including those required only during stages of ontogeny, like metamorphosis in amphibians, use to operate on identical metal ions (if any are involved);
- many protein sequences are well-conserved in genetic history (which includes binding preferences towards certain metal ions for enabling function in metalloproteins) while
- in arthropods, larval stages may even differ in metal kind of oxygen transport protein (either hemocyanin [Cu] or hemoglobin [Fe]) from adults, especially if the latter live in quite another environment, like dragonflies do; the “switch” can be either way round.

Given these facts, the biogenetic law suggests we are in a position to do something in an somewhat indirect manner we cannot do by studying fossils anyhow: reconstruct which functions metals and some non-metals like Se, I, had in animals which are long extinct. For non-animals, application of the biogenetic law is less reliable even for histology, and thus let alone chemistry. As the present patterns of essentiality were constructed probably step-by-step during evolution, we would anticipate the same step-by-step patterns in selective transfer of elements from egg (-liquid or -yolk), environment or maternal womb into an embryo or fetus. The problem now obviously is about data, or clever ways to obtain or infer these data.

In marsupial mammals, very unripe, premature animals are born meaning they can grow to several hundred times the weight at birth while feeding on milk alone. This can succeed only if milk (in its typical composition) provides everything in terms of all amino acids, sugars, lipids and trace metals the offspring is made of just before or when finally leaving the poach. Hence, e.g. the iron content of great kangaroo milk is some 100 times higher than in both human and ewe’s milk (Griffiths 1983). Assuming monotremes or marsupial mammals are forms which predated evolution of a fully functional placenta which can more effectively supply a larger fetus, the chemical requirements met by recent marsupial milk are likely to be similar to those conditions in early (Triassic to Jurassic) mammals or mammal progenitors. F.e., the high demand in iron might suggest the partial pressure of O_2

was lower in Mesozoic atmosphere except for the very last stage of Cretaceous (Maastricht). It supported active flight in pterosaurs much bigger than anything living which managed to fly on muscle power before or afterwards (*Pteranodon sternbergi*, Fig. 3.5a, 7.5 m wing span, estimated weight 15–26 kg) in Jurassic times; flightworthy Pliocene megabird *Argentavis magnificens* (Fig. 3.5b, 6.2–7 m wing span, weight 60–80 kg), man-powered ornithopters of similar weight (some 65 kg "pilot + engine" plus 40–50 kg of device). Other chemical features of kangaroo or platypus milk might reveal yet more information on Mesozoic conditions. The ability of recent tadpoles, newt- or salamander larvae to keep on growing while breathing through gills, becoming fertile and reproduce quite as if they had undergone "normal" metamorphosis does strongly suggest iodine which is a part of thyroxine (Fig. 3.6) and possibly also Cu were not available all the time when tetrapod vertebrates evolved. Into which environmental conditions might this translate? Analysis of organisms and their essentiality, metalloprotein features during larval stages will (likely) tell us!

Human embryos share the typical properties of almost all animals in biochemical terms from the very beginning. They depend on dioxygen and requiring a multitude of hormones including sources of some essential elements from the very first cell divisions; yet it is not at all certain that this applies in all conditions vertebrates, let alone, other animals or members of yet different kingdoms live and grow in: e.g. amphibians need thyroxine (and thus iodine) not during their entire life-cycles but only to accomplish metamorphosis. If the thyroid gland is resected in tadpoles they will not die (as mammals would do before long) but simply stay larvae, but these larvae then are capable to reproduce (neoteny) while growing

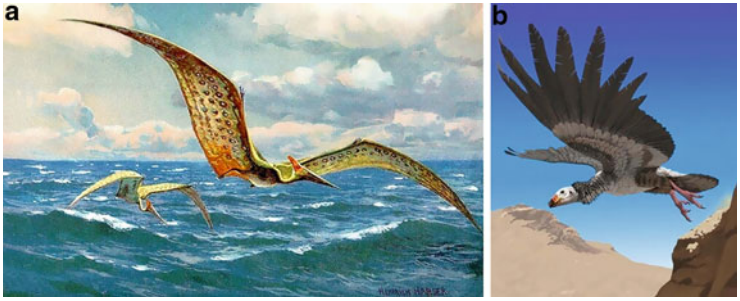

Fig. 3.5 (**a**) Painting of *Pteranodon* (pterosaurs) by Heinrich Harder (1858–1935); (**b**) *Argentavis magnificens* is one of the largest flying birds ever known. Courtesy images of Wikipedia

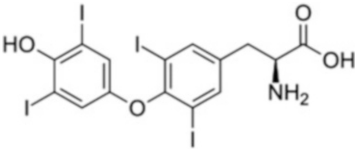

Fig. 3.6 Structure of thyroxine

much beyond the typical size at which they would else undergo metamorphosis. Keeping in mind there are many species of amphibians which undergo metamorphosis only if their hatching pools start falling dry but otherwise retain the neotenic mode of living including reproduction, one is posed to ask in which sense of the word iodine is essential for amphibians at all. Additionally, the metalloproteins required to introduce iodine into tyrosine amino acid to eventually make thyroxine—depending on Cu—are not needed if metamorphosis is avoided for one reason or another. Hence in frogs or toads or newts (like Mexican axolotl) I is not really an essential element but just serves to adapt them to air-breathing semi-terrestrial life (iodine is essential thus for toad populations capable to inhabit desert regions which see rain-caused flooding only once in rather large periods of time). Requirements for Cu will have a peak only during metamorphosis while otherwise amphibians would happily go with traces of it at most.

But even this is not the entire story: What happens if organisms can still cope with quite different chemical conditions (which is more than euryoicy: man or rat can live in quite different climates, but both are obligate aerobes)? What is different with "really euryoicic" organisms in their responding to "really big" chemical challenges, such as switching from aerobic to anaerobic conditions? How do they change their metabolisms in terms of expression of metalloproteins which are needed as enzymes when using O_2 (or doing nitrate-respiration) only? This response, individual rather than evolutionary adaptation, obviously will have an impact on their gross chemical compositions even though probably not a single hitherto (i.e., in aerobic conditions) essential element will completely vanish from function or even from analytical detectability.

Examples of living creatures which can adapt to grossly different ambient oxidation potentials and can make alternative use of different terminal electron acceptors, include common baker's yeast (*Saccharomyces cerevisiae*) and even small ($\approx$0.4–1 mm total length) animals of phylum *Loricifera* (the most recently discovered animal phylum of all). This is not a single exotic species but these fully anoxic loriciferans, living in an environment enriched by H_2S etc, are assigned to belong to novel species which represent three different genera, namely *Spiniloricus* (the one shown in Fig. 3.7), *Rugiloricus* (somewhat smaller) and *Pliciloricus*. Besides, exuvia of copepods and some nematodes other relatives of which are known to endure both prolonged anaerobic and hypersaline conditions, were found in the about 40 m thick brine layer and below in sediment. It is difficult to estimate whether either corresponds to organisms actually living and even reproducing in these deep-ocean brine "pools". Anyway, loriciferans are known to be fairly abundant in the Atlantic Ocean but had not been observed in the Mediterranean, either elsewhere or in whatever biochemical conditions.

During adaptation to anaerobic conditions their demands for metals included in some oxidoreductases will **change** accordingly. Effects are anticipated to be rather pronounced since respective oxidoreductases are more or less-substrate-specific. Loricifera in the Mediterranean live in an environment of 410 mM Mg^{2+} (almost eight times the average marine level) and some 5 M NaCl (nine times marine) obtained from leaching of underlying evaporates (left behind from Pliocene-times almost complete evaporation of Mediterranean Sea). As expected, their trace

Fig. 3.7 Anaerobic Loriciferans which (can) spend their entire generational cycle without oxygen in a sulfate-brine medium (Danovaro et al. 2010). These are the only animals (and hence metazoans) so far known to be capable to do so while there are lots of facultatively anaerobic monocellular organisms (Mentel and Martin 2010)

element will respond to this challenge also (though they cannot be directly compared to populations living nearby having access to O_2 and, moreover, represent novel species). The anaerobic Loricifera are distinguished by **hydrogenosomes** (Mentel and Martin 2010) which very much resemble those of strictly anaerobic unicellular organisms rather than having mitochondria in their cells which translates to more Ni and less Mn therein. In these Loricifera changes between “normal”, oxygenic populations dwelling in Atlantic Ocean sand interspace fauna and those in sulfate- and H_2S-rich anoxic brines at the bottom of the Mediterranean (some 3,300 m deep) near Crete are considerable, to say the least. The data given in Table 3.1 are relative contents of Na, Mg, Si, P, S, Ca, Fe, Cu, Zn and Br in the body parts of Loriciferans from the Atalante basin compared to the Atlantic Ocean (the analyzed elements given here add up to 100 %, regardless of the almost sure presence of yet other elements and probable differences in total content).

Regrettably, neither Mn nor Ni were measured in this experiment. Atlantic Ocean-derived, that is, aerobic, Loriciferans **totally lack Mg and Fe** while the Cu content is larger except for the abdomen. The role of Br in anoxic populations is enigmatic, whereas higher (any) Fe levels in parts of body of the latter (Mediterranean, anoxic) would be involved in sulfate reduction. The latter process also requires P for activation while total S levels are similar among either population. Given this it is likely the lower relative P levels in anaerobic Loricifera indicate lower levels of both metabolism and reproduction rates than with dioxygen-breathing cousins, as is common in ecological stoichiometry [P levels refer to reproduction rates (Sterner and Elser 2002)] and would be expected from poorer

Table 3.1 Elemental composition of Loriciferans from the L'Atlante basin and oxygenated North-East Atlantic deep-sea sediments

Region	Body part	Na%	Mg%	Si%	P%	S%	Ca%	Fe%	Cu%	Zn%	Br%
Atalante basin	Abdomen	0.0	0.0	22.3	9.6	30.6	4.5	0.0	22.5	10.6	0.0
	Posterior	0.0	6.5	31.3	9.9	19.7	2.6	5.2	5.2	1.8	17.7
	Whole	4.6	6.5	21.1	9.1	36.4	2.0	5.2	2.6	1.0	11.5
Atlantic Ocean	Abdomen	15.9	0.0	20.4	8.92	29.5	16.3	0.0	9.22	0.0	0.0
	Posterior	0.0	0.0	4.2	17.1	29.4	33.1	0.0	7.2	9.0	0.0
	Whole	4.94	0.0	10.7	12.3	31.0	28.4	0.0	5.9	6.8	0.0

Reported are the relative contents (given in percentage) of Na, Mg, Si, P, S, Ca, Fe, Cu, Zn and Br in the abdomen, posterior lorica and whole body of loriciferans (Danovaro et al. 2010). The values given are not absolute concentrations of the 10 elements but at up to 100 %, hence are relative shares. Relative amount of zero however, i.e., Mg, Fe implies an absolute concentration of zero, too metabolic performance (energy [=ATP] yield) of sulfate vs. O_2 reductions. (Much) lower Ca levels likewise suggest decreased cell budding rates in anaerobic populations, too, in accord with P levels. Cu rather than Fe would be used for O_2 transport in these animals, while in other animals rather modified haems (based on Fe porphyrines) are used to control and transport. Insofar occurrence of Fe in parts of anaerobic Loriciferans is quite telling.

3.2 Essentiality Pattern of Elements Versus Taxonomy: The Footprints of Evolution of Biota, Atmosphere

Regardless whether elements are essential, destructive or something in between or even more involved in biochemistries of a multitude of different organisms, there is another condition which must be met, too: the respective element must be **available** to organisms which make use of it and remain so over very long (geological) periods of time. Bioavailability means an element or organic cofactor is present whenever needed in the ecosystem where the organisms live. The set of requirements may differ when a species switches among ecosystems during ontogeny, like with amphibians or dragonflies.

Elements might be excluded from availability to the biota sooner or later by all

- redox precipitation after increase of ambient redox potential once the atmosphere became enriched with dioxygen (Precambrian oxygen disaster) [e.g. Ti],
- plate tectonics "leaching" certain siderophilic elements down into the deeper mantle of Earth (e.g. PGMs, Hf),
- radioactive decay,
- depletion of possible ligands in late stages of chemical evolution or by these ligands being eaten by an early biota (elements which form very stable carbonyls or cyanocomplexes in reducing conditions, like Ni, Co) or
- increased levels of gegenions which precipitate them effectively.

So it is quite conceivable that several elements formerly essential lost (at least large parts of) their former roles in biology afterwards or just are doing so (cp. Williams and Frausto Da Silva 1996).

Feedback is a crucial feature in bioinorganic chemistry and ecological stoichiometry likewise as both auto- and heterotrophic organisms must obtain all the elements they are made of and which they use in biology from outside by assimilation or eating food and drinking water. Given this, one might consider a (any!) living being as a device which combines many different chemical elements "trying" to accumulate more of these elements while reproducing, implying there is feedback on the level of elements also. Owing to metabolism elements will be absorbed from soil, food and atmosphere while after death certain elements are returned to the soil or water. When a plant or animal (including marine or limnetic plankton) gets eaten, transfer of elements to both environment and predator takes place, more or less closing the cycle of matter. Such nutrient feedback was shown capable of shaping entire ecosystems (Sterner and Elser 2002) even though for most elements the fraction of them bound to living biomass is just minute at every point of time. Accordingly the biota can hardly act as a buffer for keeping elements bioavailable. Yet not all cycles are fully closed: some organic carbon is retained in fossil fuels, while bioredox processes of iron or sulfur produce minerals. Photochemical hydrogen loss to outer space tends to be reduced by the biota as oxygenic photosynthesis eventually affords ozone in the stratosphere which strongly reduces direct water photolysis by absorbing short-wavelength UV radiation and converting H atoms into OH and HO_2 radicals which are way less mobile; coupling of hydrogen to CO_2 in photo- or chemosynthesis likewise keeps it from escaping to outer space. Hence the D content of water and organics on Earth now is lower than both on Mars (156 ppm [Vienna Standard Mean Ocean Water VSMOW] vs. 778 ppm [water from Martian clays]) and as it would be if there were no life on Earth.

There are elements which are essential for almost every living being even though there are some stunning exceptions: several arthropods can do without iron (the same holds for certain bacteria), Mo may be replaced by W or K by Rb; anaerobic breeds of Loricifera (Sect. 3.1.2) even thrive without containing Mg although living in Mg-rich brines. There is disagreement about how the set of essential elements were initially (or at some crucial point during biological evolution) selected (e.g. Egami 1974; Ochiai 1987). On the other side it is obvious from the data that it cannot be simply traced back to selectivities coming from the stepwise change and increase of complexation properties from partly reduced CNO species (water, CO, CN^-, NCO^-, $RCOO^-$, glycine, urea etc.) during chemical evolution (Fränzle 2010). Obviously essentiality is related to both the level of structural (biochemical and histological) complexity of an organism—with larger numbers of required elements in multicellular organisms than in unicellular ones but against the odds of naive reasoning also in heterotrophs vs. autotrophs—and to its metabolic "tasks".

Elements with $Z \gg 26$ (i.e., heavier than Fe, such as Cu, Zn, Se, Mo, and so on) tend to be much rarer in both interstellar medium and on Earth due to the pathways of stellar nucleosynthesis and the nuclear binding energy curve which causes exothermic nuclear fusion to end at $Z \approx 26$ (iron[11]). Due to photolytic reversal of stellar element synthesis (nuclear photoeffect) in dense cores ($\rho > 10^7$ g/cm^3) of dying massive stars (>10 solar masses) at some 3–5 bio. (!) degrees K, the process of stellar fusion making heavier elements actually stops before reaching the most stably bound nuclides ^{58}Fe and ^{62}Ni. Rather it provides substantial abundances of lighter Fe and Ni isotopes and of Ca, Ti, Cr, and Mn instead when silicon ($^{28;29}$Si) gets processed. However, there is no direct "bonus" for essentiality of elements to be obtained from some larger abundance and thus $Z \leq 26$ (see the extremely

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[11] These Ca to Ni nuclides soon after (the entire "equilibrium process" takes a few days at most) are either ejected in a supernova or "swallowed" and locked up forever into the ultradense central "wreck" of such a star (neutron star or stellar black hole).

abundant and rather accessible Al, Ti[12]) which means heavier or rarer elements might be "used" as well although they are less abundant (e.g. Mo, Cd, I) if they offer suitable chemical properties. Yet one can take it for sure that no now "extinct" radioactive elements could ever have attained biological/biocatalytic functions during biological evolution as they, including Tc, Pu, and Cm, had become most rare owing to radioactive decay much before life evolved on Earth. The only such nuclide left behind into biogenesis would be minute traces of ^{244}Pu ($T_{½} = 83$ My, mainly undergoing α decay besides of a little branch into spontaneous fission) which nuclide persists till today.

Many elements other than the eight "classical" metals (as well as non-metals Si, As, Se, Cl, I) are required just by certain kinds of creatures. Insofar as this fact is restricted to some taxonomic groups one can draw further conclusions on features and pathways of evolution; this is a mainly untold story which hence will be addressed in more detail below. F.e., eukaryotic cells are now considered to have originated from stepwise acquisition of endosymbionts which had been either "common" or cyanobacteria, while, to be more specific, most Mn-dependent enzymes in animals are located within mitochondria. Those bacteria capable of running their catabolic metabolism in a way which now is exploited for bio-assisted fuel cells, donating either electrons or nucleoside triphosphates to some support or environment outside the cell if not even for "extracellular" Mn-using enzymes (like in wood-degrading fungi) which were hence the most likely precursors of mitochondria or at least are late representatives of the latter. Accordingly, descendants of them probably brought the necessity to use manganese—and its very specific if not exciting chemical features in mechanisms of oxidation of both water and of refractory organics—into what was to become eukarya, and eventually animals, fungi. Most distinctive in manganese chemistry is its ability to eliminate O_2 from highly oxidized oxo- or oxohalido- or oxo-polymer species when electrons are removed by photochemical transfer or just by exposition to Lewis acids: Mn_2O_7 is an explosive green liquid while MnO_3Hal (Hal = F or Cl), MnO_2Cl_2 give away O_2 gently upon storage (Cotton & Wilkinson 1982; Kolditz 1986) and a solution of permanganate in acetonitrile likewise releases O_2 when Lewis acids such as BF_3 are added (Yiu et al. 2011). Oxomanganese clusters will produce O_2 from water in a photochemical manner if covalently coupled to $[Ru(bipy)_3]^{2+}$ or other common (MLCT) photooxidants, which system is closely related to photosystem II in biology.

Before turning to the possible relationship between major "achievements" in evolution, access to certain elements as controlled by geochemical conditions and complexity of individual living beings (either histological or in terms of metabolic accomplishments) we should begin with some more general remarks.

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[12] Al does co-catalyse (along $MnCO_3$) the transformation of molten glycine into some vast array of "significant" compounds whereas Ti (as either titanous sand, or perovskite $CaTiO_3$) was probably involved in early photoelectrochemical processing producing amino acids and other compounds (see before). Yet neither was introduced into biochemistry of any known organism, although Ti would have offered a possible entrance into primitive photosynthesis.

We are quite accustomed to the notion that metal ions are absorbed by biomass, be this to the better or to the worse of the organism involved, but how stable actually is such an assembly? This problem has two different features, namely

- retention equilibria, or partition of metal ions between biomass and the environment and
- stability and properties of e.g. metal ion protein complexes.

To start with the latter, condensation of amino acids into peptides and eventually proteins is endothermic, and many metal ions catalyze hydrolysis.[13] Accordingly, if not for steric constraints, it is the very presence of metal ions which destabilizes biopolymers towards hydrolysis. Hence, as a rule, metal levels are low inside of biomass (mass fractions $\leq 10^{-4}$ except for bones and comparable supportive structures), and often actively kept so low. **Selectivity** can be described by parameters which explicitly refer to complex formation stability, treating a given (more or less homogeneous) biomass sample, say an organ, as a kind of bidentate ligand. Anyway Cu^{2+}, the strongest-binding divalent cation, must be tightly controlled during transport through the digestive system and biomass, otherwise it would stick to every protein rather than be allocated to those which require it for function, like to laccases, monooxygenases or haemocyanin. Devastating brain diseases in humans, such as Wilson-Menkes syndrome, give an idea of what can happen if this control by specific transporters (chaperons) does fail.

Nevertheless it happened several times during evolution that access to certain elements was altered by gross biogeochemical changes, and ecosystems (average) complexity soon responded to it, but we should remain sceptical about a direct causal relationship. However, we can state that some larger or smaller parts of biota (the mass extinction event which took place in late Ordovician was almost as grave as at the end of the Permian, and either considerably more devastating than that which wiped out dinosaurs, pterosaurs, ammonites etc. in Maastricht/Paleocene times) did make it through such crises, and it is likely that novel forms to be seen in the fossil record only afterwards sometimes made use of chemical elements which had been "useless" to prior biota. Of course, this is hard to prove even in the few cases where soft tissues were conserved in fossils:

Measurable relics of enzyme activities in fossil samples go back to Miocene at best (some 20 mio. years; i.a. Dose and Rauchfuß 1975; Eglinton et al. 1983; Abelson 1959). Note that certain metal ions which are rather common in both metalloproteins and sediments, in particular, Zn^{2+} and Cu^{2+}, do promote hydrolysis of amide bonds and thus degradation of peptides; moreover Cu^{2+} catalyses subsequent decarboxylation of free amino acids or of the C termini of smaller peptides. Besides of the most robust, simple amino acids commonly produced in simulation

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[13] Of course, catalysis works either way round (enhancing rates of both forward and backward reactions as to keep equilibrium position identical to that observed without any catalyst at same conditions [T, p, pH and so on]): if there are dehydrating agents or conditions, like cyanate or polyphosphate ions or NaCl brines, Cu(II) complexes of amino acids and peptides will promote peptide chain prolongation.

experiments just proline and leucine are detected in Oligocene sediments, i.e., a little older ones; the total concentration being about one-sixth (i.e., 500 nM/g sediment DM) of those in recent matter (Erdmann et al. 1956). Some polypeptides which surely do no longer exhibit either catalytic behaviour nor metal loads identical to the original ones[14] were isolated from 350-mio.-year old Antrim shales (Dose and Rauchfuß 1975).

If you happen to find some elements in a (younger or even older) fossil sample, you hence cannot tell whether it was actually involved in biological functions of catalysis (or became absorbed *post mortem*): while the control and metal cation activation pathways of nerves and muscles are probably the same ever since these organs were developed for the first time (i.e. in uppermost Precambrian), matters are different with biological catalysis of several even fundamental transformations of small but crucial molecules, ions or functional, e.g. in phosphatases. Be aware that both muscles and nerves—either depending on strict control of ion concentrations around for proper function—were developed during evolution in a medium distinguished by fairly high to very high levels of all Na, K, Mg and substantial Ba (causing irreversible contraction of muscles), namely seawater.

Hence it is more straightforward to look for events which could change availability of elements many of which are now known to have their roles in bio (inorganic) chemistries of some creatures at least. Probably the most distinctive—and most grave—events of this kind were

- the Great Oxygenation Event, the
- beginning of the Cambrian and
- periods of intensive trapp volcanism, e.g. during late Ordovician and Maastrichtian (uppermost Cretaceous, igneous rocks then mainly located in India) times.

Corresponding effects of **impacts** of asteroids are less obvious, producing

(a) direct inputs,[15]
(b) excavating material from lower Crust and upper Mantle layers, and

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[14] Note how simple it is to prepare apoenzymes by having metalloproteins interact with effective chelating ligands such as EDTA (Vallee and Williams 1968); afterwards the apoprotein can be supplied with some other metal ion. In porphyrines this is a spontaneous process, replacing Mg from chlorophyll with e.g. Ni^{2+}, VO^{2+} (Treibs's red geoporphyrin), In^{3+}, and other ions of appropriate diameters.

[15] Besides the famous (Alvarez et al. 1980) iridium and osmium enrichments which were directly attributed to contents of a ≈ 10 km-large impactor, there are significant changes in amounts of e.g. V, Cr, Sr, Mn and other elements in both sediments and biosamples (late dinosaur eggs) some of which are involved in metabolism. However, the isotopic composition of Ir from the KT boundary layer matches that of common terrestrial samples deposited before or afterwards, including native alloys like iridosmium, ruthenoiridosmium or minerals like (Fe, Ru, Ir)As_2 (some 63 % ^{191}Ir, remainder ^{193}Ir).

Fig. 3.8 A large heap (about 1,500 long and >100 m high, several hundred m width at basement) of *grey* depleted ores from a mine in Central Cyprus, now inaccessible as such for its location. Therefore the above heap which experienced sulfide-oxidation-based bacterial leaching which occurs next to an aquifer below the uppermost "step" is exploited now. The climate there is fairly dry, causing periodic droughts of the acidic mine tailing creeks forming up the heap; to the back of the observer there is Campo San Martin, the largest UN Peace Forces barracks on the island. Image courtesy of Stefan Fränzle

(c) causing rain acidification and thus increased leaching of metals from sediments via NO_x formation in the stratosphere[16]

Figure 3.8 gives an illustration from today (photo was taken on Cyprus Island in 2008) what it might have looked like when O_2 first attacked open-lying sulfide minerals in the Great Oxygenation event and later (formerly euxinic) marine sediments and suspended particles during the Avalon period (upper Precambrian). In fact, quite recent work (Crowe et al. 2013) showed that there was air oxidation of both U and even Cr to hexavalent states 2.96 bio. years ago, with an estimate of then atmospheric O_2 level of some 60 μbar (the total density of the atmosphere was close to the present one then). The bright blue, green and brownish "stripes" denote oxidative leaching of Cu, Fe and possibly additional metals (it is a deposit of depleted copper ores [remaining Cu < 0.2 % DM] located next to the inner-Cypriote *de-facto* border between the small cities of Skouriotissa [Rep. of Cyprus] and Lefke [TRNC]); these metals thus get accessible to organisms which need higher concentrations of them, like arthropods or laccase-using fungi (the almost colorless flows probably are elemental sulfur).

Free dioxygen doubtlessly changed conditions of access to trace metals to a considerable extent, and some of the metals would only operate as biocatalysts if combined with it or with H_2O_2 at least (this holds for V, mostly also Cu). For

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[16] The rather small Tunguska event of 1908 produced so much nitrogen oxides in the stratosphere as to reduce the ozone levels—then measured by obtaining blank spectra of nighttime skies—by some 50 % for several years (Toon et al. 1992).

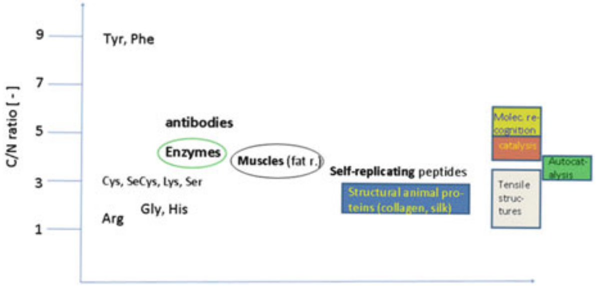

Fig. 3.9 C/N ratios for single amino acids (*left*) and proteins displaying various functions. There is no *horizontal axis* inscription as there is no parameter changing from *left* to *right*, unlike the ordinate which gives the C/N ratio. On the extreme *right*, functions of proteins are listed with respect to C/N

anaerobic creatures, the C/N ratio of ecological stoichiometry depends sensitively on the ambient redox potential even though the nitrogen content of "actual" enzymes (i.e., biocatalysts) is almost constant at some 16 %. For C/N ratios of different kinds of proteins, see Fig. 3.9. For the prototypic self-replicating peptide, the "leucine-zipper" from yeast (Lee et al. 1996), $C/N = 3.62$, whereas nitrogen contents vary with function both considerably and in a way as to discriminate the functions. As far as clear-cut metal ions are involved (i.e., in most cases except for enzyme catalysis and tendon proteins, silk) this should be related to protein sequences (but in antibodies, $C/N \gg 5$ which is far higher than Cys and His mainly capturing Zn^{2+} ions) but not in a manner which we can now readily understand. Amino acids which contain ligand-active groups in their side-chains vary in C/N over a wide range from 1.5 [arg; guanidine] to 5 [glu; carboxylate] and even 9 [tyr; phenolate].

This is to say that

(a) most of the C in anaerobic organisms (for which $C/N = 20–200$) is locked up in lipids (or long-chain ethers in Archaean cell-walls) and sugars rather than in nucleic or amino acids or within some N-containing polymer made thereof, and
(b) the specific metal ions required to cause the typical activities of the said kinds of proteins (e.g., Ca and Mg in muscles, Zn in self-replicating peptides) [also] respond to differences in gross composition of the proteins (recall that different C/N in amino acids also means different possible ligands in AA side chains to bind metal ions inside some protein are present).

Oxygenation of deeper ocean took place only very much later, during the Avalon period about 575 mio. years ago. If this model is valid, those groups of obligate anaerobes which must "hide" from any trace of O_2 and which are not connected with facultatively aerobic or at least O_2-tolerant ancestors, should operate their kinds of metabolism using those elements only which had been fairly accessible already before. Perhaps the roles of W (often replacing Mo), Ni and (substantially more of it than in vertebrates) Se in archaeans, especially methanogenic ones, are related to this. Even when the issue of controlled access of well-defined ions to some organ is left aside, it is by no means obvious how certain organs control uptake of elements in a more general way. By now, the available body of knowledge (which is mainly restricted to plants and algae) points to some effects of climate on this fractionation, but this is a topic of pending and ongoing research yet.

A most interesting (and probably prolific) period of change of both complexity of animals and likely uses of trace metals by them covers the period from Upper Precambrian (after Cryogenium) up to Middle Cambrian, even taking into account that telling fossils from that period—except for precursors of arthropods (trilobites)—are rare if not even restricted to one single site for the early Cambrian [but not the preceding times of Ediacaran which are globally represented (Droser et al. 2006; Seilacher 2008)]. First cases of formation of hard outer shells or exoskeletons which may or may not draw and depend on biomineralization, date back to the uppermost Precambrian. By then, all life was confined to aquatic settings, except perhaps for some lichens or algae already growing on moist solids onshore. Hence everything we can state about possible biomineralization and element use is related to aquatic organisms (not exclusively animals) and the corresponding fossil record.

Let us begin with the earlier (still Proterozoic) part of matters. The Ediacaran ecosystem (if a global distribution of already rather evolved living beings represented in fossils taken from a couple of mostly shallow-ocean sites only can be taken to represent some possibly globally similar ecosystem at all, which is highly doubtful) often was described as “peaceful” (Seilacher 2008): no hard shells, essentially no predators either. Matters changed in a truly dramatic way during the Cambrian: hard shelled animals evolved, and predation among animals of different to similar sizes became an issue, soon bringing about creatures such as *Anomalocaris* (Fig. 3.10) which was able to destroy trilobites even though itself not in command of biomineralized parts or organs (Nedin 1999).

Some of the statements, e.g. implications by existence of nerves [Na, K] and muscles [Ca, Mg] in almost all animals, are pretty general and far-reaching. Among these animals from $\geq$500 mio. years ago, benthic invertebrates are very well documented in the fossil collections, while plankton invertebrates (and plants) are less so, but still fairly well, whereas swimming animals are rarely found, except for cephalopods and (substantially later on), arthrodire fishes (MacAlester 1982).

Yet, even in the best of cases, for Middle Cambrian ages, there are just two sites in the World known to give a full record of benthos organisms which permits to reconstruct the local ecosystem beyond mere speculation, in particular: the famous Mt. Burgess shale layer from British Columbia (Canada, Fig. 3.11).

At this site, “soft” or chitin-clad animals did prevail. Some of them (e.g., Hallucigenia in Fig. 3.12) had mineral-made “stings” which were used either to avoid being eaten (much like modern sea-urchins) though otherwise the animal much looked like a worm (rather than being spherical or radially-symmetrical) or for locomotion (a kind of stiff legs), the real function still being open to controversy. Anyway, there is evidence for ample production of Ca-based biominerals in lobopodian worms at a period of time where biomineralization was rare otherwise, and recent lobopodians do not promote biomineral formation either.

In addition, the Vendian and Cambrian saw the development of most present classes of marine invertebrates (except for bryozoa which would evolve only in

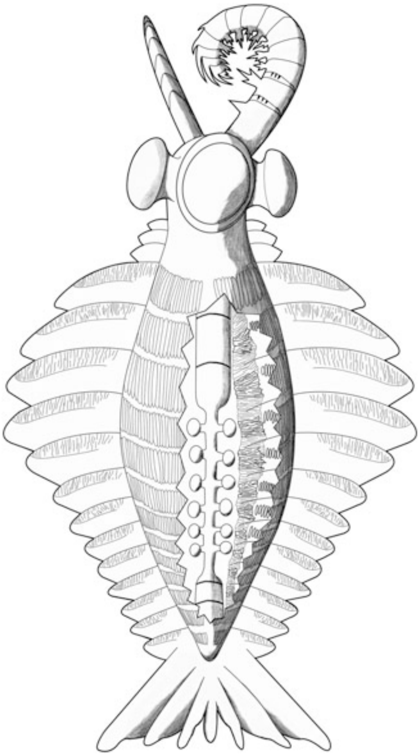

Fig. 3.10 Reconstruction of *Anomalocaris canadensis* (literally "anomalous" [strange] shrimp [although this animal was much larger than any recent or extinct shrimp at up to 1 m total length] and it is not clear whether it actually was an arthropod, as shrimps are). Image courtesy of Daley and Edgecombe (2014)

Ordovician [MacAlester 1982]), and tunicates and chordate animals which probably looked much like modern amphioxus. Embryological as well as biochemical arguments suggest the latter chordates, represented in middle Cambrian by *Haikouichthys* or *Pikaia*, and more complex "genuine" vertebrates (having a segmented chorda) are more closely related to echinoderms than to arthropods or annelids even though the latter have a head-to-end body organization rather resembling that of vertebrates. Given this, one should expect similarities in geobiochemistry of Middle Cambrian times to allow formation of either vertebrates, tunicates and echinoderms from unknown precursors which implies that there are certain common features of element use common (and novel) to them which distinguishes them from all arthropods, annelids and mollusks. The most obvious among these is the means (and carrier metal, Fe vs. Cu) of dioxygen transport but it also extends into modes and biochemical pathways of formation of hard, sometimes up to often even biomineralized, structures.

There were some, rare echinoderms already, besides a possible cephalopod (*Nectocaris*, Fig. 3.13) which yet had but two arms and neither an outer shell (like nautiloides) nor an inner stiffening construction (like recent sepia has).

Concerning our topic of element use in biology, it should be noted that, while (putative) ancestors of vertebrates like *Haikouichthys* or *Pikaia* (Fig. 3.14) date

Fig. 3.11 Walcott Quarry of the Burgess Shale showing the Walcott Quarry Shale Member. The *white parallel vertical streaks* are remnants of drill holes made during excavations in mid-1990s. The Burgess Shale Formation, located in the Canadian Rockies of British Columbia, is one of the world's most celebrated fossil fields. It is famous for the exceptional preservation of the soft parts of its fossils. At 505 million years (Middle Cambrian) old, it is one of the earliest fossil beds containing soft-part imprints. Image courtesy of Wikipedia

back some 510 mio. years, and both already possessed a kind of skull or at least a solid brain[17]-protecting structure (made of whatever material) although there were neither jaws, nor a hard chorda. Predation activity not really implies dealing with biominerals for successful "attack" or scission of prey animals: predatory marine snails or wood-boring "worms" (actually mussels) succeed in drilling holes into aragonite (β-$CaCO_3$) shells or into wood by radulae made of chitin, without that

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[17] It is an open matter whether brains of arthropods, mollusks (especially, cephalopods which are quite bright), and vertebrates are homologous organs, given that the probably last common ancestors still lacked anything of the kind. Nevertheless, brain function requires a highly developed common action of quaternary ammonium ions (acetyl choline, in synaptic gap), Na and K cations, Cu proteins (oxidizing indoles and benzenoid aromatics to produce neurotransmitter phenols and indophenols) and Zn ions, peptides, possibly also others such as Li^+.

Fig. 3.12 *Hallucigenia sparsa*, fossil from Mt. Burgess shale layer from British Columbia and reconstruction. Image courtesy of Wikipedia

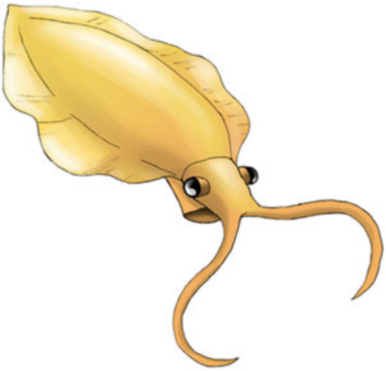

Fig. 3.13 *Nectocaris*, 505 mio. years old, some 4 mm "mantle" length, possibly the earliest cephalopod, known from the "middle Cambrian". Image courtesy of Citron-CC-BY-SA-3 via Wikipedia

substantial fortification by diverse (Ca, Zn, Mg) carbonate fibers[18] found today in e.g. mandibles of large crabs and lobsters.

Accordingly, *Anomalocaris* (Fig. 3.10), which was clad into thick chitin layers and had a mouth organ made from the same stuff reminiscent of a drilling plate, would have been in a position to cut everyone else living there—including trilobites—into pieces without processing lots of calcium or other metal ions itself to produce bones or "real" teeth. If *Anomalocaris* did not contain products of biomineralization in its mouthpieces, the former fact puts upper limits on levels of all Al, Co(II), and Cu(II),

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[18] Although, in terms of essentiality, one must distinguish between functions of some element in enzymes or cofactors such as cobalamine (Co), molybdopterin (Mo; this complex is the only speciation from of Mo higher animals can absorb to obtain "enzymatically useful", active Mo in e.g. oxidoreductases or aldehyde oxidase), selenocystein and structural, osmotic and other features, formation of such fortification fibers (much like in glass- or carbon fiber-reinforced plastics) requires passing some well-defined element to a certain location within some biopolymer sample.

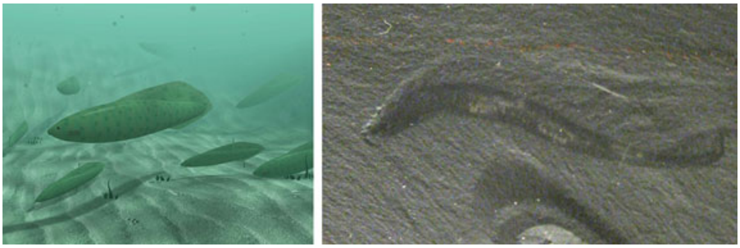

Fig. 3.14 Reconstruction of *Haikouichthys* (*left*) and two fossil specimens of *Pikaia gracilis* (*right*). Neither *Pikaia gracilis* nor its contemporary *Haikouichthys* is fully established to be a "thoroughbred" (if jawless) vertebrate already, either is 3–4 cm long, and both did live close to either shore of what now is the Pacific Ocean: Haikouichthys in China, Pikaia in Canada (British Columbia). Image courtesy (*left*) Talifero via Wikipedia; (*right*) Jstuby via Wikipedia

and probably other metals, in the Cambrian ocean. Later anomalocaridids, such as *Schinderhannes bartelsi* (Upper Silurian) had "fortified" mouth and biting organs.

Moreover, the common conclusion that only biomineral production would offer a chance to start predation in short-term response to formation of hard shells (which need not have been made from minerals either) is misleading, and thus one cannot reconstruct changes in metal-ion processing biochemistry from onset of predation and corresponding change in complexity of ecosystems. Production of Ca phosphates for teeth-analogs commenced during early Cambrian also (in conodonts) meaning we must and can view upon the problem from a more general geobiochemical limitations point of view.

Interestingly, both vertebrates and echinoderms use hydroxyapatite rather than $CaCO_3$ for their hard structures (bones, stings, teeth), as do the earliest conodont-bearing animals which evolved at the same time. Bryozoa and calcite-fortified algae developed only later, briefly before onset of Ordovician. While there had been RNA and DNA—and by inference nucleoside triphosphates—long, long before the Cambrian, the controlled deposition of insoluble phosphates from ATP or GTP into biominerals commenced only then. Ca^{2+} was available from the ocean obviously, and there are different kinds of phosphatases which either use Mg, Zn, Mn(II) or Fe(II) [purple acidic phosphatases] for their activity. Concerning the local chemical environment, it should be noted there will be no precipitation of phosphates like apatite or $AlPO_4$ from mainly organic media like lipids unless substantial amounts of water are admitted. Formation of phosphate-based solids (bones, teeth, stings, conodonts and so on) then could be imagined to biogeochemical conditions enabling fairly unlike organisms to divert PO_4^{3-} from the very high throughput of NTPs (some 1,500 Mols/day in an average human!) into spatially controlled deposition. Conodonts are not precursors to vertebrate teeth (Janvier 2013, Fig. 3.15) but came into existence at about the same time. The controlled precipitation of $Ca_5(PO_4)_3(OH)$ might be accomplished close to membranes but mainly such formed of aquated proteins given the problems of precipitating phosphates from lipid-like media like ester solvents.

Apart from the peculiar processes concerning biomineralization and O_2 transport which obviously started around the early Cambrian, our ideas on use of essential

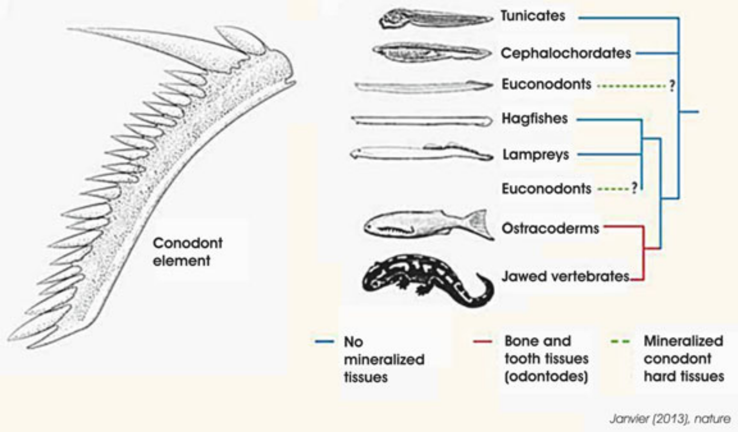

Fig. 3.15 Conodont supporting structures and the possible taxonomic status of conodontophoran animals: something related to cephalochordata or lampreys? The *right side* shows two possible taxonomic relationships of euconodonts, either with Lampreys or with Lancelets. Source of image: Janvier (2013)

elements are substantially flawed especially insofar as metals in enzymes are concerned. These flaws, of course, come from incomplete fossil records which likely produce selection effects in our ideas on what conditions then were like concerning formation of biomineralized structures from certain elements (Ca, Sr, Si, etc.). Concerning non-metals, it is fair to say that phosphates, rather than halides Cl^- to I^-, kept on being the principal leaving groups in alkylations while the latter would perform much better in electrophilic substitutions and alkyl halides are biologically readily available, in particular produced by marine plankton algae and by fungi. The use of Co in vitamin B_{12} (super-reduced state, that is, Co(I)) did not change this, nor did evolution of metalloenzymes which—from the view point from an organic chemist—would run considerably better on alkyl halide intermediates than on phosphate esters, e.g. CO acetate synthase from *Moorella thermoacetica* (a clostridium [Riedel et al. 2010]). Obviously phosphate release by polyphosphate hydrolysis is so crucial for control of almost everything which happens inside any kind of living cell that better alternatives would produce too many obstructive side-effects [recall that evolution by random mutation and selection would not identify global optima to “solve a problem” but only gets to local minima within reach of a given attractor (Rechenberg et al. 1998)].

Yet there is indirect evidence of how optimization tool place. To give an example, early (that is, Vendian or Tommotian, >530 mio. years BP) sponges could not control uptake of Si by dissolution of silica sand and reprecipitation, unlike the more advanced forms; they would rather grow around heaps of sand and use this for “passive” (not related to nor depending on solution-phase metabolism) fortification of tissues. E.g., Ediacaran Tribolozoa such as *Tribrachidium* or *Skinnera* probably were small (1–4 cm diameter) primitive sponges, overgrowing sand grains to form an inner supportive structure instead of depositing silica in needles actively, while first $CaCO_3$-depositing organisms from upper Ediacarium of Namibia produced small "baskets" (*Namacalathus*) or series of conical $CaCO_3$ structures located one in the next (*Cloudina*), neither being capable to add more carbonate at the edges, meaning that these outer skeletons would not grow with time. Although they are consistently assumed to belong to the animal kingdom, their taxonomic position still is enigmatic (Seilacher 2008).

However, exactly this fact provides a hint of what might have happened: many organisms, among them bacteria, lichens, and others attack smaller or larger grains of solid silica by Si complexation using o-phenyl phenols (=2-hydroxybiphenyls). How can they obtain such substances? They are quite uncommon in the environment, and plants or lignite (soft coal) layers providing them still were not existent either. The most obvious way to get o-phenyl phenols is enzymatic hydroxylation of biphenyls or derivatives thereof, in particular of fluorenes or carbazoles.[19] This enzymatic hydroxylation of biphenyls or their derivatives is accomplished by laccases and other aromatic-compound hydroxylases which commonly contain Cu (one atom per molecule) and make use of O_2. Some then contemporary creatures like arthropods, mollusks (including trilobites, *Anomalocaris* and *Nectocaris*) surely used Cu even for dioxygen transport, so fairly plenty of it must have been available, while laccases in either fungi or more advanced animals do not need too much of Cu. Hence when more modern sponges replaced archaecyathida some 516 mio. years ago it is likely that Cu-depending enzyme-based hydroxylation of (certain, "activated") benzenoid arenes and biphenyls and fluorenes was already feasible. (Of course) no trace of the corresponding enzymes is left behind in the fossils now available. Even Cu isotope data ($^{63}Cu/^{65}Cu$ ratios, the value being about 2.24 in the isotopic standard mixture) in modern remains probably would not allow to distinguish between Cambrian-times isotopic fractionation during resorption and use and later-on absorption by the would-be fossil. But another reaction (i.e., dissolution of silica by hydroxybiphenyl compounds which must be made somehow in a metabolic way) provides an educated guess of what was available by considering what it takes to "prepare" these very intermediates inside of tissues. The data are obscured, anyway, and this is probably even a very lucky example of indirect information on element interactions (in modern organisms, similar links could be inferred from inorganic total analysis of some creature or organ thereof, but then the [mostly organic] intermediates of metabolism are also available).

As far as sponges are concerned, the biosynthetic pathway of isocyanides R–NC (R = terpene backbone or aryl group)—which likewise draws upon electron transfer from oligocyclic organics while formamides or similar "reasonable-looking" precursors are not involved—thus also points to similar reactions. However, the RNC products are powerful metal ion ligators and can thus alter the metal patterns inside corresponding tissues considerably. Especially since sponges lack a broader

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[19] As far as hydroxylation is induced by direct electron transfer from an aromatic or PAH or hetero-PAH compound towards Cu(II), no weaker oxidant than O_2 (or nitrate, nitrite at best) can induce the e^- transfer cascade, and the series of **increasingly difficult** 1e-oxidation (increasing redox half-wave potential) is aniline < phenol < fluorene < biphenyl < carbazol ≪ alkyl- or halobenzenes (Lund 1957; Miller et al. 1972).

histological diversity inside of them and will passively coordinate dissolved metal ions. Given present conditions, this predominantly holds for freshwater and estuarine sponges simply because local "heavy metal" ion concentrations exceed those in the ocean by orders of magnitude. Metal RNC complexes keep stable upon both oxidation or reduction of the M^{n+} centers over far larger ranges of redox potentials and formal oxidation states than do metal carbonyls or –phosphine complexes.

Let us return to the actual sequence of events now: except for some Precambrian "pioneers" (which are commonly interpreted as almost sessile animals) forming hard inner or outer structures still were unable to modify them with time (i.e., let them grow). Different kinds of animals started to use different elements one by one during the Cambrian. With later-developing groups (e.g., demosponges, fortified by protein and SiO_2) having a different element biochemistry sometimes readily replacing the former ones (in this case, Archaeocyatha [mainly present between 525–516 mio. years BP]), having $CaCO_3$ shells which survived fossilization in their original shape, hence must have been calcite rather than aragonite now produced by molluscs. This is why the latter are bound to crumble during transformation into considerably more dense calcite[20] ahead of fossilization which means that negative imprints are left over, not the very shells of snails, cephalopods or mussels).

3.3 Metal-Forming Elements in Biology

Processing Ca for shell formation started in the early Cambrian 542 mio. years ago with the above sessile animals and with brachiopods, while just before and at the very beginning of the Cambrian there were

(a) a glaciation period (Baikonur glaciation) and
(b) a series of first largely negative and then positive excursion of $\delta^{13}C$ values in biogenic organic matter (Magaritz et al. 1986).

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[20] $\rho_{arag} = 2.73$ g/cm^3, $\rho_{calcite} = 2.93$ g/cm^3 which means a contraction of some 7 % takes place during change of crystal structures which, moreover, are not closely related but imply a substantial rearrangement of ions. Ostwald's famous phase rule then means, if there was calcite in Archaeocyatha, like in bones and teeth of today's vertebrates, biomineralization was effected either slowly, including catalysis of the said rearrangement, or it was done in a manner which was entirely different from that in mollusks. Be it as it was, Archaeocyatha were the first organisms to produce reefs, yet were replaced by sponges already some 516 mio. years BP while likewise "primitive" reef-builders like cnidaria even made it until today (unlike rudites) through several periods of ocean acidification by increased CO_2 (implied by thermal history of ocean waters during the times from Ordovician till today)—which should not be taken as an advice to be clumsy or reckless on CO_2 enrichment in both troposphere and ocean: obviously some kinds of coral-forming polyps can live isolated, without a stable exoskeleton, in the same manner as *Hydra* does, but we would soon painfully notice the effects—from fishery turnover breakdowns to catastrophic attack on shorelines by tropical storms—if the large reefs East of Australia and Belize and all the smaller ones would get dissolved by acidification!

There are two coupled equilibria after Magaritz et al. (1986):

$$CO_2 + 2H_2O \leftrightarrow HCO_3^{-} + H_3O^{+} \text{ and}$$

$$Ca^{2+} + 2HCO_3^{-} \leftrightarrow CaCO_3 \downarrow + CO_2 + H_2O$$

Thus a compound in which two oxygens are bound to C is converted into another which keeps three O per C and then is removed from solution. Exchange by either step gets faster the higher the temperature will be. Stronger bonds in which (vibration) excited states are less populated are less likely to be cleaved by decomposing HCO_3^{-} into CO_2. The strongest bonds are those among the heaviest isotopes of both carbon (^{13}C) and oxygen (^{18}O), and the difference in vibration excitation extents gets the larger the colder the surroundings are. Thus “isotopically peculiar” bonds tend to survive into precipitation of calcite or aragonite the more the colder the surroundings are, too, causing coupled isotopic fractionation as long as just a part of C and O gets locked up into carbonate. It does not matter whether both steps occur in living beings (say, formation of a mussel shell or an elephant’s tusk) or in inorganic setting (making a hanging stone in a karst cave); you can deduce local temperatures in either case (this is how it got proven late [Maastricht-times] dinosaurs and pterosaurs actually were homoeothermic). Coupling or uncoupling of $\delta^{13}C$- and $\delta^{18}O$ data additionally provides data on body temperature in which biominerals were produced, permitting to show that, while mammoths (data were obtained from both tusks and bones) had essentially the same body temperature as recent elephants, and crocodiles would live and grow in waters substantially cooler than 36 °C, some dinosaurs probably were homoeothermic indeed, as had been inferred from presence of fur or feathers and activity before. It is likely hence, that their use of certain essential elements in catabolic metabolism and redox processes in dinosaurs more resembled birds (taken to be successors of dinosaurs) and mammals than contemporary reptiles.

Often such events of $\delta^{13}C/\delta^{18}O$ changes in carbonates produced by or next to living beings are linked to substantial changes in biodiversity such as mass extinctions (Magaritz et al. 1986), and so are perhaps more telling than the trivial fact that living beings on Earth (a) mainly consist of carbon and (b) changes in chain of trophic length will alter the extent of sequential isotopic separation of C in biogenic matter (such as evolution of grassing and prey-catching animals in the Cambrian case, or mass-extinctions hitting marine plankton massively, as well as grassers [Frasnian-Famennian transition]).

The latter fact suggests a thorough change in internal structure of the corresponding organisms which took place during this time while concomitant formation of an outright trophic pyramid meant more and more membrane passages in metabolism: like in protocols for isotopic separation where a small fractionation across some membrane or along a thermal gradient gets amplified by repeating the corresponding structure and passage of some share of the original mixture of isotopomers of some compound time after time until volatiles such as $^{10;11}BF_3$, $^{28;29;30}SiF_4$, $^{235;238}UF_6$ or $^{12;13}CI_4$ are almost completely fractionated to enrich the lighter isotope, biology would achieve the same if separation effects were not “obscured” by joint presence of heavier or lighter isotopes of several elements combined in one kind of “food” molecules.[21] The necessity to pass something through membranes—be it a molecule, ion or complex—brings about some isotopic fractionation, commonly selecting the lighter isotope or isotopomer, as do precipitation or partial (acidic or oxidative[22]) dissolution. Once there are several layers of cells and membranes in between them and separating some “interior” from water and a digestive apparatus or from gills, this separation effect will increase even though there might be also chemical or climatic changes which bring about different fractionation patterns (the linked $^{13}C/^{18}O$ fractionation in carbonates can be used to pinpoint and determine palaeotemperatures, including the body temperatures of organisms assumed or contested to be homoeothermic, such as advanced dinosaurs or pterosaurs). Every trophic level, every increase in histological complexity translates into yet more membranes contributing to isotopic fractionation.

Anyway, the use of **Ca** in large amounts (formerly it was required in control of cell budding already, and photosystem II—being universal in its structure and role in oxygenic photosynthesis—contains one Ca^{2+} besides of manganese also) predated that of Si by and in sponges. However, carbonates which may or may not be biogenic in precipitation may correspond to either

- change in ocean pH,
- extent of extraction of CO_2 from HCO_3^- for photosynthetic “purposes” (which latter would be related to improvement of carboanhydrase activity, that is, use of primarily Zn [or, Co, Cd] in marine phytoplankton) or
- length of trophic chains until nutrient recycling takes place. The latter, obviously linked to the evolution of animals, however is likely to produce but a small effect given > 80 % of ingested plant reduced C are oxidized to CO_2 on second trophic

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[21] E.g. CO_2 for plants and cyanobacteria where there are both ^{13}C and $^{17;18}O$ or sugars for which the same holds. In amino acids and peptides, there is ^{15}N additionally, while methanotrophic organisms would perform better in $^{12;13}C$ isotopic separation as D (^2H) is much rarer (about 0.016 %) than the above heavier C, N, and O isotopes. Biogenic metal (Mg, Fe, Zn, Cr, U) isotopic fractionation is feasible for the same reason: “exotic” isotopes ($^{25;26}Mg$, $^{66;68}Zn$, $^{54;57}Fe$, ^{235}U) use to be much more abundant than $^{17;18}O$ or ^{15}N, meaning that biological processing of stable complexes which do not undergo complete M-ligand separation in digestion will fairly efficiently enrich or deplete the above nuclides in biomass thereafter, provided there is but partial resorption, as is quite common. ^{58}Fe, ^{234}U, or ^{54}Cr are too rare for this to be observed.

[22] Of course, one then must distinguish between the phases produced during such treatment (the effect can only occur during **partial**, incomplete dissolution): upon acidic etching of calcite, CO_2 (gas) will be depleted in ^{13}C, meaning a relative enrichment of this heavier carbon isotope in both dissolved HCO_3^- (liquid) and remaining calcite solid. The calcium isotopes behave similarly, with ^{40}Ca becoming enriched in the supernatant whereas heavy isotopes $^{43;44;48}Ca$ tend to stay in the solid (normally, the ratio $^{40}Ca/^{44}Ca$ [46.47 in isotopic standard] is measured, while the tiny traces of ^{46}Ca in the mixture [≈0.004 %] escape precise determination of isotopic shifts and ^{42}Ca is omitted and use of ^{43}Ca [about 0.14 % of mixture] additionally allows for NMR investigation of this fractionation). To give another example, H_2O_2 oxidations of both elemental sulfur and certain heavy metal sulfides produce $^{34}S/^{32}S$ or $^{36}S/^{32}S$ fractionations which are identical to those observed in biological sulfur redox metabolism, and thus—given photochemical formation of H_2O_2 in palaeoatmosphere and its corresponding presence in rainwater—hence it is impossible to tell when sulfate bioreduction commenced in Archaic times.

level already; yet it is possible to use C isotopic data (and those for N, Ca, Sr) to reconstruct former feeding habits of extinct animals (or, in forensic medicine, of unidentified human bodies even if they are badly burnt or almost reduced to the skeleton).

Keep in mind that arthropods, mollusks, horseshoe crabs and some others do not employ Fe for dioxygen transport and activation but rely on Cu for these purposes (haemocyanin, laccases, monoxygenases). While most specimens from the Mt. Burgess Shale fauna (Middle Cambrian; s. Fig. 3.11) can readily be attributed to phyla which are still with us, these creatures still were soft-bodied; construction of hard shells and hence increased Ca, P, etc. metabolic turnovers had still to be developed, after some precedents in upper Precambrian and a kind of "break" thereafter. Yet representatives of the soft-bodied Burgess types of animals made it into the Ordovician (Fezouata, Morocco) regardless of probably increased predation intensity (as a matter of fact, very "soft" animals like nematode worms exist till today even if unprotected by poisons etc. otherwise). On the other hand, from biophysical constraints on size, shape, and organization of heterotrophic organisms (Nachtigall and Wisser 2006) it is quite straightforward first to have advanced O_2 transport systems and only then to develop body covers which massively reduce dioxygen supply by simple diffusion, necessitating development of all gills, mouth and digestive intestine except for symbiosis in certain marine tubeworms.

During the Ordovician, there was a second massive radiation of animals in the Sea. Even though novel chemical bases of skin cover and –protection came into existence with reptiles, birds and mammals (scales, feathers and fur all made from mutually fairly similar S-rich proteins) later-on, this would not imply novel ways of biochemical catalysis to make them. Cystein is produced from phosphoserine by nucleophilic substitution with sulphide produced by sulphate bioreduction which in turn relies upon Fe thioclusters (ferredoxines) which, however, are likely to be among the oldest enzymes known and accordingly common to almost all organisms living today. More advanced vertebrates thus do not differ from either fishes or amphibians with respect to essentiality patterns, except perhaps for iodine (little can be said now about lancelets [cephalochordates] or cyclostomes [hagfishes, lampreys] which both are difficult to keep in tanks and thus were not exposed to element deprivation experiments so far).

The very origins of vertebrates (something like *Pikaia* in Fig. 3.14, similar to lancelets [Middle Cambrian of Canada]) and of insects and other arthropods (*Opabinia*, from the same excavation site) and mollusks are identical in age (some 510 mio. years BP), accordingly the difference should not be due to one or the other element (Cu or Fe) be better available at a given point of animal evolution. Mutual distances in taxonomic relationships and the comparison to echinoderms rather suggests the "decision" which metal to be taken for O_2 transport (and omission of the "chemically logical" Co alternative might date back into late Precambrian). Moreover, making Fe reversibly react with dioxygen is not too simple (Collman 1977), and it is stunning that **no** aerobic creature uses **cobalt** for O_2 transport given the properties of Co(II) amino acid or –peptide complexes

(McLendon et al. 1976) while there are not only cobalamines like vitamin B_{12} but also a wealth of Co-based hydrolases and anhydrases.

The adaptive radiation (and size increase, formation of hard body covers/protective shells) of aerobic heterotrophic metazoans

- obviously started from thin-layer animals which possibly had no necessity to chemically capture and transport O_2 at all but could rely on simple diffusion inside of them and
- took place at some small fraction of the present O_2 partial pressure (which is some 213 mbar) while the latter increased (rather than decreased, to a first approximation **disfavoring** evolution of complex transport structures in terms of both chemical O_2 transporters and liquid media [blood or hemolymph] employed to transport and distribute the scavenged O_2 inside some smaller or larger body).

Simple reasoning from biophysics then suggests that making hard body covers almost impermeable for dissolved gases went along evolution of dioxygen transport mechanisms while early Cambrian animals were not significantly larger than their late Precambrian (Ediacaran, Vendian) ancestors. Whether there are holes in a chitin or Ca carbonate cover (preceding trachea) or some membranes are actively stretched out of the gas-closed inner parts (gills, pleopods and the like), from then on effective internal O_2 transport would inevitably take availability of chemical transporters which are suspended in some fluid circulating in the body. When thin worms would evolve into either vertebrate- or (more likely) arthropod precursors, they already had to have (either Cu- or Fe-)based transport agents. The Fe-based systems are much more complex and demanding in terms of avoiding irreversible oxidation of the metal center (precluding later release of O_2) than either Co or Cu-based ones (see the synthetic "picket-fence" porphyrins after Collman 1977 in Fig. 3.16). So it is likely that the Cu-based structures evolved first, with either later-on becoming the basis of many and diverse oxidation catalysts in later biology.

The so-called Cambrian explosion which indeed is no longer considered to be one was limited to one kingdom of biology (animals) only while little less than a billion years before separation of multicellular kingdoms took place. This brought about remarkably diverse patterns of essentiality. Here, events were not really simultaneous, unlike in Middle Cambrian: most "strange creatures" from Mt. Burgess (British Columbia) site were formerly considered to be so exotic as to represent extinct phyla of animals which did not make it for long now are taken to be simple polychaetes, arthropods, coelenterates and so on. Conversely, what was taken to be imprints of late Precambrian jellyfishes for a longer period of time is fully enigmatic now, no longer even sure to be animals at all!

In this manner essentiality lists of elements (Table 3.2) probably grew one by one during evolution, with hardly any hitherto essential elements left behind or omitted after some point of time; it is intriguing that, given the much higher synthetic demands associated with autotrophy, plants (both higher green plants and humble algae, mosses) depend on less elements than heterotrophic animals or fungi. Meanwhile the composition of the atmosphere did change with time and biological activity, implying that solubilities of certain elements changed considerably.

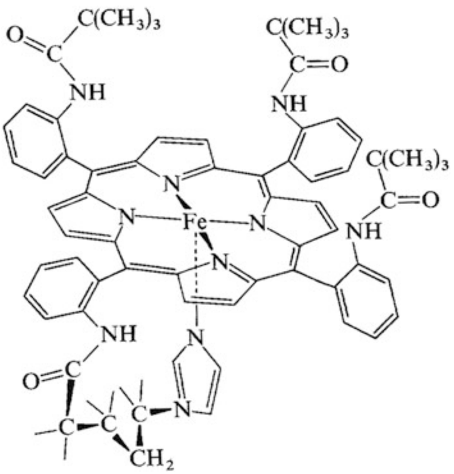

Fig. 3.16 "Picket-fence" porphyrin: The four bulky pivaloylanilido groups in between the pyrrol rings of the porphyrin block approach of a second Fe ion or similar complex; thus the originally O_2 adduct cannot dimerize to produce a peroxide-bridged Fe(III) dimer (it is a synthetic complex rather than the exact haemoglobin or myoglobin while these O_2 transporters make use of the same kind of sterical blocking of dimerization). This structure is favorable for reversible O_2 binding and thus its transport while the latter, lacking this pronounced sterical congestion, will activate peroxides [derived from either O_2 or H_2O_2 (due to atmospheric photochemistry, H_2O_2, which can be readily detected in rainwater, was present and available even before O_2 enriched in the atmosphere. E.g., it now also occurs in the Martian atmosphere which contains but traces of O_2 variable with time. On Earth, porphyrins are found in very old sediments, shales and oils also, and thus one can imagine some heterotrophic creature consuming algal or cyanobacteria cells to replace Mg in chlorophyll thus taken up by Fe(II) and then make corresponding meaningful biological oxidations without using anything but rainwater-derived hydrogen peroxide, even before 2.3 bio. years before present)] via O-O bond splitting and formation of $Fe^{IV}O$ porphyrines. Possibly the latter, arguably more simple and straightforward way of using O_2 predated its transport by Fe haem systems, or both evolved side by side. Fe ("ferryl(IV-)"-haem peroxidases are very distributed among, animals, fungi, and bacteria. Source of image: Collman (1977)

Ochre formation in aerated water bodies commences at a Fe^{2+} concentration of some 3 mg/l while, excluding O_2 or other oxidants or UV radiation (Braterman et al. 1983; Horvath and Stevenson 1992), much higher levels of this ion could be sustained even in almost neutral—rather than highly acidic—solutions. Hence "injection" of substantial O_2 into the atmosphere by increased oxygenic photosynthesis some 2.3 bio. years ago caused substantial depletion of dissolved Fe[23] (while first banded iron formations [BIFs] are much older) while other elements became more mobile by oxidative

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[23] Unless pH and carbonate content of ocean water then were about the same as today. In the latter case, siderite $FeCO_3$ and iron(II)hydroxides would limit dissolved Fe considerably, in addition Fe(II) photooxidation and H_2 release would rapid occur upon UV exposure of the solids (the exactly stoichiometric solids are white but turn green to olive to reddish soon under illumination *if solid*) reducing Fe availability even before gaseous O_2 was present.

Table 3.2 Catalytic chemistry on precursors of bioorganic chemistry in parentheses (Fränzle 2010, extended)

Substrate	Functional group involved, co-reactants (C)	Products	Prebiotic; catalyst	Present-time biochemistry (metal ion in enzyme)	Technical organic chemistry; catalyst	Side-reactions, by-products, catalyst "poisons" (P)	Remarks, "matches"
CO	$C = H_2$, NH_3	HCN, hydrocarbons, alcohols, amino acids, other RCOOH	Transition metal ions (little defined)	archaea: W, Zn; CO dehydrogenase: Mo/Fe/S (aerobic bacteria) or Ni/Fe/S (anaerobic bacteria)	Fe-oxide phases, Ni metal, clays (FTT synthesis)	Water-gas shift affords CO_2, methanation; P=S	Fe
CO_2	Electron sources; biology + sugar phosphate	Carboxylates, esters	$C = H_2$: Fe(II)	Mg (rubisco); Fe (formate dehydrogenase[a]) of yeast; W (or Mo) + Se (clostridia and other bacteria)	Cathodic reduction (Cu- or Pb- or In cathodes)	Release of H_2, CO	Cathodic reductions require very low potentials, while affording oxalate rather than compounds rich in CH bonds
Hydrocarbons	$C = NH_3$	Nitriles including HCN	Apparently several (photooxidative attack by $[Fe(OH)]^{2+}$?)	CH bond activation by high Fe oxidation states in haem [$c' = O_2$ or H_2O_2]	Bi_2O_3; Mo	NO, CO_2 P=S	Seen in complicated multicatalyst prebiotic systems; saturated hydrocarbons like CH_4 are no ligands, hence interact with metals only in an indirect manner or after oxidation

Aldehydes	–CHO	Sugars	Ba^{2+}, Pb^{2+}, clays; cofactor/ template = $HOCH_2CHO$	Sugars are not made from RCHO in present biology	No (synthesis accomplished by means of enzymes only)	Disproportionation (OH^-, Al, Zr)	CC linkage to yield sugars vs. hydride transfer without forming new CC bonds (esters at most)
	$C = NO_3^-$	Amino acids	Fe(III) [photo-chemical]	Sugar consumption in nitrate respiration: Mo in first step	No		
	R-CHO = sugar or glycol, glycerol aldehydes; $c = NH_3OH^+$	Amino acids, mainly glycine	Several metal ions in the mixture, probably active: Mo, V (pH = 6)	No equivalent	Not used		CC bond cleavage occurs; ala > gly with methyl glyoxal, glyceraldehyde and ribose only. Best precursor HCO-COOH
N_2	$C = H_2$ or labile hydrides	NH_3	HCHO + light $\{MoO_3\}$, produces amino acids; FeS, $c = H_2S$; reduced vanadium in alkalinic conditions	Fe (alone or + Mo or + V [nitrogenase])	Fe oxides promoted by K carbonate and other additives (Haber-Bosch process) or Os/TiO_2		Active iron sulfides are probably not pure; similar roles of Fe and V

(continued)

Table 3.2 (continued)

Substrate	Functional group involved, co-reactants (C)	Products	Prebiotic; catalyst	Present-time biochemistry (metal ion in enzyme)	Technical organic chemistry; catalyst	Side-reactions, by-products, catalyst "poisons" (P)	Remarks, "matches"
Phosphate	Condensation agent	Oligophosphates	Alkaline earths, best: Be^{2+} or Mg^{2+}	Phosphate kinases: Mg or Mn^{2+}	Uncatalyzed high-T process		Mg
Amino acids	For peptide linkage: C = ATP	Peptides	Cu^{2+}, NaCl (solid)	Mn, Co (dipeptidases); Zn (carboxypeptidase) but Co^{2+} is superior to Zn in catalytic performance	No (synthesis accomplished by means of enzymes only), lab-scale work by Co(III)-complexes		Peptide formation by Cu(II) is autocatalytic
		Organic acids	Mn/Al (solid $MnCO_3$)	Mo + Se (reductive dissemination)	Not used		Similarities of thermal "prebiotic" pathways with Krebs tricarboxylate cycle
2-keto acids	NH_4^+, reductants	Amino acids	Cp. aldehydes, particularly for gly formation from HCO-COOH: Several metal ions present in the mixture, probably active: Mo, V (pH = 6)	Transamination by reduced pyridinium salt; added metal ions use to disturb reaction	Ru- or Ir complexes with chiral co-ligands (mostly phosphanes)	Amines from decarboxylation	

1-alkynes	Trimerization	Benzenoid aromatics, pyridines	Probably transition metal ions	Not observed	Mo or other metals, Ni carbonyls (Reppe chemistry)	Hydrolysis	Seen in complicated multicatalyst prebiotic systems (yet containing no Ni); match with Mo?
	$C = H_2O$	Aldehydes, methyl ketones; then amino acids via Strecker synthesis	? (but increased yield of alanine, methyl hydantoine from systems containing both C_2H_2 and metal ions compared to metal-free systems)	Not observed	Cu^+, Ag^+, Hg^{2+}	Cyclotrimerization	Seen in complicated multicatalyst prebiotic systems (yet containing no Ni)
Nitriles	Electrons	Amines	Not observed	Cp. N_2: Fe (alone or + Mo or + V [nitrogenase])	Ru complexes (studied for hydrogen storage in recyclable liquids)		
	$C = H_2O$	Carboxamides	Not specifically looked for	Co^{2+} (bacteria)	Hydrolase enzymes containing different metals are applied		Co^{2+}
		Peptide linkages (nitrile = AAN)	clays	Not observed	Not applied		

[a] Like any catalyst, (must) work(s) either way round, also enhancing kinetics of backward reaction. Formate dehydrogenase thus was applied for CO_2 hydrogenation to produce formate at a p-InP photocathode

degradation of sulphides or pnictides or even of oxoanions, thus becoming more accessible to the biota (provided the latter could stand dioxygen).

When trying to compare our knowledge on prebiotic chemistry and its catalytic features (sofar now identified) to present biochemistry, we should

1. focus on cases where there are identical substrates, yielding ”biorelevant” compounds like sugars, amino acids or organic-conjugated polyphosphates or precursors thereof, and
2. do a second, parallel comparison to technical organic chemistry (if there are equivalents)

This is the purpose of Table 3.2. Photoelectrochemical processes are deliberately omitted from the list as they are

(a) uncommon in technical organic chemistry and
(b) sometimes related to elements in the semiconductor surface which never (Ti, Nb, In, PGM nanocolloids on illuminated interfaces) or rarely (Cd, Sr) turned up again in biochemistry, hence—if representing realistic features of prebiotic chemistry at all—were not adopted into bioinorganic chemistry for long nor would become fundaments of a primitive kind of photosynthesis in (hypothetical) early autotrophs.

Identity of substrate (if it behaves as a ligand) and of potential catalyst/precatalyst means identical binding energy and to a first approximation similar catalytic activity/turnover rates; however it is a tenacious difficulty in bioinorganic “modeling” (by preparing respective compounds rather than do *in silico* simulations only) that model complexes centered around the same metal ions having similar ligands rather would not promote the same reactions[24] while efficient homogeneous catalysts, e.g. for N_2 reduction, differ from the biological counterparts (nitrogenases) in both respects: Mo, W, V, or Re are used instead of Fe for binding and processing dinitrogen, and useful ligands are phosphanes rather than iron sulfido clusters and amino acid side chains.

Notwithstanding this, a comparison among all cases might reveal something on differences between early Earth, Mars conditions and contemporary bioinorganic chemistry (parts of which operate in unpolar lipid membranes or among valine-, (iso-)leucine-, phenyl alanine etc. residues, thus essentially work within a hydrocarbon medium) vs. technical organic chemistry is telling even though the latter may be operated in either polar (aqueous-based “green chemistry”) or unpolar conditions over a range of temperatures and using organometal reagents which are apparently almost avoided by biology.

It is probably fair to state that there is substantial „deviation“ among the three scenarios (bioinorganic, prebiotic, technical-organic) under consideration here. The more interesting are the actual or likely “agreements” (matches) observed for

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[24] “Positive exceptions” are mainly centered around certain elements, in particular Cu (hydroxylation of aromatics, peptide/polyamide linking) and V.

substrates CO, N_2, nitriles, alkynes, and phosphate. Apparently (except for phosphate) a covalent triple bond—irrespective of ligand-forming properties (which are more pronounced in CO, nitriles than with the other two)—does constrain possibly catalytic interactions among these substrate and metal ions. This happens as to dictate common kinds of interaction; it should be pointed out that V, Fe or Ni do not tend to produce side-on-π bonds towards alkynes or nitriles which would increase hydrolysis rates of the latter ligands whereas Mo might do so (CO and N_2 are bound in a linear or bridging fashion also). For the majority of cases, however, differences in conditions obviously more than outweigh for "best" pathways which should be identified by evolution as well as by systematically looking through the PSE in technical chemistry. Concerning the metals where there are "matches", Mg and Mo are almost universally essential whereas this not hold for either Fe or V (N_2 binding, -activation, -reduction) which as such is limited to few kinds of organisms. CO aqueous oxidation bound to Fe or Ni does not pose harsh criteria to occur (Hieber's famous[25] base reaction).

3.4 Essentiality/Toxicity of Elements

The classical argument on the relationship of essentiality dates back to sixteenth century even though its author—Theophrastus of Hohenheim, also (and better) known as Paracelsus—did not yet know anything about essential elements in nutrition yet came about effects of speciation of some element strongly influencing toxicity. It reads: "Everything acts as a poison depending on its dosage. Nothing is incapable of acting as a poison, and it's just the dose which converts everything into a poison". Accordingly everything is toxic if administered in excess, with substantial differences in width of therapeutical concentration ranges; e.g. selenium should not be given and consumed without constant medical surveillance as its therapeutical range (the interval between lack of supply and intoxication by the very agent) is very small.

Essentiality of chemical elements was established one by one (and sometimes, e.g. with Cr, cast into doubt some time later again). With many elements, toxicity of not-too-large doses was seen before there was any indication of essentiality (Fig. 3.17). So it happened that the role of selenium in humans was reappraised several times. The final (1966) "correction" was due to discovery of selenocysteine as a proteinogenic amino acid and Se–H bonds—which are weak and strongly reducing—being involved in reconstitution of glutathione and hence cleavage of ROS. Interestingly, there is one Se-cys residue at most in each protein chain.

As a rule, an excess of some essential element will be the more dangerous when it does interact considerably strongly with some kind of biomass. Oral Cu intoxication effects are limited by its causing pronounced vomiting in most subjects. This

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[25] One of the few cases of a name reaction in inorganic (rather than organic) chemistry.

Fig. 3.17 The public image of the "toxic" elements versus "essential" elements. Image courtesy of L.N. Vernie, Selenium in carcinogenesis

is employed by adding Cu^{2+} salts (usually, the sulfate) to toxic agent pills (analgetics, sleeping pills) to exclude their abuse for committing suicide or homicide by orally administering large amounts of them. This mechanism of protection against overly metal supply is quite common though not always as effective as with Cu (or Cd): weakly coordinating toxic ions (Tl^+, Ba^{2+}) can be administered orally in amounts sufficient to kill readily, while many pharmaceuticals which strongly interact with biomass then to act as cytostatics, f.e. cisplatinum and derivatives thereof, must be administered intravenously, yet violent vomiting frequently occurs during cancer chemotherapy. Apparently there are sensors in the body—possibly located in the upper digestive tract (throat, esophagus, stomach)—which respond to complexation of metals.

As mentioned before, biomass does behave as a ligand; accordingly, metals which form very stable complexes at appreciable reaction kinetics will be most toxic (Paquin et al. 2003). Among the essential ones, this holds for Cu,[26] Co mainly; among the non-essential ones, uranium (UO_2^{2+}), the other actinoids (apart from their radiotoxicity!), terbium and beryllium should be mentioned. It is not just since Be would be "mistaken" by cells and bioorganic compounds and enzymes for Mg (or Zn[27]) why it is so tremendously toxic. Likewise, with the actinoids U, Np, and

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[26] The same happens during induction of metallothionein biosynthesis: once heavy metals or other electrophilic agents like halocarbons react with some specific segment of DNA, gene expression does take place, producing MT which may or may not scavenge the toxic reagents. Some ions, like Bi^{3+}, are so effective in inducing MT as to render them essentially harmless (except if biomethylation takes place), while others including mercury will compromise this mechanism as to product outmost damage.

[27] Even though the ionic radius of Be^{2+} is much smaller than those of either Mg or Zn, there are similarities with Zn and Al pertinent to bioinorganic chemistry: e.g. heating of carboxylates or nitrates produces tetrahedral unpolar molecules with an M_4O center and the oxoligands bridging the six edges of the tetrahedron giving $[M_4O(\mu_2\text{-}RCOO)_6]$ (M=Be or Zn) which are not just lipophilic but do even dissolve in certain hydrocarbons (Cotton and Wilkinson 1982). Neither Al nor Mg nor Ca form similar compounds.

Pu chemotoxicity exceeds radiotoxicity for nuclides of sufficiently large half-lives ($^{233;235;236;238}U$, ^{237}Np, and $^{242;244}Pu$).

There is an overlap among essential to toxic elements of course which goes beyond the statement by Paracelsus: often ultratrace essential elements have a small width of therapeutic dose exactly because they are involved in quite a number of crucial metabolic transformations, like Mo in redox biocatalysis or Se in reductions. In either case the therapeutic window is so small as to really caution against unmonitored submission of these elements, with the risk somewhat reduced in Mo as it can be used by the human body only if bound to pterin[28] before. It is an open question whether this argument can be inverted, as therapeutic widths are larger in both established (V, Co [both vitamin B_{12} and non-cobalamine applications in e.g. hydrolases]) and putative (As, Li) essential elements than with Mo or Se. It cannot be generally concluded that something which is of no use will be rather harmless in larger amounts because it may still interfere with enzymes e.g. by replacing other essential elements, e.g. replacing Zn with Cd. In some cases enzyme activity may be maintained or even increased, or isofunctional enzymes may employ different metal ions or co-factors (phosphatase, hydrolases, hydrogenases), but as a rule such replacement is obstructive (Vallee and Williams 1968). Hence there is a relationship between toxicity and strength of binding to common ligands including apoproteins: the higher the affinity towards ligands, the higher chemotoxicity will be (e.g. Be^{2+}, Pd^{2+}, Hg^{2+}, UO_2^{2+} or Pu^{4+}). Some elements are tolerated only because there is tight control of their transport through the body by means of chaperones (Ni, Cu) (Tottey et al. 2005).

3.5 Ecotoxicological “Identity Cards” of Elements: Meaning and Scope[29]

Obviously what can be done (catalyzed) by a given metal ion or non-metal element depends on its chemical properties; the mere fact that there is a universal set of biocatalyst elements suggests there is a connection with the universality of certain chemical features in biology on Earth. Interestingly, organometal chemistry is almost insignificant in biochemistry even though many elements undergo biomethylation in appropriate conditions, and many oxidoreductases operate around Mg or Zn ions with the latter never changing their oxidation states, let alone doing something similar to Grignard-, Barbier- or Reformatsky reactions *in vivo*. Hence you cannot appreciate the subtleties and features bioinorganic chemistry, let alone apparent paradoxes like those mentioned before unless you

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[28] Given this, it is blunt nonsense to administer Mo e.g. as ammonium heptamolybdate as is usually done in preparations of multimineral food augmentation tablets (this author possesses samples of this kind); here molybdenum would only be toxic but not at all employed.

[29] Fränzle and Markert (2002a, b).

try to cover key features of the chemistry of one element before and besides considering its role in biology. That is what "identity cards" were constructed for.

Ecotoxicological "identity cards" were developed some ten years ago by Fränzle and Markert (2002a, b), originally to give a summarizing account of chemical properties and biological/biochemical effects of a number of chemical elements. "Identity cards" are meant to link the body of knowledge on

- oxidation states,
- speciation forms including methylated compounds (if persistent in aqueous media) of some elements (starting with As, Sn, Tl, reproduced here in tabs. 3.3—3.5) and
- their respective biocatalytic to toxic properties to biochemical properties and
- the issue of essentiality.

Are there certain chemical features which render it more likely that some element is essential or at least beneficial to living beings—and if so, to which ones? Of course, the most simple cases are such where there essentially is no speciation, no redox state change or -multiplicity, no complex formation, no alkylation in protic media, no acting as a ligand or component of insoluble salts. This refers to the heavier alkali metals, for example. They may yet be essential although K and Rb can be completely replaced by each other in many kinds of organisms; in stark contrast, noble gases have no "positive" biological role even though the same features—except for lack of charge—apply and neon is isoelectronic with Na^+, argon with K^+. Other elements have quite a number of oxidation states in biomass (often two, like with Fe or V, sometimes even three, e.g. Mo), or cations/oxoanions can be converted into ligands by multiple biomethylation and/or reduction steps (Ge, Sb, Bi, Te).

Let's discuss the ID-Cards of As, Sn and Tl in the following and let's have a look to their *toxicological* aspects (Fränzle and Markert 2002a, b; Markert et al. 2013d). We will start with As.

Arsenic is known to reduce the otherwise very high toxicity of (the essential element) selenium towards rats, dogs or poultry as well as in yeast except for SeO_4^{2-}; this holds for both inorganic and organic As compounds. Corresponding work dates far back to the 1930s: Lardy and Moxon (1939) showed that arsenite prevented inhibition of yeast fermentation caused by selenite. Arsenate and arsenite tended to increase the toxicity of selenate in this system. Moxon and DuBois (1939) administered 5 ppm arsenic and several other elements in the drinking water of rats to study their effect on 11 ppm selenium as Se-wheat. Fluorine, molybdenum, chromium, vanadium, cadmium, zinc, cobalt, nickel and uranium all increased the observed toxicity in the selenium-treated groups.[30] Tungsten gave some protection against liver damage and mortality, but complete prevention of selenium

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[30] The toxicity increases observed with Mo, Cd, Zn or Ni show that Se is not reduced to HSe^- ion and thus cleaved as metal selenide but takes another biochemically active form the activity of which is increased by addition of "hard" heavy metal ions.

toxicity was only obtained with 5.0 ppm As as sodium arsenite. Other studies (Potter et al. 1939) demonstrated that arsenic in the diet would maintain liver glycogen stores in selenized rats at levels similar to the controls and much higher than in animals receiving just selenium. DuBois et al. (1940) showed that administering 5.0 ppm As to rats, from either arsenite or arsenate, was effective in overcoming the effects of 11.0 ppm Se from Se-wheat, but arsenic sulfide was not “effective” (insoluble and not bioavailable). The authors (Moxon and his co-workers) stated (unpublished data) that arsenite was protective against Se from Se-wheat, selenite and selenocystine. This study also showed that arsenic would protect rats that had previously been fed selenium diets for 20 days”. Thus, there are complex interactions. The “identity card” of As is given in Table 3.3.

The ecotoxicological “identity card” for Sn species (Table 3.4) summarizes chemical features of both inorganic and organic speciation forms of tin. Tin undergoes biomethylation only to a limited extent, but stannane SnH_4 is the strongest known reductant to be produced in any non-photochemical biochemical process. There is no verified biological function of tin in any organism.

Table 3.5 represents a so-called ecotoxicological “identity card” for Tl. Based on the ecotoxicological identity cards of As and Sn from Fränzle and Markert (2002a, b) (s. Tables 3.3 and 3.4) this card is meant to give a first-hand description of properties relevant to biological and toxicological features of a certain chemical element and its geobiochemically plausible speciation form. After Markert et al. (2013d) Tl^+ differs from alkali metal ions such as K^+, Rb^+ by having a free electron pair additionally, which was taken up after reduction of Tl^{3+}. Having a free electron pair at the metal ion, complex formation is poor with Tl(I) [mutual repulsion with ligand electron pairs]. Due to that free valence electron pair, Tl^+ ions are shaped rather like an egg than being spherical. The net charge is positive while the negative valence electron pair is located on one end, making the entire atomic ion a dipole, and thus, although complex formation is feeble, much less pronounced than in monovalent coinage metals, will cause havoc when competing with K^+ ions (of similar net diameter) in e.g. nerve membranes: they would slip into these nerve cell membrane channels but turn a little, thereafter blocking passage for K^+ (or, Rb, Ag) ions while slowly accumulating until nerve function breaks down altogether. The typical aspects of thallium toxicity, other than the conspicuous but reversible total body hair loss some 12 days after ingestion, are thus all related to neurotoxicity: first hyperesthesia, then loss of tactile sense, blindness, paralysis, unconsciousness and finally failure of the sine node of the heart, that is, cardiac arrest. Most likely, the first effect of Tl ingestion is also related to K/Tl antagonism in both sensory and motor nerves (of the guts and colon): obstipation, which of course increases the share of Tl absorbed from a poisoned meal, this situation being aggravated by Tl reabsorption from guts via the enterohepatic cycle, which, however can be blocked by Tl absorbers orally given (Prussian Blue).

In central nervous system, there is enhanced production and release of catecholamines after Tl ingestion, probably related to both tremor symptoms and psychical illnesses associated with Tl toxicity, namely, depression but also psychotic episodes. Tl(I) sulfateTl_2SO_4 formerly was used as a rodenticide (not arising any

Table 3.3 Ecotoxicological "identity card" for As species (Fränzle and Markert 2002a, b)

Kind of speciation	Inorganic As (III)	Inorganic As (V)	AsH_3	$RA_sO_3H_2$	R_2AsO (OH)	R_3As	R_3As^+-CH_2X~
Environmental concentration (ocean)	16 nmol	70 pmol			Presumably larger than that of inorganic As ($R = CH_3$)		
Environmental concentration (applies to fresh water)		About 7 nM	Extremely low		Occurs in rain water, rather stable	Low (undergoes rapid oxidation in air)	
Chemical aspects							
Preferences and strengths in complex formation	Low	Arsenate is a ligand possibly competing with phosphate	Only as ligand (precipitation of metal arsenides M_xAs_n with soft metals)	Poor ligands	As ligand	Highly efficient ligands	None
Tendency for ion formation	Low (weak acid)	High (rather strong acid)	No	High (acid)	Yes	No	Is a cation
Lipophilic properties (used to describe membrane toxicity and narcotic action)	None	None	?	Low (behaves as a tenside)	Extremely high	High	Depending on X
Model-theoretical considerations							
SNA: strong cycles possible?	Yes	Probably not	No		(As catalyses auto-catalytic cycles with C transfer in marine organisms)		
Biological considerations							
Essentiality	Yes	If reduced?	No		?	No	Yes
Toxicity	Very high	Yes	Extremely high	No	?	Yes	No
Binding to (as examples)						"Soft" metals	
Reversible biomethylation?	–		–	No	Probably no	Yes	Yes
Maximum extent of biomethylation in					Vertebrates	Fungi	Marine organisms

Table 3.4 Ecotoxicological “identity card” for Sn species (Fränzle and Markert 2002a, b)

Kind of speciation	Inorganic Sn (II)	Inorganic Sn (IV)	RSn^{3+}	R_2Sn^{2+}	$R_3Sn^{+/-}$	R_4Sn
Environmental concentration (ocean)		4 pmol (all tin species combined)	(methylated tin species prevail in estuars)			
Environmental concentration (applies to fresh water)	low (undergoes rapid oxidation)	<1 nM	?	≤ 100 pM	Low	Below 0.5 nM
Chemical aspects						
Strenghts/preferences in complex formation	Low	Medium	Probably bridging among sulfur centers		R_3Sn^+ binds to thiogroups; R_3Sn^- is a versatile soft anionic ligand	Selective affinities (e.g. to fluoride)
Tendency for (cat-)ion formation	High	Low	Very low	Very high	Restricted (ions form only if appropriate leaving groups are present, e.g. chloride or nitrate)	None
Lipophilic properties (used to estimate membrane toxicity and narcotic action)	Low	Absent	Low	?	Extremely high	Very high
Model-theoretical considerations						
SNA: strong cycles possible?	No	Yes				
Biological features						
Essentiality	No	Probable	No	No	No	No
Toxicity	None	None	Probable	High	Very high	Low
Binding to (as examples)		Gastrine?	$(S; Se)_x$ cluster		S species	Unlikely
Reversible biomethylation?	Demethylation of $Sn(CH_3)^4$ to trimethyltin species is observed in mammal liver cells (entailing toxication), but generally photochemical degradation is more probable					
Terminal state of biomethylation in					Fungi	Bacteria

Table 3.5 Ecotoxicological “identity card” for Tl species (Markert et al. 2013d)

Formal oxidation state	+ I	+ I	+ III	+ III	+ III	Negative
Principal speciation form	Tl^{+}_{aq}	Complexes of Tl(I)	Tl^{3+}_{aq}	Complexes of Tl(III)	Organometallic, e.g. $(CH_3)_2Tl^+$	Zintl ions like Tl_4^{4-}
Remarkable chemical features pertinent to biochemistry and toxicology	Non-spherical ion, tends to “lock” in ion channels	usually unstable towards hydrolysis (data in Nriagu 1998)	Strong oxidant, attacking e.g. alkenes, cycloalkenes, styrenes like cinnamic acid and alkynes (oxythallation)	branching in relative stabilities between O donor and other complexes[a]		Do not occur in biomass, hardly stable in aqueous media
Origins, fates			Possibly formed by very strongly oxidizing enzymes or environmental peroxides (H_2O_2; PAN), NO_2, NO_3 radicals; reduction by alkenes, phenols, e.g. humic acids or photolysis		Biomethylation by unidentified marine and sludge organisms, very resistant towards all oxidation, hydro- and photolysis; pathway of cleavage in marine environment must exist but is unknown	direct reduction of Tl or Tl alloys by solvated electrons in solvents like NH_3(l), amines or THF

In environmental compartments	Present, also minerals lorandite $TlAsS_2$, crookesite Cu_7TlSe_4; volatile Tl compounds (TlCl, Tl(OH)) released in cement production	Some are abundant	Not identified, presumably short-lived	Not detected so far	Common in ocean (up to 48 % of total Tl), others like TlR_3 or Tl(I) organics would be far less stable	Absent
In animals	Neurotoxic, tends to accumulate in nerves, causing reversible hair loss, is also resorbed transdermally		Fast reductive cleavage by oxythallation or thiolate reduction would be likely			
In plants	Accumulated by rape leaves, pine trees, certain flowers (up to $> 1\%$!), less so by grapes and cabbage; root absorption is common and occurs readily					
In bacteria			Like with plants, animals			
Other, unidentified or unspecified organisms					See above for oxidative (Challenger-type) methylation of Tl(I)	

[a] Unlike most other transition-group, main-group, REE, or actinoid metal ions, stabilities for chelator—ligand complexes of thallium (both common oxidation states) and Hg(II) cannot be calculated directly from the equation

suspicion by rats because it does neither taste nor smell anyhow but being frequently abused for homicide for these very reasons also; 1 g will kill an average adult human) with the bright green emission of Tl employed to correct the emission spectra of neon or argon gas discharge lamps into a more whitish overall appearance. While there was the distinctive green band in the spectrum of such lamps only 30 years ago, this kind of Tl use meanwhile was outphased also.

Elements which do no good to any living being yet have some bioinorganic chemistry, usually displaying ion-biomass interactions even if only destructive ones. With thallium, Tl(III) is likely to do the same kind of oxythallation transformations of many biogenic organics in vivo which is known and useful in preparative organic chemistry.

Arsenic may be essential for some organisms even though the purported replacement of P by As in DNA could not be corroborated. In both As and Tl, biomethylation apparently acts as a detoxification pathway for both bacteria and metazoans. In Sn, biomethylation is difficult and done by just few organisms. Generally speaking Tl is highly poisonous for animals (while several plants enrich it to remarkable levels without any apparent harm) for its compromising nerve functions—including that of the sine node which controls heartbeat autonomous[31] from other nerve system—by Tl^+ getting into ion channels of nerve membranes instead of K^+, then to "stick" there.

The ID cards are not meant to give a full account of possible functions or effects of an element in its possibly various speciation forms and oxidation states but should point out certain chemical features which may or may not be related to observed modes and kinds of biological/biochemical action.

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[31] This is why hearts can be transplanted at all without microsurgically connecting them to the recipients nervous system: fitting to arteria and venes will do.

Chapter 4
Stoichiometric Network Analysis: Studies on Chemical Coordinative Reactions Within Biological Material

Abstract SNA, introduced in the 1970s by Canadian chemist Bruce Clarke and derived from matrix stability analysis, can be used to identify feedback structures in chemical and other reaction networks which are due to autocatalysis. Autocatalysis in turn is a type of feedback which resembles the chemical processes underlying cell-budding or whole-organism reproduction: first and rather continuously absorb certain kinds of matter from some reservoir and process them in a complicated chemical network to finally obtain more of the compounds constructing this network which in case of living organisms is actively kept together by the outer linings of the organism is both about biological reproduction and autocatalysis in "humble" chemical systems like acid-catalyzed oxidations releasing more protons in protic solvents. As effective feedback relies on certain network topologies and limited presence of competing reactions in either case, SNA can provide certain statements on limiting conditions which must be obeyed to keep chemical entities involved in biochemistry as reproduction takes place on and on and evolution goes on. It can be shown that these criteria essentially limit the number of essential elements while powerful yet rare and selective possible catalysts like PGMs or rhenium are as efficiently excluded from bioinorganic chemistry as abundant elements which could run just few biorelevant transformations (most notable, Al and Ti).

4.1 Definition of SNA and Its Historical Approach

Stoichiometric Network Analysis (SNA) was developed from approaches originally applied in theoretical economics (Clarke 1975). In Clarke's (1988) own words, SNA is

> "... a systematic, general approach to the qualitative, non-linear dynamics of chemical reaction mechanisms and other systems with stoichiometry. The advantage of a qualitative approach is that no rate constants are needed to determine qualitative feature of the dynamics. If one is interested in stability, the approach yields inequalities among the steady-state concentrations and the rate of flow through sequences of important reactions. These parameters are often the ones most easily measured experimentally. By comparing such experiments with the inequalities derived from stoichiometric network analysis, one

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> can often prove that certain mechanisms cannot account for oscillations or other types of observed dynamics…The existence of steady states of zero concentration…applies to chemical evolution."

Matrix-stability analysis from which SNA was constructed was primarily meant to investigate whether self-supportive measures in economy bring about "stable" growth kinetics or oscillations. I.e., both the familiar fairly periodical ups and downs of conjuncture as well as long waves on a $\approx$ 60-a time scale (Kondratieff 1926). While such oscillatory phenomena are quite common in economics, they are considered "exotic" in the realm of chemical kinetics even though

- chemical oscillators can now be made "by design" knowing (kinds and kinetics of) key reactions which produce certain autocatalytic feedback species (either dissolved or heterogeneous, e.g. particulate MnO_2) and
- self-replicating molecules, some of them purely synthetic and capable to assemble from simpler sub-units (Terfort and von Kiedrowski 1992), thereby exhibiting autocatalysis, can likewise be made and their behavior (kinetics) be investigated in the lab.

The focus in these phenomena inevitably rests with **autocatalysis**, and SNA was designed to identify the autocatalytic entities involved (*autocatalysis*: some among the reaction products itself is the catalyst). That means that in most analyzable systems, it is just one—usually H_3O^+, adsorbed CO or formyl HCO or a labile bromine oxide such as BrO, BrO_2—which is linked to one or few feedback modes in one or another way (Eiswirth et al. 1991a, b). Oscillations or bistable behavior can be a feature of such chemical systems. Oscillations actually were observed in certain biochemical systems such as the glycolytic enzyme complex, but not with prebiotic model reaction networks so far. For the matter of chemical and prebiological evolution it is more significant that autocatalysis provides a kinetic advantage over other networks in exploiting and processing limited resources. It only works when causing Darwinian evolution to take place and the corresponding entity/network exhibiting autocatalysis to take over in competition once there is some method to store information on its structure and/or how to make it. This need not be or involve nucleic acids already but anyway depends on autocatalysis and thus any method (like SNA) which is focused on identifying the feature of autocatalysis in a reaction network; it will be useful to identify possible key actors in advanced phases of chemical evolution. An early model—purely theoretical and much before synthetic replicators were even pondered to prepare (in 1971)—was Eigen's hypercycle. In fact, Clarke later went on to analyze the hypercycle and its predicted dynamics in SNA terms, noting (in 1980) that it was a critical cycle capable of outcompeting others but itself fairly liable towards perturbations.[1]

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[1] In SNA theory, one distinguishes among strong cycles (autocatalytic reaction order > combined orders of reactions which remove or inactivate parts of autocatalyst), critical cycles (autocatalytic reaction = combined orders of reactions which remove or inactivate parts of autocatalyst) and weak cycles (autocatalytic reaction < combined orders of reactions which remove or inactivate parts of autocatalyst).

Generally speaking, SNA can be—and already was—applied to understanding reasons of uncommon dynamic phenomena in all

- chemistry (*loc.cit.*, and Clarke 1980),
- economics (Fränzle and Grossmann 1998),
- ecosystems stability (Fränzle 2000),
- description of spread of infectious agents, and even
- nuclear astrophysics (steady states in energy production of stars, Clarke 1980).

But you need not do modeling all the system (which yet was done considering the entirety of enzymes in a bacterium cell [Schilling and Palsson 1998] indeed!) by larger or smaller computers but can make use of certain theorems and rules derived from SNA. F.e., one can predict by qualitative arguments to see whether presence and activity of some autocatalyst in any of the above kinds of systems exhibiting reproduction or non-linear kinetics is here to stay and persist.

In biology, this autocatalytic agent means either

- a certain kind of enzyme, e.g. a class of metalloproteins using a certain ion
- or some taxonomic (rather than chemical) species which will make it through many generations of reproduction or become excluded from either metabolic or trophic networks if some limiting conditions are met

Mathematically speaking, SNA is about matrix stability analysis. Non-linear chemical kinetics are obviously involved in selection of certain chemical pathways over others (cp. Eigen 1971; Eigen and Schuster 1977). The property of SNA to "single out" chemical species involved in causing non-linear kinetics makes it most useful to identify possible key compounds or patterns of chemical pathways even given the limited knowledge on details of then chemical (geochemical, cosmochemical) conditions. Table 4.1 gives an overview of authors who worked on theoretical and experimental achievements related to the field of SNA.

4.1.1 Autocatalysis in Biology

Concerning biology and genetics, and thus autocatalytic/reproducing features of nucleic acids, recall the saying that "an organism is the method of its genes to multiply themselves". This is the principal argument of socio-biology even though you may not like the consequences of this method to analyse evolutionary fitness on

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The latter are called weak as autocatalysis, and accordingly replication cannot be sustained in these conditions; according, neither oscillations nor bistability or selection among competitors would be ("successfully") observable. This may happen in entire ecosystems when too many resources are consumed (e.g. by man interfering [excess fishery, wood logging], washout of nutrients, massive predation in key levels of a trophic pyramid with the resources not being resupplied by excretion when the latter takes place elsewhere [sinking below some halocline, excretion of piscivorous birds or mammals far off a lake or river]).

Table 4.1 Theoretical and experimental achievements related to non-linear (chemical) kinetics, mathematical foundations of SNA and its applications in chronological order

Date (year)	Author(s)	Result, method	Remarks
1886	Landolt	Clock reaction: iodine clock (contains iodate, HSO_3^- and some starter acid)	First observation that (acid-based) autocatalysis brings about non-linear chemistry, with two compounds reacting one after the other rather than competing. Elemental iodine appears and discolors solution after about 1 min. Iodine clock can be made to oscillate by adding another reductant (e.g. $[Fe(CN)_6]^{4-}$) and a proton buffer
1895	Hurwitz	Matrix-based systems stability analysis	Hurwitz method (convex event space analysis) is mathematical backbone of a method later called SNA (Clarke 1975, 1980)
1899	Ostwald	First observation of chemical oscillations in heterogeneous system (corrosion of cobalt metal in acidic chromate solution)	p-type Co oxide layers formed by oxidant etching preclude continuous electron transfer into oxidizing solution while being unstable themselves towards solution attack; hence the system switches between two states both of which are unstable, causing potential oscillation at the Co electrode
1910	Lotka	Theoretical concept for oscillatory behavior of both predator–prey and chemical systems	It is very hard to actually construct a Lotka-like chemical oscillator system: for problems of Lotka kinetics in population dynamics/-ecology (Fränzle 2000)
1916	Morgan	HCOOH decomposition by sulfuric acid will occur by periodically peaking CO release	First homogeneous chemical oscillator actually observed (pulsed evolution of CO gas)
1931	Onsager	There **can be no oscillations** around some chemical equilibrium state (reciprocity relations)	Concentration oscillations are limited to autocatalysts (mainly pH oscillations) and [other] intermediates of a reaction; deliberate addition or removal of such intermediates can induce or stop oscillation in both batch and throughflow systems
1951/ 1959	Belousov	Oxidations of citric, malonic acids (or other CH acids such as acetone, cyanoacetic acid, pentane-2,4-dione) by bromate in mineral acid (pH ≈ 0–1) occurs with periodic changes of both redox potential (shown by color changes of either redox catalyst or redox indicators	Paper became just little known; original redox catalyst systems producing color changes were $Ce^{III/IV}$ or $Mn^{II/III}$, both having similar aqueous acidic potentials of some + 1.5 V versus NHE (1.3 V versus SCE) but can be replaced by almost every one-electron transfer

(continued)

Table 4.1 (continued)

Date (year)	Author(s)	Result, method	Remarks
		such as ferroin) and of intermediate (BrO_2 etc.) concentrations; now called Belousov-Zhabotinsky (shortly BZ-) oscillator type reactions in honor of (also) Anatoli Zhabotinsky who re-discovered Belousov's work in 1970/1971	agent of similar potential, e.g. $[Ru(bipy)_3]^{2+/3+}$ or $[IrCl_6]^{2-/3-}$. Final approach to chemical equilibrium occurs in a linear rather than oscillating manner (see Onsager's reciprocity theorem), final products are multiply brominated acrylic and fumaric acids *NHE*: Normal hydrogen electrode *SCE*: Saturated calomel electrode
1969	Hughes et al.	Chemical wavefronts in acid-autocatalyzed gel systems	First example: 5 M nitric acid/ SCN^- (forms red front of ON-SCN which slowly propagates through an unstirred system). For reaction mechanism, see Jones et al. (1996) Quite similar chemical waves of Ca^{2+} concentrations on cell walls are observed and involved in cell budding
1974	Clarke	Application of matrix stability analysis on non-linear chemical systems; derivation of a number of theorems	Term "SNA" was coined only later
1980	Clarke	General overview	Eigen's hypercycles as a theoretical model of chemical evolution pertinent to RNA world are also discussed, identifying them as a critical cycle. Stoichiometric features of a chemically coupled system of proteins/amino acids and nucleic acids are shown to produce unstable ("slowly exploding") dynamics which was interpreted as to require cell budding
1985	Epstein et al.	Rational design of chemical oscillators starts using SNA and similar methods	Halogenates, $ClO_2^{0/-}$, IO_4^- or MnO_4^- are combined with a pair of "competing" reductants (often sulfur compounds like SH^-, SCN^-, $S_2O_3^{2-}$ **and** CH-acidic organics)
1988	Clarke	First application of SNA to problems of chemical evolution	
1998	Schilling and Palsson	Full-scale quantitative description of a metabolom and its dynamics using the entire set of enzyme kinetics in *Escherichia coli*	Some 2,400 enzyme-run reactions and their kinetics included in model
2000	Fränzle	Proof that ecosystems and biocoenoses chemically connected to their neighbors cannot attain steady-state conditions but are metastable at best	

(continued)

Table 4.1 (continued)

Date (year)	Author(s)	Result, method	Remarks
2008	Fränzle	Derivation of 3**F**unction rule from qualitative SNA arguments	Does apply to every autocatalytic system including hypothetical “exotic”, e.g. extraterrestrial life-forms; for details of argument see elsewhere in this volume or Fränzle (2010)

population levels. Given this, DNA can be considered to behave as an autocatalyst: DNA, via several intermediates, is used to make more DNA, but the same holds for the essential elements required by some organism which then develops, grows, behaves in order to retrieve and make useful more of them. The law of mass conservation demands there must be an external source from which the very autocatalyst or its components can be taken and assembled/processed. Accordingly, there can be no autocatalysis in a closed system unless it is internally heterogeneous—and reproduction and excitation in living systems depend on their being an open system undergoing metabolic matter exchange with their environment also.

What was stated about DNA above, could thus be extended to metals and non-metals to be obtained from food, soil, minerals, aqueous solution or even air (uptake from deposited aerosol) to be used in metalloproteins- and DNA-, RNA-syntheses and -readout, like Zn^{2+} or Mg^{2+}. Each level of systems hierarchy will matter then, but matters can be much more simple: assume some reaction which is executed by an enzyme or some cluster of cooperating enzymes, f. e. like formation of ethanol and CO_2 from glucose or mannose (which are isomers of each other and linked to each other in malt sugar, maltose):

$$C_6H_{12}O_6 \rightarrow 2\ C_2H_5OH + 2\ CO_2 \uparrow$$

By this reaction alcoholic beverages are produced given that the starting mixture contains all N, P, and the trace metals yeast cells need to reproduce, especially Zn, so that the equation may be expanded to give:

$$C_6H_{12}O_6 + N, P, S, Zn,\ Mg,\ \ldots\{\text{yeast cells}\} \ \rightarrow 2\ C_2H_5OH + 2\ CO_2$$

$$\uparrow + \textbf{more yeast}\ \text{cells}$$

where some of the glucose (+ trace metals, N, P, S,…) is turned into yeast cell biomass. Note that

(a) this reaction is autocatalytic in its beginnings but in the end inhibits itself (the yeast cells will die if ethanol content exceeds some 13–15 %)

(b) the autocatalytic nature of this reaction (owing to yeast cell budding) makes sure ethanol will be produced ever the faster until there is no more glucose, mannose, maltose left over, ending up with some really dry wine (or stout beer) except for case a) or killing yeast cells by heating the mixture and

(c) the entire thing could be done in another (non-biological yet still) autocatalytic fashion either if there were some catalyst formed from ethanol molecule precursors (say, a polyester), some co-reactant and possibly a trace metal present in the mixture (say, ruthenium)

Now consider a reaction (like the above) which is exothermic, thus accessible to efficient catalysis while possibly occurring spontaneously without a catalyst also, and occurs in presence of some biological agent (creature). As the biological autocatalytic branch is enhanced with time provided the corresponding organisms can grow and multiply, their share of the entire turnover of some substrate (e.g., Fe^{2+}) will steadily increase with time until the biota does almost all of this transformation. Hence, as soon as some organism "invents" some novel metabolism-related transformation of a hitherto biologically inert substrate—and external conditions are such as to meet basic living preconditions are kept—this resource is going to be rapidly exploited unless for protection by sediment covers. For reasons of clarity of argument we here focus on reactions which turn out to proceed both: run by some organism and by simple inorganic or organic chemistry at reasonable rates.

4.1.2 Rules, Structures and Effects in Ecosystems

The respective set of metabolic processes exerted on a given sub-set of substrates in turn defines one "ecological niche" within some ecosystem by its trophic demands and network structure/position. So there is multi-level autocatalysis by reproduction of organisms, and these are likely to use fairly abundant elements for the respective transformations rather than those which would appear best-suited to the catalytic chemist (for corresponding lists and comparisons, see Ochiai 1968; Fränzle 2010).

Normally, in an ecosystem total biomass of the next-higher trophic level (TL + 1) is about 10–15 % (one-tenth to one-seventh) of that of the given trophic level TL. Only some part of the biomass thus produced is "shuttled" into offspring; another part of the "missing" 85–90 % becomes simply oxidized to obtain metabolic energy just to keep the consumer alive, converting most of available plant or bacterial or phytoplankton biomass back into CO_2 and soluble odd-nitrogen species or N_2, N_2O. By definition there can be only one level of producers whereas consumers might arrange in three or even four more trophic levels. Essential trace metals contained therein are released from food biomass and can be used by the predator/grazer for its own purposes of running metabolism and permitting reproduction. Hence it holds for carbon (C content is about constant among trophic levels):

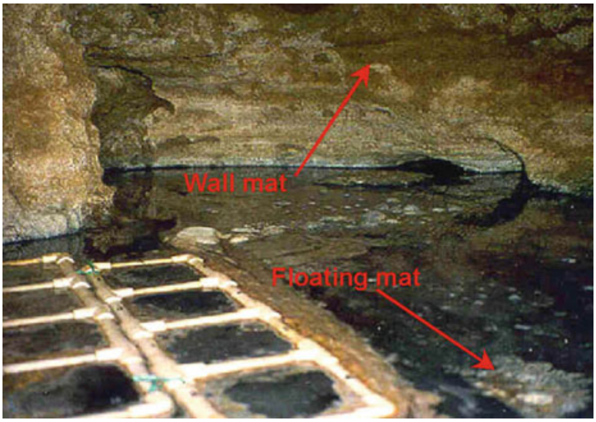

Fig. 4.1 Microbial mats in Movile cave, Romania. A mat is a complex microbial habitat, comprised of fungal hyphae and an assortment of bacteria. The mat is very thin (like wet tissue paper) and is kept afloat due to air bubbles. There are also submerged mats sticking to the ground of this pond which cannot be seen in this picture. The white deposits along the shoreline are mainly elemental sulphur (S_8). Image courtesy of Kumaresan et al. (2014)

$$7\ \mathrm{C}_{\mathrm{org(TL)}} + \mathrm{n\ oxidants}\ \rightarrow 6\ \mathrm{CO}_2 + \mathrm{C}_{\mathrm{biom(TL+1)}},$$

while the fate of n depends on the respective C/N ratios (cp. textbooks of ecological stoichiometry).

SNA exactly states what might happen then, due to the very fact there is autocatalysis in this system, and going to take over dynamics. This means SNA can be used to analyse and predict ecosystems dynamics particularly for rather contrived systems with strange redox biochemistry and/or extant chemosynthesis, like in famous Movile cave (near Mangalia, Dobrogea, SE-Romania, Fig. 4.1). The Warwick University research group concerned with Movile cave describes the situation as follows (Kumaresan et al. 2014):

> Movile Cave is a totally unique environment, situated in the south of Romania… In spite of being totally sealed and being devoid of light, the Cave is a thriving ecosystem filled with all manner of life, from tiny crustacea to isopods, molluscs and arachnids. On the rest of the planet, ecosystems are supported by **primary producers**, such as plants or algae, which convert carbon dioxide from the air into living matter that can be eaten by higher organisms—this process is driven by light and is known as **photosynthesis**. In the dark reaches of Movile Cave, the primary producers are bacteria that convert carbon dioxide into living matter in the form of vast floating "mats" on the surface of the Cave waters. Primary production in the dark is driven by chemical energy obtain by the bacteria from the oxidation of sulfur compounds and ammonia in the Cave waters—a process called **chemosynthesis**…to better understand the roles of chemosynthetic and methanotrophic bacteria in the floating mats of Movile Cave and their interactions with other species at the base of the food web. Limited productivity of some ecosystem commonly causes an increase in biodiversity[2].

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[2] Yet compare Movile cave biodiversity to that seen in some usual soil mesofauna.

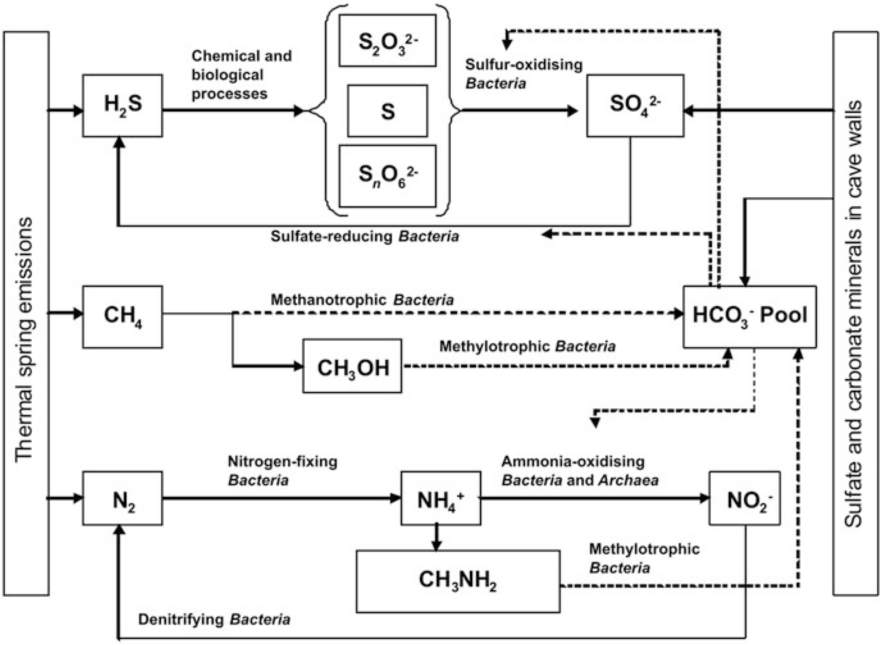

Fig. 4.2 Reaction network within Movile cave. Note the reactions to the *left* involving N_2, CH_4 are really hard to accomplish unless for photo- or radiochemistry so every organism getting capable of doing them will take over dynamics while then secondary steps, and H_2S and thiosulfate oxidations and methylotrophy based on both CH_3OH and methyl amine are much simpler (there, chemical processes are indicated to take place and compete with biology). Accordingly, as the unique arthropod biota of Movile cave necessarily is mainly aerobic, as are many of the bacteria degrading ammonium ions and methanol, and they feed on the microbial mats they must compete with inorganic processes for sustaining themselves while the primary producers are in a better position. Image courtesy of the Murrell Lab, University of East Anglia

As here in- and output and the lines of production (chemosynthesis) and trophic connections are fairly easy to spot, it should be looked upon in some more detail. There is but limited inflow of reactants from different sources: CH_4, NH_4^+, and H_2S from warm springs in the cave, CO_2/HCO_3^- from (probably bioassisted) weathering of its walls while some O_2 must come from outside. Oxygen is required for running S oxidation by "chemical and biological processes" (Fig. 4.2) beyond the pyrrhotite + H_2S/pyrite system, and the diverse arthropods inside the cave for sure are not fully anaerobic.

Normally, matter exchange is less contrived but much harder to understand also with respect to its ramifications to "mode of operation" of single species within an ecosystem. This is why we selected this truly peculiar example. Due to the interaction of autocatalytic (i.e., metabolic for this purpose) and other modes to fulfil some reaction chemistry will dramatically change locally once an access is made for living beings to thrive somewhere; this is about i.a. mining sites where sulphide oxidation first produces sulphuric acid (+ substantial biomass) and the former then etches away and mobilizes large amounts of Al and heavy metals, compromising living conditions especially for fishes and aquatic arthropods, with the latter being even less tolerant towards acidic conditions than many (limnetic) fishes, requiring to maintain pH ≥ 5.

4.2 SNA Analysis of Eco(systems) Stability

To constantly gather the entire set of components required for its replication is the kind of situation life on Earth is concerned up to this day: the amount of C in active biomass is less than that in atmosphere CO_2 now and similar considerations concerning the biosphere from tropopause down to upper sediments hold for all other essential elements except of P and Zn. Hence still today biomass, living matter, can be considered a kind of seed operating within some much larger amount of the elements required to make it yet being in a less-energetic form. This way of reasoning immediately reminds one of that brilliant vision by Vernadsky (about 1930) that "living matter… is going to use and activate all the atoms it can use with time" (Levit 2001) but in the same moment implies life did not get very far with it till now, except for biological cycles of P (especially in limnetic ecosystems, Fig. 4.3) and Zn, to a lesser extent Cu.

Accordingly autocatalysis, and thus reproduction, is effectively limited by some external force. Given the rather poor efficiency of photosynthetic carbon reduction,

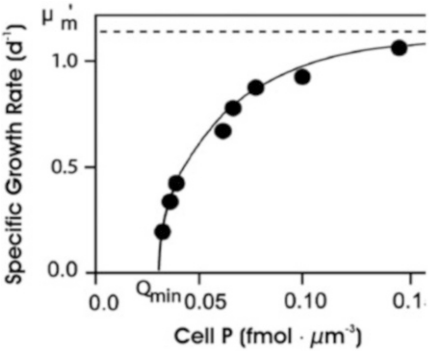

Fig. 4.3 In limnetic plankton algae, total P content is linked to metabolic efficiency in terms of reproduction rates but not in a linear manner but asymptotically approaching some limit value (Rhee 1973). Phytoplankton cells cannot grow and reproduce infinitely fast, the limit given by the efficiency of photosynthesis which also limits photophosphorylation and CO_2 reduction regardless of the total phosphorus content. The limit of growth is about one cell division per day also in optimized technical cultures of *Spirulina platensis* and the like

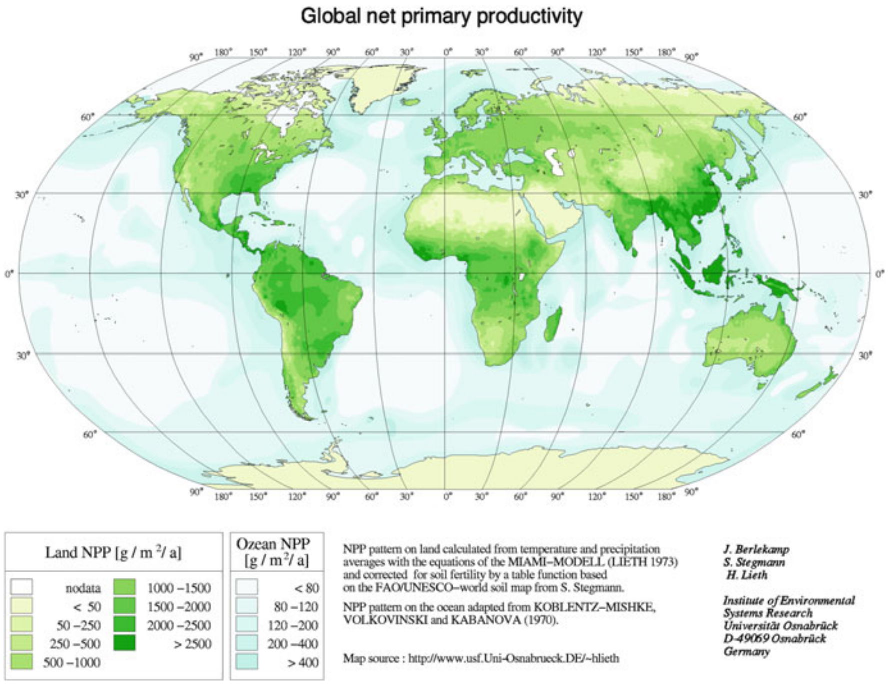

Fig. 4.4 Rio Model 1995 (corrected for effects of soil fertility) for global net primary (photosynthetic) productivities. GIS/Arc Info Map. Image courtesy of Lieth (1995)

the flux of energy may well be what limits this. Lieth's global maps of photosynthetic net productivity (Fig. 4.4) however, suggest this is not quite the full story as the most prolific source of biomass on this planet is the circum-Antarctic sea where photosynthesis is even more inhibited by its mostly taking place under some cover of ice.

Where there is plenty of sunlight, climax ecosystems might have formed since long the net productivity of which is essentially **zero**. And here comes in another statement from SNA (Fränzle 2000): ecosystems, which unlike the organisms they are mentally constructed of, do not reproduce in any manner, can be shown to be **metastable** at most:

By first approximation, a climax system will hardly produce anything material which can be transported out of the system (e.g. dissolved or actively swimming in rivers) without compromising it. "Inside" it, there are many heterotrophs also using certain rarer elements (rare especially in regions like Amazonian hylaea in spite of very efficient and rather fast recycling) like V (fungi) or Co (animals, certain bacteria) while the other (for them) essential elements have very many enzyme functions; hence the entire organism is a set of strong AC cycles as long as there is steady supply of the nutrients and thus is bound to display non-linear behavior, even beyond reproduction (reproduction as such cannot remove excesses of AC functions in a manner as to produce linear kinetics[3] once again). This intrinsic non-linear dynamics will be coupled and communicated to the environment by metabolic interaction of any kind of organism.[4] Moreover, there are mutations and evolution in most of the organisms in such a climax ecosystem which make change their—if not pathways—at least kinetic parameters of some metabolic turnovers. Hence, once climax and efficient intra-biocoenosis-recycling of nutrients reduce "net output" to almost zero, there is no more way to keep the system stable or even only to display stable dynamics. Accordingly, arguments from SNA predict that such climax states are rather-short-lived, metastable at most: in fact, most of Amazonian hylaea recently was discovered to oscillate between the present "zero-net production" rainforest and some much more savanna-like state in a bistable manner, with the latter savanna-state even allowing for long-term agriculture run in such areas.

As for the essential trace elements, one has to consider effects of biochemical weathering of bedrock or other resources on vertical transport and bioavailability and their possible seasonal (outside humid tropics) or other periodical changes. Ongoing humification of soil organics has a similar effect as the polymer will retain metal ions in a form no longer accessible to plant roots while earthworms can degrade (depolymerize and oxidize) humics to re-mobilize ions hitherto "trapped" in them. Accordingly, we (or the collective of living beings on this entire planet or within one ecosystem) would never get lost in a situation of permanent zero-net-production climax but autocatalytic features of the subsystems, in particular of living beings, will serve to keep things changing.

In fact, the above-mentioned collectives (that is, biocoenoses) cannot do so at all or bind all of the available matter—except for P where ecological stoichiometry likewise argues for it being the limiting factor in turnover, and perhaps Zn, Cu—in a

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[3] The terminal approach towards equilibrium occurs in a linear manner even with oscillator systems. Yet "normal" animals and fungi (except for anaerobic metabolism) use assemblies of food and oxidant initially rather far from equilibrium, and, as far as fungi are concerned, catalyst/substrate/oxidant systems may come very close, if not identical to, actual chemical oscillators (namely $Mn^{2+/3+}$/malate or some amino acid or malonate or phenol/H_2O_2 except for a second oxidant added (IO_3^- in [Briggs-Rauscher-kind] oscillators, or MnO_4^- if you prefer Mn-related autocatalysis) and the pH of operation being not that acidic (that is, 3–4 rather than ≈ 1) in wood degradation.

[4] Even symbiotic photoautotroph-heterotroph assemblies like lichens (alga or cyanobacterium/fungus), stony coral polyps (coelenterate animal/alga) or chemoautotroph-heterotroph endosymbiotic systems (clams or worms in black-smoker habitats) do (and, for the latter must [S demand]) continuously exchange matter with the environment restraining from constructing closed-loop cycles for anything falling short of fast growth. Hence a coral reef **depletes** its environs from phyto- and small zooplankton (and Ca^{2+}, Sr^{2+}, HCO_3^- ions, of course) while photosynthesis does provide just a part of organic carbon and way too less dioxygen even to cover demands of the polyps, let alone the fishes, crustaceans and so on inhabiting the reef. Therefore symbiosis will not stabilize it towards external perturbations but multiply the risks (it can stand some predation of polyps by *Chaetodon* and parrot fishes and mechanical destruction by storm waves but declines when the water gets too warm for zooxanthelle survival or too acidic for actively maintaining the carbonate backbones).

manner which would make Vernadsky's assumption (conjecture) a reality within several billion year's time but ensures almost every spot on Earth to be actually inhabited by living beings. Doing it to the extremes of thermal hydrolysis of nucleoside triphosphates and NA backbones (110–120 °C) as well as to the point when pressure alone induces the Maillard reaction in cold ($T \approx 2$ °C) environments (little more than 1 kbar, corresponding to conditions next to bottom of the Mariana Trench). Another example are situations where the array of possible biochemical reactions is essentially limited by catalytic metal ions forming chlorocomplexes rather than promoting biochemistry. Hence it is the thermodynamic control of speciation of most of the theoretically "biophilic" kinds of matter which keeps it from actually being introduced into organisms, meaning that average biological turnover times are very long for most of these elements, and average stoichiometry of biomass is far from biosphere average which means most of the corresponding elements can never come even close to Vernadsky's ideal situation.

As for individual metals in individual species—rather than ecosystems considerations—we "switch on" replication and thus autocatalysis with the organisms "tapping" resources of their autocatalyst precursors in a manner which is fairly typical of certain larger groups (kingdoms, phyla, families), somewhat modified by environment (though it is obviously more straightforward to obtain trace metals from ambient water [like fishes, mollusks, sponges, algae etc. do] than from aerosol deposition [e.g. mosses, lichens] and more reliable in composition than food would be. This expectation holds for limnetic conditions at sufficiently low pH only, not for the ocean): if they do both grow and regularly reproduce, it is taken for granted they could obtain everything they needed.

Nevertheless it must be considered (calculated) which share (percentage) of elements becomes finally bound to the biota from regions which directly interact with photosynthetic organisms (primary producers) and hence are accessible in terms of metabolic exchange and uptake. For the biota (most of which are green plants and phytoplankton, of course) in total this share will range from minute parts to some 25–30 %. Furthermore understanding these figures takes a closer look on relationships of the figures towards the PSE (e.g. comparing different REEs, or Si and Ge, Al and Ga, the PGMs or Zn, Cd, Hg), to matters of essentiality (yes/no/for some organisms only: is there an impact on uptake share?) and pathways of uptake which is the purpose of Table 4.2.

In addition features of resorption pathways should be considered: if several elements which all form tetrahedral oxoanions in common ambient conditions, are resorbed by plant roots by means of the (f.e.) sulfate carrier, relative uptakes (and in effect the part of the element entering biomass) will not agree but depend on

- charge of ion at soil water pH,
- diameter of ion (here, differences among the tetrahedral oxoanions are small), and
- reduction already occurring in microroots (e.g. Cr(VI), Se(VI), Re, PGM [Ru, Os, Ir] oxo-/hydroxoanions).

Table 4.2 An overview of the contents and percentages (shares) of some ambient elements which are bound to biota. Modified according to Markert (1996)

Element	Total content in biomass (g)	Biomass content/m^2 (g)	Ocean water (μg/m^3)	Total content of uppermost 100 m of ocean/m^2 (g)	Soil (average)	Total content of top 3 m of soil (g)	Sum of biomass, top-soil and upper ocean (g/m^2)	Share in biomass (%)
Ag	3.7×10^{11}	7.5×10^{-4}	2.0	2×10^{-4}	0.5	3.3	0.86	0.09
Al	1.47×10^{14}	0.3	30	3×10^{-3}	About 4×10^4	About 3×10^5	About 8×10^4	4×10^{-4}
As	1.84×10^{11}	4×10^{-4}	1,240 [99.6 % As (V)]	0.124	1.5	10	2.7	0.015
Au	1.84×10^9	4×10^{-6}	0.02	2×10^{-6}	10^{-3}	6.6×10^{-3}	1.7×10^{-3}	0.23
B	7.4×10^{13}	0.15	4.6×10^6	460	About 20	About 130	About 380	0.04
Ba	7.4×10^{13}	0.15	15×10^3	1.5	500	3,300	860	0.02
Be	1.84×10^9	4×10^{-6}	0.22	2.2×10^{-5}	6	39.6	10.3	4×10^{-5}
Bi	1.84×10^{10}	4×10^{-5}	0.03	3×10^{-6}	0.25	1.7	0.43	0.01
Br	7.36×10^{12}	0.015	6.9×10^7	6,900	40	264	7,000	2×10^{-4}
C	8.19×10^{17}; other data: 6.1×10^{17}	1,670 or 1,250	2.78×10^7	2,780	480	3,100; plus atmospheric CO_2 and CH_4: some more 1,700	5,800–6,200	Some 25 %
Ca	1.84×10^{16}	40	4.25×10^8	4.25×10^4	1.5×10^4	10^5	5.6×10^4	0.7
Cd	9.2×10^{10}	2×10^{-4}	72	7.2×10^{-3}	1	6.6	1.7	0.012
Ce	9.2×10^{11}	1.9×10^{-3}	0.7	7×10^{-5}	50	330	86	2.2×10^{-3}
Cl	3.7×10^{15}	7.5						
Co	3.7×10^{11}	7.5×10^{-4}	1.2	1.2×10^{-4}	8	52.8	14	5.5×10^{-3}
Cr	2.76×10^{12}	5.6×10^{-3}	218 ([chromate(VI)]	0.022	50	330	86	6.5×10^{-3}
Cs	3.68×10^{11}	7.5×10^{-5}	315	0.032	3	20	5.2	1.5×10^{-3}

Cu	1.84×10^{13}	0.038	150	0.015	20	132	34	0.11
Dy	5.5×10^{10}	1.1×10^{-4}	1.1	1.1×10^{-4}	5	33	8.6	1.3×10^{-3}
Er	3.68×10^{10}	7.5×10^{-5}	1.2	1.2×10^{-4}	1.6	10.5	2.73	2.8×10^{-3}
Eu	1.47×10^{10}	3×10^{-5}	0.18	1.8×10^{-5}	1.2	8	2.1	1.4×10^{-3}
F			1.34×10^{6}	134				
Fe	2.76×10^{14}	0.56	30	3×10^{-3}	About 3×10^{4}	About 2×10^{5}	About 5×10^{4}	10^{-3} similar to REEs
Ga	1.84×10^{11}	4×10^{-3}	1.2	1.2×10^{-4}	28	185	48	8×10^{-3}
Gd	7.36×10^{10}	1.5×10^{-4}	0.9	9×10^{-5}	6	40	10.3	1.5×10^{-3}
Ge	1.84×10^{10}	4×10^{-4}	5.7	5.7×10^{-4}	1	6.6	1.7	0.023
H								
Hf	9.2×10^{10}	1.9×10^{-4}	3.5	3.5×10^{-4}	5	33	8.6	2×10^{-3}
Hg	1.84×10^{11}	3.8×10^{-4}	0.14	1.4×10^{-5}	5×10^{-4}	3.3×10^{-3}	1.25×10^{-3}	30 (highest value in all PSE)
Ho	1.47×10^{10}	3.0×10^{-5}	0.37	3.7×10^{-5}	1	6.6	1.7	1.8×10^{-3}
I	5.5×10^{12}	1.1×10^{-2}	6.0×10^{4}	6.0	3	20	10	0.11
In	1.84×10^{9}	4×10^{-5}	0.01	10^{-6}	0.01	0.07	1.8	2.2×10^{-3}
Ir	1.84×10^{8}	4×10^{-7}	3×10^{-10}	3×10^{-14}	1.5×10^{-6}	10^{-5}	3.0×10^{-6}	13
K	3.50×10^{16}	72	4.11×10^{8}	4.11×10^{4}	14	92.4	3.04×10^{4}	0.24
La	3.68×10^{11}	7.5×10^{-4}	5.8	5.8×10^{-4}	26	172	45	1.7×10^{-3}

(continued)

Table 4.2 (continued)

Element	Total content in biomass (g)	Biomass content/m^2 (g)	Ocean water (μg/m^3)	Total content of uppermost 100 m of ocean/m^2 (g)	Soil (average)	Total content of top 3 m of soil (g)	Sum of biomass, top-soil and upper ocean (g/m^2)	Share in biomass (%)
Li	3.68×10^{11}	7.5×10^{-4}	1.85×10^5	18.5	40	264	82.3	9×10^{-4}
Lu	5.5×10^9	1.1×10^{-5}	0.24	2.4×10^{-5}	0.3	2.0	0.5	2.2×10^{-3}
Mg	3.68×10^{15}	7.5	1.32×10^9	1.32×10^5	1,000	6,600	10^5	7.5×10^{-3}
Mn	3.7×10^{14}	0.75	20	0.002	440	2,900	750	0.10
Mo	9.2×10^{11}	1.9×10^{-3}	10^4	1.03	2	13	4.2	0.045
N	4.60×10^{16}	94	8.72×10^6; of which $NO_3^- = 4.2 \times 10^5$	Total 872, nitrate 42	5	33; air column above 8×10^6	Odd and org. N: 134, allowing for N_2 assimilation: 8×10^6	Value in between 10^{-3} and 70 % depending on assumed efficiency of N_2 assimilation
Na	2.76×10^{14}	0.57	1.11×10^{10}	1.11×10^6	2.3×10^4	1.5×10^5	8.6×10^5	6.5×10^{-4}
Nb	9.2×10^{10}	1.9×10^{-4}	5	5×10^{-4}	24	158	41	4.5×10^{-4}
Nd	3.68×1011	7.5×10^{-4}	3.4	3.4×10^{-4}	20	132	34	2.2×10^{-3}
Ni	2.76×10^{12}	5.7×10^{-3}	490	0.049	50	330	86	0.007
O								
Os	2.8×10^8	6×10^{-7}	2×10^{-3}	2×10^{-7}	$<10^{-6}$	$\ll 10^{-5}$	$<3.4 \times 10^{-6}$	About 20
P	3.68×10^{16}	75	64	6.4×10^{-3}	500	3,300	933	8.0
Pb	1.84×10^{12}	4×10^{-3}	2.8	2.8×10^{-4}	23	152	40	0.010
Pd	1.84×10^9	4×10^{-6}	0.06	6×10^{-6}	<0.03	<0.20	<0.05	≥ 0.01

Pr	9.2×10^{10}	1.9×10^{-4}	0.7	7×10^{-5}	8	53	14	1.4×10^{-3}
Pt	9.2×10^{7}	2×10^{-7}	0.05	5×10^{-6}	0.04	0.26		About 10^{-4}
Rb	9.2×10^{13}	0.19	1.2×10^{5}	12	90	600	165	0.1
Rh	1.84×10^{8}	4×10^{-7}	0.08	8×10^{-6}	$<10^{-6}$	$\ll 10^{-5}$	About 10^{-5}	4
Ru	1.84×10^{8}	4×10^{-7}	5×10^{-3}	5×10^{-7}	3×10^{-6}	2×10^{-5}	6.0×10^{-6}	7
S	5.52×10^{16}	113	9.23×10^{8}	92,300	260	1,700	440	0.12
Sb	1.84×10^{11}	4×10^{-4}	200	0.02	1	6.6	1.7	0.02
Sc	3.68×10^{10}	7.5×10^{-5}	0.72	7.2×10^{-5}	7	46	12	6.3×10^{-4}
Se	3.68×10^{10}	7.5×10^{-5}	100	0.01	5	33	8.6	9×10^{-4}
Si	1.84×10^{15}	3.8	2.9×10^{6}	290	1.5×10^{5}	10^{6}	2.6×10^{5}	1.5×10^{-3}
Sm	7.36×10^{10}	1.5×10^{-4}	0.59	5.9×10^{-5}	5	33	8.6	1.75×10^{-3}
Sn	3.68×10^{11}	7.5×10^{-4}	0.5	5×10^{-5}	1	6.6	1.7	0.044
Sr	9.2×10^{13}	0.019	8.0×10^{6}	800	200	1,320	930	2.1×10^{-3}
Ta	1.84×10^{9}	4×10^{-6}	<2.5	$<2.5 \times 10^{-4}$	1.5×10^{-3}	0.01	2.6×10^{-3}	0.15
Tb	1.47×10^{10}	3.0×10^{-5}	0.18	1.8×10^{-5}	0.7	4.6	1.2	2.5×10^{-5}
Te	9.2×10^{10}	1.9×10^{-4}	0.07 [70 % Te(VI)]	7×10^{-6}	0.05	0.3	0.08	0.02
Th	9.2×10^{9}	1.9×10^{-5}	0.02	2×10^{-6}	11	73	19	10^{-4}
Ti	9.2×10^{12}	0.019	6.7	6.7×10^{-4}	3,300	2.18×10^{4}	5,700	3.3×10^{-4}

(continued)

Table 4.2 (continued)

Element	Total content in biomass (g)	Biomass content/ m^2 (g)	Ocean water (μg/m^3)	Total content of uppermost 100 m of ocean/m^2 (g)	Soil (average)	Total content of top 3 m of soil (g)	Sum of biomass, top-soil and upper ocean (g/m^2)	Share in biomass (%)
Tm	7.36×10^9	1.5×10^{-5}	0.2	2×10^{-5}	0.5	3.3	0.9	1.7×10^{-3}
U	1.84×10^{10}	4×10^{-5}	3.3	3.3×10^{-4}	1.5	10	2.6	1.5×10^{-3}
V	9.2×10^9	1.9×10^{-5}	2,000	0.2	100	660	170	1.1×10^{-5}
W	3.68×10^{11}	7.5×10^{-4}	10	10^{-3}	2.5	16.5	4.3	0.017
Y	3.68×10^{11}	7.5×10^{-4}	17.5	1.75×10^{-3}	23	150	39	1.9×10^{-3}
Yb	3.68×10^{10}	7.5×10^{-5}	1.2	1.2×10^{-4}	2	13	3.4	2.2×10^{-3}
Zn	9.2×10^{13}	0.19	360	0.036	50	330	86	0.22
Zr	1.84×10^{11}	4×10^{-4}	15	1.5×10^{-3}	235	1,550	403	10^{-4}

The data of column two was taken from Table 2.2

This reduction will shift resorption equilibria which otherwise simply depend on anion exchange as carriers are polymeric (protein-based) cations attracting anions like sulfate and the competitors by electrostatic interaction.

Element Inventories in Biomass Versus Ocean Soil Contents
Assumptions:

- photosynthesis in oceans extends down to some 100 m, below of this there is no live phytoplankton while net productivity from other sources (in particular, chemosynthesis near black smokers) is negligible on an average and does not re-transport matter to surficial biomass (although several species of dented whales and seals can dive and hunt below >2,000 m of water, there is no indication that they use resources of black-smoker communities, neither do the calmars the above marine mammals use to hunt down there)
- rhizospheres, and thus phytoremediation works just to three m below soil surface; vertical mixing beyond is very small during life-time of an average organism
- soil density is 2.2 $g/cm^3 = 2{,}200\ kg/m^3$, that of ocean water is 1.03 $g/cm^3 = 1{,}030\ kg/m^3$
- biomass is spread over entire Earth surface except of large ice shields, that is, total relevant surface is $\approx 4.9 \times 10^{14}\ m^2$
- oceans are 74 % of total surface while non-iceshield-covered lands are 26 %

4.2.1 Modeling of Coordination-Chemical Properties with Respect to Chemical Evolution[5]

Chemical properties—including the selectivity and strength in retaining possible substrates as ligands to metal atoms or—cations—are related to catalytic properties (*ligands* = substances that bind to metal ions). Metal ions or related metal compounds (clays, solid carbonates, borates, metal sulfides, ambient mineral photosemiconductors) are involved in producing “prebiotic” compounds from simple precursors. These might be e.g.

- HCHO, with or without a reactive N source,
- formamide (cp. Saladino et al. 2012), or
- Miller/Urey substrates (moist CH_4/NH_3 or CH_4/N_2 or $CO/N_2/H_2$); for unattributed effects of multiple ion additions (Kobayashi and Ponnamperuma 1985),
- HCN; concerning effects of hexacyanoferrate “doping” on HCN formation and –processing (Keefe and Miller 1996), metal-free autocatalysis of HCN oligomerization (Schwartz et al. 1984)

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[5] Fränzle (2010).

with additives (as a rule metal ions) thereby acting as either catalysts or as stoichiometric reagents (e.g. $Fe_xS + H_2S$, ferrous carbonate). Yet, either kind of process is likely to involve complexation of some intermediate(s) to metal ions, and thus be influenced by the extent and mode/selectivity to which this happens (Beck and Ling 1977; Beck et al. 1977). Accordingly there should be some relationship between quantifying descriptions of complexation and the effect/involvement of metal ions into transforming some part of the energized matter into compounds or anions pertinent to our question. Moreover, the tendency of intermediates and products which accumulate with chemical evolution going on to act as a ligand does increase considerably (Fränzle 2010).

Fränzle (2010) developed a method to predict ***complex formation constants*** applicable to seawater conditions also to aqueous-organic media (*complex formation constant* = measure of the reactivity for the particular metal ion-ligand complex: $\mathbf{-log\ k_{diss}}$). One conclusion is, that for metal-forming elements pathways of transport through and strength/stability of binding to biomass are closely connected to their coordination properties. This defines the current endeavour: we are to express these coordination properties in a way (quantitatively) which allows to account for such abundance correlations, biochemical functions and catalytic uses likewise. This requires a method of description which does not just address one "biochemical" ligand or another but encompasses the entire range of materials seen in biological materials and their interconversions.

Corresponding numbers thus must describe properties of some metal ion—be it essential, slightly or highly toxic—with respect to almost all kinds of donors. Some representation which borrows from data directly related to quantum chemistry will be most versatile for understanding reasons of essentiality provided it can link some easily measurable term to complex formation constants in a quantitative way referring to electronic properties of the complex thus formed.

This approach thus relies upon the following matters of fact:

- Complexes of one identical central ion with different ligands use to differ with respect to stability. Stabilities of complexes containing ligands bearing similar or identical functional groups are very much similar, however. Hence, polarity effects e.g. among amino acids almost cancel their complexes producing closely similar complex formation constants in these pairs of complexes for a multitude of metal ions each (e.g. Kiss et al. 1991; Sovago et al. 1993; Irving and Williams 1953; Irving and Rossotti 1956). As a result, binding stabilities just depend on the particular coordinating group, that is, carboxylate or an amino group while hydrophilic or hydrophobic behaviour (e.g. log k_{OW}) of the entire ligand molecule or anion is insignificant. Thus, the same "focussing" on the very binding (ligation) site may apply to very large ligands—that is, to apoproteins or other macromolecules.
- Upon exchange of a ligand by another there will be a change of both binding (hydrolytic) stability and of metal-centered orbital energy levels, causing the conspicuous changes of colour which are so typical for reactions in coordination compounds, classically accounted for by ligand field theory (Figgis and

Hitchman 2000). Such energetic changes of highest occupied or lowest unoccupied orbitals also influence the tendency of complexes to give away or take up electrons which in turn can be measured as a change of redox potentials which occurs due to exchange of some ligand.

Originally appropriate scales—that is, ligand-based electrochemical series describing redox potential changes—were developed in the Brighton-based workgroup of Chatt (starting in 1974, see especially Chatt et al. 1980a, b) and almost simultaneously by others (Sarapu and Fenske 1975; Bursten 1982). In 1990, Lever defined a kind of electrochemical series of ligands which refers to potential changes in the Ru(II/III) couple (solvent: acetonitrile). Accordingly the principal term was called the **ligand electrochemical parameter E_L(L)**. It gives the amount by which the redox potential in the Ru(II/III) couple changes upon some ligand replacement (when a ligand X gets substituted by Y). For multi- or oligodentate ligands this value has to be multiplied by denticity (hapticity) to obtain the change of potential which is actually seen (Lever 1990). The potential-changing effect is additive: replacing one carboxylate moiety by an aminomethyl donor site in a ligand system consisting of two carboxylates close to each other (oxalate, malonate turned into glycinate) produces an effect half as large as with replacing both sites (i.e. replacing oxalato ligands with ethylene diamine). The "absolute" scale also is derived from an assumption/observation (Chatt et al. 1980a; Bursten 1982; Lever 1990; Rocha et al. 2002) of ligand additivity: for the famous redox couple $[\mathrm{Ru(bipy)_3}]^{2+/3+}$ (bipy = 2,2′-bipyridyl), a complex which is used for photochemical water splitting, with six pyridine donor sites the standard potential is +1.56 V, for the respective Ru aquaion it is +0.24 V. Thus $E_L(L) = 1.56/6 = +0.26$ V for (half of) a 2,2′-bipyridyl ligand or other pyridine and $0.24/6 = +0.04$ V for water ($[\mathrm{Ru(H_2O)_6}]^{2+/3+}$ as standard compound).

The intention of the model after Fränzle (2010) is to predict complex stabilities by means of the equation:

$$-\log k_{\mathrm{diss}} = x \times E_L(L) + c \tag{4.1}$$

– log k_{diss}: complex formation constant; ***E_L (L)***: ligand electrochemical parameter; ***c***: intrinsic binding stability; ***x***: ligand sensitivity.

C is an acronym of **c**onstants, alluding to the fact that this part of bonding does not depend on the electrochemical ligand parameter while the sensitivity x does. X thus refers to the identity of the ligand (binding atom, its own chemical environment/ charge (e.g. nitrite, amines, nitriles, pyridines, dinitrogen) and number of links to the metal center.

Data on complex formation constants $-\log k_{\mathrm{diss}}$ were taken from Irving and Williams (1953), Moeller et al. (1965), Izatt et al. (1971), Furia (1972), Kiss et al. (1991), and Mizerski (1997), plus values scattered elsewhere in the literature, while E_L(L) values are derived from Lever (1990). Once c and x are known, it becomes feasible to calculate/predict the behavior of certain metal ions in another ligand environment including biomasses or to calculate an effective ligand electrochemical parameter for biomass by way of the before mentioned equation.

When the concentrations of the metal ions in serum, cell sap or ambient water (aquatic organisms) are known, it can be determined whether some metal ion can become attached to a certain site, e.g. within a protein, at all. The end is to calculate and predict hydrolytic stabilities of complexes in biota or compartments of the biosphere, corresponding to equilibrium between $[ML_{(aq)}]^{o+}$ forming from L and the simple aquaion (aquacomplex) $[M_{(aq)}]^{n+}$ and those two components.

The first ligand exchange denotes the fact that several ligands with hapticities 1–3 can bind to a single metal ion. However, in cases of either low ligand concentrations or low stabilities the M-L-system will remain in this first step mainly; thus, many more complexation constants were determined for the first than for "higher" (subsequent) complexation steps. Both the complex formation constant ($-\log k_{diss}$) and the electrochemical ligand parameter (E_L(L)) do barely depend on substituents on "external" sites, whereas different ligands—differing with respect to E_L(L)—also differ in their complex stabilities: both complex formation constants and redox potentials change upon exchange of some ligand by another, say fluoride by chloride or CO by phosphines, with the reaction supported by the product complexes having larger stabilities. A "colloquial" complex consists of one central ion and one or several ligands. For the most simple case (one central ion, one ligand other than water) the equilibrium constant according to the Eq. (4.1) corresponds to$-\log k_{diss}$. This latter values refers to a relationship between metal ion and ligand whereas E_L(L) describes the ligand alone. Accordingly, the property on this relationship between metal ion and ligand provides information on the other component of the system, that is, the metal ion, when E_L(L) is known. For this purpose combinations (complexes) of one given metal ion with different ligands of identical hapticities (e.g. oxalate, glycinate end ethylene diamine) are investigated, taking the E_L(L) values for the latter ligands. c and x values thus obtained are specific for the metal ion and the given hapticity: e.g., for binding of monodentate ligands to REEs, rather similar c and x values are obtained while in bidentate systems, differences among these ions are quite considerable. Following an approach by Irving and Rossotti (1956), data for ligands of unlike denticities, e.g. F^-, CN^-, glycinate, iminodiacetate, citrate and EDTA, complex stabilities of which ligands correlate linearly with that for another central ion, may be used to determine additional c and x values for other metal ions by multiplying the regression data with c and x for well-studied metal ions. Thus, it is possible to determine c and x for some "exotic" metal ion—e.g. Be^{2+} or Sc^{3+}—even when only one single complex formation constant is given for a certain hapticity.

4.2.2 Application of Modeling: Possible Derivation of Essentiality/Toxicity of Certain Metal Ions

Fränzle et al. (2012) stated already that with every organism, there are elements, including some minimum set of metals (usually, K, Mg, Ca, Mn, Fe, Mo, Fe, Cu, and Zn), required to maintain a number of biological functions, including

- catalysis,
- information processing (not restricted to nerve membranes in animals but also covering e.g. the ethylene receptor controlling plant flowering and fruit growth/ ripening, in which C_2H_4 gets bound to Cu(I)) and
- obtaining information (magnetite in bacteria, migrating birds, sea turtles and others).

In biocatalysis, this function is often related to attracting some substrate and/or a reaction partner of this by complexation and easening a chemical transformation by having it occur right within or next to the ligand coordination sphere. Of course, this kind of reaction critically depends on the “right” stabilities of complexes which combine all the substrates and the peptide/protein backbones which is also attached to the metal ion (and retains it within its polymer structure). Often, among chemically related elements like Be and Mg, Ca or most of rare earth elements/Tb the crucial difference between harmless or even essential and “highly toxic in general” just is that Be and Tb form “too stable” complexes (Fig. 4.5). The central region of Figure 4.5 is called after Fränzle (2010) the “Window of Essentiality” and was created after the description in Sect. 4.2.1. Equation (4.1) is used as a kind of background information to determine or estimate complex stabilities and in turn partition of the element. As c and x, accordingly, are parameters which influence partition and the chance to use some element altogether, it may be anticipated that only some combination(-range)s of x and c can permit efficient autocatalysis and thus biocatalytic essentiality. Therefore, just try to do some mapping of biochemical properties in the c/x plane for the distribution of essential elements. A look on Fig. 4.5 will show that there is some relationship between x and c for divalent ions and another for trivalent ions even though x and c can plausibly be identified with π- and σ-bonding properties of a metal ion, respectively (see the large $E_L(L)$ of strong π-acceptor ligands like CO, ethyne, phosphines or phosphites and the decrease of x from Cu(II) towards Zn(II)). With the present knowledge on the spectra and distributions of essential elements and on other effects of chemical elements such a c/x/ “function” plot may reveal common features of the essential metals with respect to metal ion-protein interactions.

As was already pointed out before, chemical evolution converts poorly coordinating (except for CO, CN^-) gaseous and dissolved species into such which bind more strongly to metals. When comparing different molecules which could be formed from the more colloquial elements encountered in atmosphere and liquidosphere of some terrestrial planet, however, this might be an unwanted or unaware-of (experimental rather than Darwinian!) selection effect: wanting to

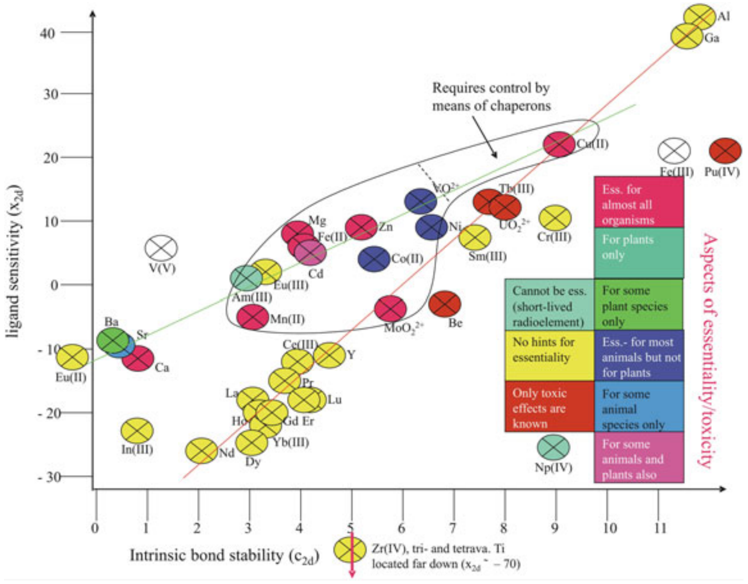

Fig. 4.5 A 'Window of Essentiality' of metal ions as identified by Fränzle (2010). The diagram shows the relationship between essentiality (in biochemical terms) and other physiological features of metal ions versus their ability and selectivity in forming complexes. The exact values of c and x (***c***: intrinsic binding stability; ***x***: ligand sensitivity) correspond to the crossing point of the lines inside the dot while the shadowing of this dot denotes existence and possibly range of essentiality (if there is any). Note the positions of strong poisons Be^{2+}, UO_2^{2+}, Tb^{3+} (which is much more toxic than other REEs), Pu(IV), Ga^{3+}, or Pb^{2+}. In^{3+} is homologous to Al, Ga but located far to the *lower left in the diagram* and not toxic at all. Further and more detailed information of this graph please find in Fränzle (2010)

obtain amino acids and nucleobases which are the monomer backbones of life as we know it we use to deliberately add some N compounds to the mixture. The N-containing compounds then obtained from such mixtures are distinguished by pronounced ligand properties, capable of readily extracting metal ions from underlying sediment or even minerals.

Yet, it is by no means certain that

(a) there were no other, amino-acid-independent chemical systems capable of reproduction and autocatalysis[6] or at least coming close to that stage of development (such as clays) on early Earth or Mars or elsewhere. Such

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[6] Concerning catalytic features of nucleic acids (so-called ribozymes), please distinguish between (rather slow) spontaneous reproduction of RNA (which is usually effected by adding some **protein-based** enzyme) and its catalytic activity which commonly means "cutting out" (resecting) some part of the RNA chain which latter implies that, although the reaction is promoted by RNA, it is not autocatalytic but autodestructive. Self-replicating peptides, on the other hand, cause other enzyme reactions besides of making copies of their own.

systems would compete with amino-acid-based ones for resources once they evolved into autocatalysis, and

(b) although strong ligand properties are useful for mobilizing metal ions into prebiotic polymers by extracting them from minerals and solutions like ocean water, it is wrong to conclude a maximum activity in this respect would provide optimum catalytic properties of protoenzymes formed in this manner (Rothenberg 2008).

On the contrary, there is ample empirical evidence for medium-intensity binding to be best for catalysis, while there are different ways of "modulating" M-L interaction energies, not the worst being steric inhibition.

Such bond-weakening can be caused e.g. by introducing bulky substituents, e.g. tert-butyl- or cyclohexyl- or 2,6-dialkylphenyl groups, into phosphanes, isocyanides etc. which extend M-P- or M-C bond lengths with respect to CO or $P(CH_3)_3$ ligands, allowing for ready dissociation of some ligand to capture the substrate of a catalytic transformation. Bulky alkyl groups in proteinogenic amino acids are likely to act similarly, reducing M-L bond energies besides of providing access for unpolar substrates into some highly polar (α-polyamide, water-containing) polymer. From the "other end" of the M-L bond, that is, from point of view of a metal ion acting in biology/biochemistry or incapable to do so other than as a poison, the "window of essentiality" (Fig. 4.5) was established which is limited to the right, that is, excludes metal ions which form **too** stable complexes.

Now, what happens during chemical evolution? Generally speaking, the affinity of intermediates of chemical evolution towards metal ions will increase with time (Fränzle 2010), but binding selectivity may be changed or introduced as well; it takes a closer look on quantitative (analytical) composition of the organic products most of which are either hydrocarbons or carboxylic acids.

As soon as metal ions spontaneously absorbed from the environment during chemical evolution will cause catalytic activity of whatever kind. A set of different but well-defined chemical reactions must be effected to keep biology, and be it the most humble kind of life-forms, running while the change discussed before suggests there is a set of ions which will do the job best or sufficiently well in the time-dependent state of complexity at the very moment reproduction commences which is about the moment of biogenesis. Empirically, among metal ions, the efficient catalysts of "early-stage" prebiotic reactions and the recent fundamental set of essential elements are very similar which suggests that in-between, around biogenesis, it was similar to either also. This means that living matter—making much use of Mg^{2+} and Zn^{2+} as catalyst ions which are rather uncommon in technical organic catalysis—was not too different then at least in terms of crucial reactions and kinds of chemical bonds from which it is now like.

Let us now look on what was (available) to be processed back then in chemical evolution, eventually to provide reproducing entities which apparently mainly used the same metal-ion biocatalysts which are the common set still today: among the products of simulation experiments, amino acids are rare with respect to both some ill-defined polymeric "goo" or "tar" as well as to hydroxycarboxylic acids, except for glycine[7], alanine, and aspartic acid. The others are trace products usually while nucleobases are even harder to obtain, commonly turning up only in conditions which in turn do not provide or even consume amino acids, except when formamide $HCO\text{-}NH_2$ is used as a starting chemical. To be more specific, look on carboxypeptidases and other kinds of hydrolases. Reconstitution experiments here show likewise (Vallee and Williams 1968) that Mg^{2+} or Zn^{2+}, besides of Co^{2+} or Cd^{2+}, are best-suited for promoting such reactions. Metals which form substantially more stable complexes with the apoprotein, like divalent (each) Cu, Pb, or Hg, form almost got completely inactive metalloproteins, as do the homologues of Mg, Ca or Sr (*ibid.*). The equation by which hydrolytic complexation stabilities can be calculated from the electrochemical ligand parameter $E_L(L)$ and a set of parameters which apply to the metal ion, namely c (intrinsic bond stability) and x (ligand sensitivity) is given in Sect. 4.2.1. Among the divalent ions, c increases according to Eu (II) $<$ Ba $\approx$ Sr $\approx$ Ca $<$ Mn(II) $<$ Mg $<$ Fe $<$ Co $<$ Ni $<$ Cu $>>$ Cd $\approx$ Zn (reproducing the famous Irving-Williams series), and x behaves similarly. We are left with the conclusion that the observed set of "well-behaved" catalysts depends on the substrate to be activated (as could be expected). Hence the above identity of catalysts effective in prebiotic systems and the most versatile ones in contemporary bioinorganic chemistry should simply mean that identical functional groups are activated and produced: in the very moment we try to mimic contemporary biochemistry by "energizing" educt mixtures of respective composition (e.g. containing substantial odd-N- and reduced S compounds), we choose the catalysts now versatile in biochemistry. It should be pointed out that this result is not at all trivial, considering the cases where

(a) activation takes place by other than bidentate complexation, and
(b) there are several catalyst elements in prebiotic chemistry not used by present-time biochemistry (Al, Ti, Zr, In, Pb) only some of which do activate substrates unlike biochemical ones (e.g. aldehydes by Al or Pb)

Thus, on one hand, bulky amino acids[8] loosening the "grip" for metal ions (for comparative data {complex formation constants of $[M(\text{glycinate})]^+$ versus

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[7] Even when starting chemical evolution experiments with CH_4- or C_2H_6-rich mixtures rather than CO_x/H_2, yields of all glycine, glycolic, oxalic and lactic acids (besides of HCOOH) are larger than those of acetic or propionic acids (Dickerson 1978); thus there is a strong trend towards introduction of groups into carboxylate side-chains which commonly increase strength of coordinative binding of metal ions.

[8] Note that commonly in complexes of amino acids, also such ones which carry ligand-active functional groups, it is the terminal carboxylate and the α-amino group which bind the metal ion while in peptides binding by suitable side-chains prevails. Thus, bulky substituents like 2-propyl (valine), 2-butyl (isoleucine) or benzyl (phenylalanine) will have a bigger impact on M-peptide interactions than on the simple M-AA complexes. Although there are cases of linkage isomerism in amino acids such as cysteine (thiolate + amine- vs. carboxylate + amine binding to Co(III)) or arginine, they are rare and unlikely to influence the pathway of chemical evolution. Thus, bulky substituents like 2-propyl (valine), 2-butyl (isoleucine) or benzyl groups (phenylalanine) bound to C_2 of glycine will have a bigger impact on M-peptide interactions than on the simple M-AA complexes.

[M(leucinate)]$^+$, [M(phenylalaninate]$^+$} see Irving and Williams 1953; Sovago et al. 1993) to improve catalysis by complexes formed from them presumably had been hardly available in competition to simple, polar, better-coordinating ones, while, moreover, it cannot be taken for granted there is any co-existence of amino acids and nucleobases at a given spot in either space (chemical setting) or time. Accordingly, it is much more likely that life started with early reproductive entities (if there ever was anything like an “RNA world” at all) of different kinds but each of them was just based on a single kind of polymers (peptides, NAs, possibly clays and yet others). All of these different forms of protolife would compete for resources, and for chances to activate their precursors for condensation by absorbing light energy for now and the next future in times of chemical evolution, only much later perhaps combining to cooperate. The more efficient some autocatalytic system becomes in exploiting some source of chemical energy and matter resources with respect to competitors, the more likely it is to outgrow them or use resources faster than them.

Hence, assuming

(a) such a competition situation of coexisting and co-evolving—probably even then linked by Darwinian selection—different autocatalytic and perhaps informatory chemical entities and clusters thereof, besides of catalytic properties to be given or even a requirement before anything like an RNA world could evolve, and
(b) considering the selection advantage of metal ions displaying rather moderate (not to say mediocre) complexation properties.

We straightforwardly arrive at the conclusion that systems containing monomers which themselves and their polymers activate metal ions are mandatory for biological systems to evolve. The more efficient some autocatalytic system becomes in exploiting some source of chemical energy and matter resources with respect to competitors, the more likely it is to outgrow them or use resources faster than them. However, this is an advantage in terms of natural selection only if there is a steady reliable source of matter and chemical energy which can be tapped by the protobiota in competing with others, arguing e.g. against “black smokers” which cease to produce hot, metal ion- and sulfide-rich waters after several decades at best. Apparently, the system of chemical compounds we consist of proved superior to competitors. The questions for the reasons of this is tantamount to estimating the chances for other kinds of life which omit or replace certain components we make use of while existing in an environment more or less similar to early Earth or Mars. F.e., nitrogen can be activated to produce compounds which facilitate extraction and binding of metal ions which permit these very reductions; the same holds for sulfate, although to a lesser extent.

Chapter 5
Significance of Water (or Some Other Liquidosphere), Soil and Atmosphere for the Chemical Evolution

Abstract In order to get chemical evolution into life, permitting for transport and enrichment of intermediates, and organizing biology into cells which then can compete as to enable Darwinian evolution, a liquidosphere is required besides a steadily retained atmosphere and a solid basis—excluding gas planets and smaller asteroids, moons from consideration as abodes of life—, and there are arguments in favor of water to form this liquidosphere: it is the most likely compound (especially given its abundance in both "near" outer space and cosmological distances) while others are either "too good" solvents (liquid HF, CH_3OH) and/or photochemically unstable. It is the very interaction among all three environmental compartments which does shape and enable life-forms to persist and reproduce while both solid and liquid phases have their indispensable roles in bringing together and processing intermediates which either are formed in the atmosphere or even trickle down from outer space. Maintaining a certain range of surface pressures and temperatures produces upper and lower limits not only for the orbit of a planet or large moon "friendly" to (origin, sustainance of) life but also to its size.

Even though chemical evolution might take place remote from any light after its being absorbed by deep oceans or overlying sediment, then driven by radioactive decay and its radiation-chemical products or geothermal effects—life existing next to a surface requires the biosolvent (water or something else) be kept liquid by sufficient atmospheric pressure.

While by now (f.e.) total atmospheric pressure on Mars does hardly suffice to maintain liquid water unless for salt brines or depressions in terrain,[1] things were apparently different early in its history (then total surface pressure is commonly

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[1] The famous "gullies" on Mars which significantly get active during winter- rather than summer times are not caused by melt-water on crater ridges but sand gets mobile by evaporation of underneath dry ice or CO_2 hydrate, rendering a, possibly salt-glued, layer of sand to behave like a hovercraft in sliding down on some gas cushion. Nevertheless there was liquid water flowing and depositing typical minerals (clays, jarosite) in depressions in earlier times, probably extending over the first billion years of existence of the planet. Now $p_{max} = 13–16$ mbar at deepest spots of Hellas Depression.

B. Markert et al., *Chemical Evolution*, DOI 10.1007/978-3-319-14355-2_5

estimated to be between 40 and 150 mbar). Such a development might cause chemical and protobiological evolution to stall. Besides some liquidosphere might also disappear by global freezing associated with decrease of greenhouse effect by either common way of atmospheric erosion—photolysis which decreases IR retention efficiencies of both reducing (photolysis of NH_3, CH_4) and oxidizing (photolysis of CO_2) atmosphere components with time or else by direct effusion into outer space.[2]

Hence we shall soon see to which extent and manner the three different environmental compartments should interact in order to advance chemical evolution to a "productive" stage and finally sustain life, that is, bringing about reproduction of some entity. This is not to suggest that photosynthesis is mandatory for a sustainable biosphere; chemoautotrophy and "heterotrophic" consumption of products of chemical evolution would also do for a quite a while, although the spatial density of biota then might be smaller (the present average level of biogenic, still or recently living organic carbon is about 1.2 kg/m^2 or 100 M/m^2 of Earth's surface, with net productivity varying by several orders of magnitude). Nevertheless there should be some chemical arguments on mutual transport of intermediates and polymers from chemical properties of either phase, helping to clarify what will work to give a "satisfactory" result or/and favoring formation of membranes or micelles. Making metal ions active in catalysis likewise requires some conditions to be met. Thus let us begin with the three phases only then to inquire into their likely forms and implications of interactions.

5.1 Water

To start with, H_2O is about the most abundant small-molecule volatile compound (this category corresponding to $T_{boil(1\ bar)} > 200$ K) in ISM, way before NH_3, HCN, CH_3OH, $HCONH_2$, HCOOH, CH_3CN or HC_2CN. It thus will form condensates (ice or liquid) readily or prevail in condensed mixtures of the above compounds: Moreover, as water is a very stable compound without low-lying dissociative excitation states, it readily forms from various oxides in presence of H_2 (which is by far the most abundant chemical compound in ISM, protostellar nebulae, gas planets and so on). Once formed, it is stable towards UV radiation down to ≤ 200 nm wavelength, permitting photoprocessing of compounds and ions dissolved or dispersed in it, including reactions of metal complexes (LMCT, mainly via $[Fe(OH)]^{2+}$, and CTTS, e.g. Bahadur et al. (1958), e.g. from iodide or reducing hydroxocomplexes, with the hydrated electron becoming "nascent hydrogen" if

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[2] At sufficient pressures, there is line-broadening of absorptions even with IR-inactive molecules such as N_2, H_2 or noble gas atoms, producing substantial greenhouse effects at $p_{tot} > 5$ bars even though IR absorption is "forbidden" by selection rules. For Mars, there is evidence for massive effusion by enrichment of heavy isotopes ^{13}C, ^{15}N, ^{18}O in both CO_2 and N_2 with respect to both condensed C, N, O compounds in Martian soil and to Earthly isotopic standards.

$pH < 11$, and both H/e^{-}_{aq} and OH capable of interesting reactions with CO_2 and CN^{-}, respectively). Upon cooling of a protostellar cloud after collapse and making the first planetesimals, more water is made by interaction of the two most abundant compounds around, namely hydrogen and CO once and for all regions where $T < 900$ K:

$$CO + 3\,H_2 \leftrightarrow CH_4 + H_2O \text{ (methanation, equilibrium then to the right;}$$

$$\text{it does shift to the left [syngas reaction] in hotter environments)}$$

So we can surely take the existence of lots of water and reaction/mineral weathering products due to its presence and chemical activity for granted, even predating the formation of sizable ($r > 100$ km) planetesimals. Owing to the apparent ubiquity of water and its broad range where it keeps liquid there are clays in many meteorites other than those attributable to asteroid 4 Vesta (Fig. 5.1) or even Mars (SNC objects). Although compounds like HCN, aminoacetonitrile, other nitriles etc. can be prepared in simulation experiments in cryogenic conditions where compounds even more abundant in ISM than water, HCN, NH_3 might condense, namely: CO and N_2, it is not obvious inhowfar liquid CO might take the role of water even though it is **that** polar solvent with by far the lowest melting-point (68 K) and does solvate transition metal ions similarly effective as water, ammonia or HCN do. Likewise the fascinating wealth and abundance of pertinent organics on Titan might "become biochemistry" (if at all) only around the cryovolcanoes which eject ammonia-containing water as a melt. Hence water is the first guess for a solvent

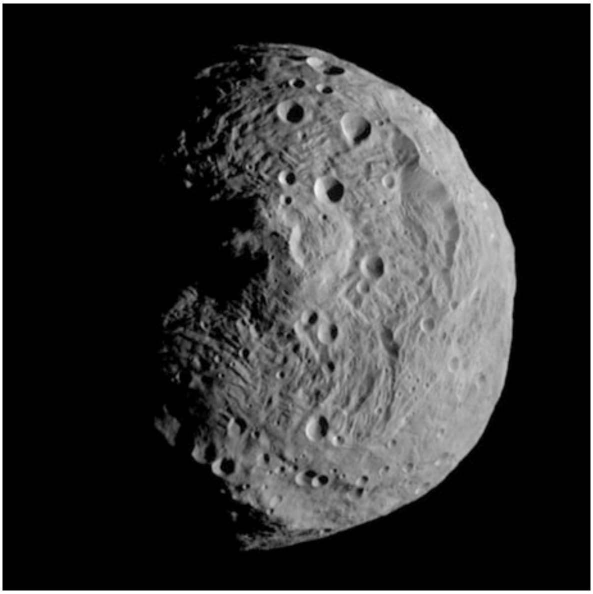

Fig. 5.1 4 Vesta is one of the largest asteorites in the Solar System with a diameter of 525 km. It is a differentiated object with both basalt/iron samples from near core (howardites) and surfacial, "moist" material among known meterorites spectra of which could be cross-checked by Dawn space probe orbiting Vesta in 2011/2012. Image courtesy of NASA/JPL-Caltech/UCLA/MPS/DLR/IDA via Wikipedia

covering parts of a reasonably warm[3] planet and its peculiar properties, some of which are unique among both organic and inorganic solvents, demand closer consideration.

Water is more than just a selective solvent which allows for dissolution of salts while long-chained organics get organized in membranes (vesicles or micelles) enabling separation of reaction compartments which also is compulsory for competition among entities and thus Darwinian evolution; this could not happen in a non-organized homogeneous phase. In addition, all the key compounds, such as amino acids, nucleosides, sugars or organic polyphosphates contain both elements of water. What about chemical evolution in mixtures which provide all the elements (C, H, O, N, S, [P]) but do not contain water, neither as

- vapor nor as
- liquid solvent or
- ice (models of "cryogenic" chemical evolution, which were empirically studied by e.g. Orgel [HCN/H_2O eutectics], Trinks, Biebricher & Trinks), and
- in a more stringently water-avoiding medium, "processing" non-aqueous formamide (Saladino et al. 2012), or
- (directly from gas phase) CO/CO_2 and a N source on acidic clays or
- iron oxides (Hubbard 1979) or
- Fischer-Tropsch reactions on $H_2 + CO + NH_3$ (Hayatsu and Inoue 1971), including HCN formation by simple clay-induced $CO + NH_3$ condensation?

All of these reactions, including the most selective ones, produce water as a primary product, and putting energy to the mixture mostly produces OH radicals which are crucial in processing and activating the other components. Hence, when including hydration water in clays (which in turn cannot form without liquid water being present for some period of time) the question what chemical evolution would be like without water is just pointless. Recent work moreover shows that large basins of water were present on Earth already more than four billion years ago, yet possibly dispersed into outer space by large impacts later. Spark discharges or ionizing radiation on CO or CO_2 can produce aldehydes and (if there is N_2) amino acids or aminonitriles with H_2 (lots of it, more than the stoichiometric amount!) as the original hydrogen source but most of this hydrogen also ends up in water, being a by-product of carbon oxide reductions in these conditions.

Apart from these details of chemistry, evidently large parts of Earth's surface (not just impact craters or other depressions as tectonic troughs would form only later when plate tectonics commenced at about the time when life originated) were covered by water, albeit probably not 70 % of entire Earth like today.

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[3] Some enzymes obtained from quite different, including thermophilic, organisms were shown (Siegel et al. 1984) to remain active in such media or in methanol containing but traces of water yet the minimum temperature for perceptible activity seems to be about 220 K. However, there is no more detectable metabolic activity in Antarctic aqueous salt brines below some 255 K (Don Juan Pond), let alone down to the freezing-points of the above water-similar solvents or even (the lowest-melting close analog of water) 1-propanol (146 K/−127 °C).

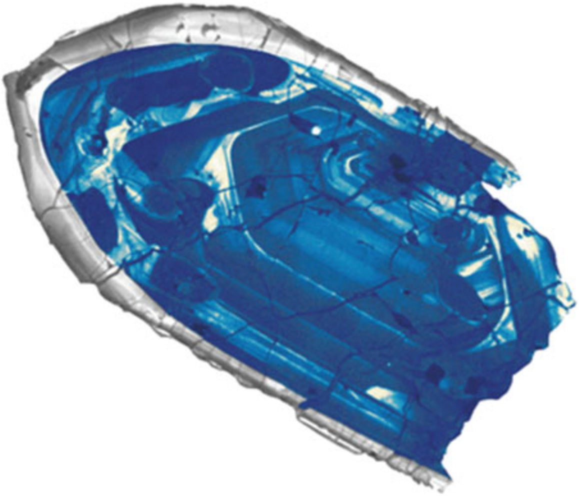

Fig. 5.2 Ancient zircon crystals, discovered in Australia in 2001, have been proved to be our planet's oldest known substance. It is providing new insight into how the Earth cooled from a ball of magma and formed continents. Image courtesy of John Valley, University of Wisconsin, Madison

The chemical problems discussed elsewhere in this volume render it unlikely that large (essentially unlimited) bodies of water were suited for chemical evolution to go on. We are left to conclude that a little less water (of which some substantial part was brought to Earth by impacts of cometary nuclei) was better; actually all terrestrial planets are fairly dry with respect to the average (solar) O/C and O/Si ratios. This does hold for Earth like it does for Mars (whose polar caps consist of CO_2 hydrate rather than pure water ice) or Venus, and of course for Mercury. Evidence for very early liquid water is conserved in zircon crystals (Fig. 5.2, Valley et al. 2014) as well as tiny inclusions in greenstone pores.

Some organic-rich meteorite bodies also bear evidence of chemical and mineralogical alteration by liquid water (molten under some surface crust) on the meteorite parent bodies. These very meteorites being here mean that liquid water was involved in chemical evolution before the samples arrived on Earth. Some organics, especially the simpler PAHs known to exist in both meteorites and the interstellar medium, do react with heated water and ammonium salts to afford amino acids as well as heterocycles. For reasons of its particular UV transmission, and OH radicals being formed by either radiation chemistry or dissolved Fe(III) to activate many organic and inorganic precursors to chemical evolution, water will be both

- a solvent, moreover organizing structures due to a more selective solution than with CH_3OH or NH_3 to name but two otherwise similar solvents, and
- a reagent in chemical evolution.

It is about the only solvent capable of suspending/dissolving combinations of multiply charged cat- and anions in soluble salts (e.g. $MgSO_4$ can be readily dissolved in water but does just dehydrate similar solvents like alcohols, acetone); given the peculiar role of divalent ions in enzymes and the ample presence of sulfate ions on Earth access to such ions for biocatalysis once again is directly related to solvation properties of water.

5.2 Soil

Soil, or rather regolith is a chemically active solid layer which extends several decimeters to many meters in depth. It might act as a heterogeneous catalyst itself (albeit less so than isolated [carved out by erosion] and heated clays or fresh volcanic ash, tephra) as well as a reservoir for elements and compounds which might take part in prebiotic chemistry. While the uppermost layer is exposed to light and UV radiation while adsorbing products from gaseous and liquid (aqueous or other) phases, a redox gradient might form which can process organic intermediates and activate metal ions while trickling downward with moisture. It acts as a solid sorbent which protects intermediates formed at the very surface (e.g. by photoelectrochemistry) from further photolysis and retains organics and some anions in certain layers, influencing and organizing further reactions.

Not too much is known for sure concerning what soils were like on Earth before the advent of life. Arguably the range of minerals and by inference also of mineral micro- and nanograins increased by origins and evolution of life on Earth, concerning both the number of different minerals (Hazen 2009) and the range of stability and sorption conditions. Conversely we would suggest the solid phases which were available to influence or even catalyze chemical evolution would be rather similar to each other and unlikely to undergo strongly exothermic mutual reactions. However (assuming for the moment that there neither is [extant] nor ever was indigenous life on Mars) the arrangement of minerals and amorphous phases detected there (Gale Crater, Mars Science Laboratory (MSL) mission 2013, Fig. 5.3), including Fe(II), sulfide, reduced C and N, and perchlorate, possibly additional oxyhalogen species, is far from being mutually stable.[4] So either Hazen's argument is misleading, or there is life on Mars, or effects of Aeolian mixing and perhaps mineral-based photoelectrochemistry were underrated.

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[4] HCN, several chlorohydrocarbons, O_2, H_2S, COS, traces of CS_2 and first parts of SO_2 start being evolved upon heating a drilled Martian sample (from within "Rocknest" site rocks) within a fairly narrow temperature range (250–450 °C). The amount of water released upon heating (some 2–3 wt-%) is similar to that which severely "compromised" the results of Viking Pyrolytic Release Experiment (likewise indicating fast formation of reduced C compounds more complex than CO, CH_4, possibly being HCN or COS but more likely simple organics like glycolic acid) when added to the test samples (which were more massive than those from Gale Crater) as vapor or "mist".

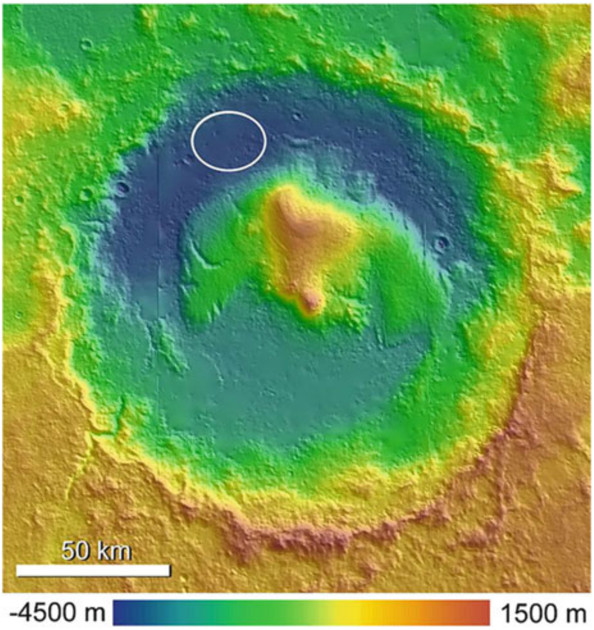

Fig. 5.3 A shaded and colorized topographic map of Gale Crater, Mars. The NASA Mars rover, *Curiosity*, of the Mars Science Laboratory (MSL) mission, landed in "Yellowknife"of Aeolis Palus in Gale at 05:32 UTC August 6, 2012. The MSL landing ellipse is indicated in the northwestern crater floor. Image courtesy of Anderson and Bell (2010)

5.3 Atmosphere

The atmosphere is less strongly involved in long-range transport of charged or nonvolatile compounds than is water, except perhaps for aerosols. Except for thermal decomposition of moist reduced iron minerals, C and N (and S) for chemical evolution are likely to come from the atmosphere, with the simple hydrides CH_4, NH_3, and H_2S being photolabile while sometimes taken to have acted as photochemical sensitizers themselves. In order to get a more reasonable understanding of what the atmosphere might have been like actually in those days, we must use geochemical constraints which (more or less) preserve the then conditions while the composition of the very atmosphere changed massively, partly due to biology itself. The most abundant element in the crust/soil of a terrestrial planet/large moon which is redox-active within the range of conceivable conditions is **iron**, and iron minerals of various kinds can be found on each of the terrestrial objects (little is known concerning Venus while its local [thermal] conditions [at least now] preclude chemical evolution and life altogether). The layer of topsoil/regolith which is in constant gas exchange with the atmosphere is some decimeters to meters thick, meaning that mass of overlying atmosphere will prevail for surface pressures similar to Earth[5] or Titan or above (let alone, Venus);

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[5] What now is the atmosphere of Earth corresponds in pressure to some 10 m of water or about 4 m of sand or pebbled rocks. For Mars, correcting for its weaker gravity it is some 15 cm of salt brine water (keeping liquid at the very surface) or 7 cm of soil; soil starts to change from rusty-red to

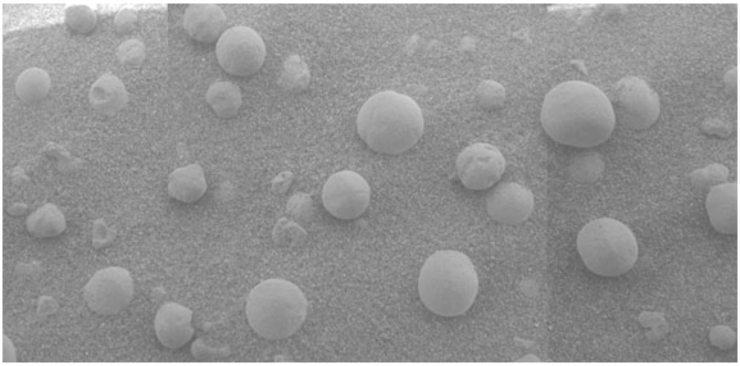

Fig. 5.4 Hematite "blueberries" (hematite perls), several mm in diameter, found at various sites on Mars. Actually, these perls are red to brownish-yellow (rust!; this is a B&W picture) but were called blueberries alluding to their size and the bluish color seen in false-color (!) photographs. For their stability there has to be a certain composition of Martian atmosphere. Blueberries shown in this photograph now lie on silicate sands. Image courtesy of NASA/JPL/Cornell/USGS via wikipedia

accordingly the minerals next to the surface (possibly buried and preserved in fossil phases like sandstones) will rather store and report conditions in the atmosphere than *vice versa*. Scientifically interesting was also the detection on hematite ("blueberries", Fig. 5.4) because terrestrial hematite is typically a mineral formed in aqueous environments or by aqueous alteration. Contemporary Martian conditions (except for T): neutral to slightly acidic soil, about 0.1 % CO (variable with time) in an atmosphere dominated by CO_2 (some 95–96 %). Hematite is stable here and turns up as small "balls" ("blueberries"), which first were spotted in 2004 by rover "Opportunity".

For an "effective" chemical evolution, the atmospheric pressure must be large enough to produce a significant temperature range of liquid state in the liquidosphere (for [pure] water, this range is zero at 611 Pa [triple point pressure], 10° at some 2.5 kPa, 30° at some 7 kPa, 100° [as you probably are aware of] at 101.3 kPa while a little more pressure will keep water liquid much above the temperatures even marginally compatible with hyperthermophilic life); other solvents with very low melting points and triple point pressures such as methanol would be favorable on smaller and colder bodies retaining just a thin atmosphere like Mars or big moons/exomoons do. The liquidosphere then will be involved in weathering solids, including minerals.

The range of atmospheric pressures under which life can evolve and sustain by now can just be estimated; very thick atmospheres like on Venus produce a

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light-grey much above, and permafrost is seen at about this level (7 cm) in the Martian Arctic. Thus even in the terrestrial plants with more thin atmospheres (Earth, Mars) the atmosphere prevails over oxidatively altered topsoil in mass of redox-active species. Oxidative gradients in terrestrial soils now form within the uppermost 1 m, and a few mm in water-logged matter.

greenhouse effect (almost irrespective of their composition) which is too pronounced to permit stability of intermediates on the surface; like in the case of Venus, “common” solvents (excluding salt melts, liquid metals, molten tellurium [the latter was actually invoked to explain radar signal features on Venus!] or the like) will no longer be capable to form liquid pools on the surface.

5.4 Interactions Among Environmental Compartments in the Framework of Chemical Evolution

We simply could not avoid alluding to interactions among environmental compartments (as we would call them for contemporary environmental systems) in the previous subchapters already. While parts of the reactions which afford significant compounds can take place in gas phase, formation of polymers as well as hydrolysis require interaction with liquids. They would reside rather in pools or creeks on the surface than just forming cloud droplets. The key intermediates of amino acid or nucleoside or sugar formations will most readily dissolve in water but only slightly and slowly so in hydrocarbon hazes which would be photochemically formed if there was significant methane beside of CO_2 or CO in the atmosphere which in turn is excluded by Fe redox speciation in oldest surface samples on Earth.

Few metal compounds, e.g. some volatile chlorides or carbonyls (Al, Fe, Ni, semi-metals like As, Sb, Ge) could come in from the gas phase into both going-to-be biopolymers and topsoil, changing pathways of matter transformation. However, their formation would require very high levels of either HCl or CO in the atmosphere, and up to now was not demonstrated in either the atmosphere of Venus or next to active volcanoes on any planet, including the “exotic” chemistry observed in Kamchatka, Kuriles volcanoes (East Russia). The same holds for metal ions (not to mention clays) catalyzing certain reactions: they must be either included in minerals or be dissolved as such or in complexes to become active, invoking solids (lithosphere and its weathering products regolith, “soil”), and as the gas phase is not really a reliable supplier for the elements in discussion (especially Zn, Mg), even when allowing for deposition and dissolution of aerosols, some soil which is going to tend life soon must be in contact and chemical exchange with both an atmos- and a liquidosphere.

On Mars, there is rapid oxidation of locally vented organics or other reduced compounds much beyond the kinetics attributable to OH radicals in gas phase. Accordingly there should be heterogeneous oxidation catalysts in either aerosol or solid surface rock. The latter turn up visibly: Mn oxides are visible on ferrous rock surfaces in Gale crater (Fig. 5.5).

Unless there was some strange process producing phase transfer reagents such as quaternary ammonium- or phosphonium salts (or long-chained carboxylates, amino acids) in a nonpolar medium, this condition of chemical exchange and metal ion/complex mobilization once again calls for some polarity in the liquidosphere.

Fig. 5.5 Mn- and Fe-oxide coatings on rocks in Gale Crater on Mars. Average Mn content surpasses that in Earth's crust. MnO_2 is a potent oxidation catalyst even at low O_2 partial pressures. Photographed with Curiosity's Mastcam. Image courtesy of NASA/JPL-Caltech/MSSS

It favors water (or methanol) as to-be biosolvents over photogenic or FTT-reaction-derived hydrocarbons. The oldest samples from Earth now are taken to be pillow lava which is a reactive substrate still today (Fig. 5.6). The fact that it persisted at least at certain areas near Hudson Bay means the conditions of (most likely still prebiotic) Earth were not so harsh as to destroy all evidence of the events of those early times but rather suggest interactions like those invoked before must have been limited at least in submerged state (pillow lava cannot form on open land). C in Isua samples apparently is carbonate rather than graphite, once more providing arguments in favor of assuming an early atmosphere in which CO_2 prevailed over both CO and CH_4, other hydrocarbons. So

- interaction among the three environmental compartments is crucial for "productive" chemical evolution although uncontrolled, unlimited dilution of intermediates or their first hydrolysis products in water bodies must be avoided, and
- only polar liquids (the geochemically plausible and stable range of which is limited, too[6]) can bring the components together which are necessary for promoting crucial steps in amino acid or sugar synthesis.

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[6] Whereas HF does occur in Venusian atmosphere and volcano vent gases, it is unlikely to prevail over water in forming liquids, its ambient-pressure boiling point being some 19 °C. Many metal ions—by dissolution of silicate or carbonate rocks—and boron would be converted into fluoro complexes which at least are not known to be catalytically active in our context. CH_3OH is sensitive towards oxidation while NH_3 undergoes rapid photolysis, and HCN is liable towards both polymerization and hydrolysis rather than supporting solution for long (notwithstanding the obvious risks associated with using either solvent [liquid HF is about as toxic as liquid HCN] both solvents and similar ones like nitryl- or arsenic halides were investigated in much detail concerning all dissolution of various organics, complex formation, redox reactions, beginning in late nineteenth century already [e.g. Fredenhagen 1902); hence water remains the best guess for

Fig. 5.6 Pillow lava rocks on the slope off Hawaii form when magma oozes from below. Pillow lavas contain characteristic pillow-shaped structures that are attributed to the extrusion of the lava under water, or subaqueous extrusion. Image courtesy of OAR/National Undersea Research Program (NURP)

Thus, except for life-forms the chemical basis of which is beyond our reasonable imagination, we are left with a combination of atmosphere, liquidosphere and soil/ bedrock which is plainly speaking astonishing similar to the ones we deal and do experiments with. This holds the more when doing inquiry into chemical evolution right here on Earth or possibly on Mars.

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prebiotic chemistry although its peculiar chemical properties are somewhat obstructive in terms of chemical kinetics (Hammett 1973; Makosza 2000).

Chapter 6
Present and Future Projects on Chemical Evolution by Means of Space Research

Abstract Having just one example of a celestial body endowed with living beings ready for our studies, studies on biology on different celestial bodies necessarily are **extrapolations** which (must) rely upon our knowledge on chemical evolution, with some of the intermediates like HCN, HC_2CN or amino acids present in meteorites, comets or planetary atmospheres elsewhere. These might suggest how things might go on/had already proceeded into formation of extraterrestrial life-forms given the conditions outlined in the previous chapter, and on chemical knowledge on possible precursors thereof and appropriate energy-sources for advancing chemical evolution (UV and particle radiations, lightning bolts, volcanoes, etc.) being present besides an arrangement of atmosphere, liquidosphere and solid ground at some site. Planets or moons within the Solar System are accessible or will soon be so for direct investigation, including lander probes, to find out whether this advanced chemical evolution did actually happen. For obvious reasons there is an emphasis on results and projects dealing with Mars and certain satellites of Saturn and Jupiter. Outside the Solar system, distances are way too large to cover them within meaningful periods of time; yet spectroscopic investigation of exoplanets will soon reach the point where additional statements become possible. Inside the Solar System, life-forms elsewhere thus should be detectable within the forthcoming decades—if they exist. Philosophically speaking, present investigation of the Solar System is going to change our perspectives of the neighborhood and ourselves quite as much as discoveries of and in other continents did in the late fifteenth to seventeenth centuries.

It is not just a marketing argument advanced by all NASA-, ESA- and Roscosmos officials that we must pursue more outer space research to learn what we came from (and, of course, what it takes to maintain some biosphere) but corresponding research, sending probes especially to Mars, Titan, it's fellow Saturnian satellite Enceladus or Jovian moons Europa, Ganymed actually is pertinent to our question. By the way, addressing other questions formerly advanced by philosophy and religions, e.g. on the origins and key properties of matter, are more expensive to investigate: just **expanding/updating** one TeV-range accelerator system would buy

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quite a number of sophisticated planetary spaceprobes. So let us conclude with a glance on the present plans concerning such spaceprobes, now that (non-)funding decisions covering the times beyond about 2035 have been made by all the above key actors, and on exoplanet research the mere distance of which obviously excludes sending probes there within the foreseeable future and technology. Unlike today, methods and capabilities of automated chemical analysis to be done aboard some robot in outer space or the deep ocean were primitive and unreliable in the 1970s or so. Although the first meaningful automated devices were not specifically designed for this purpose in the 1960s, Viking program gave them substantial impetus. Now out-in-the-field microlaboratories are state of the art, and for many purposes and sites of investigation human operators are just considered one more huge source of contamination and other analytical errors, let alone the precautions and additional expenditures which are to be taken to bring them to the measuring sites and keep, return them alive (from) there! The focus should be (remain forever!) with unmanned missions also for quite a number of ethical reasons.

As should be clear from the lines of argument advanced before in this volume, one can neither understand pathways of chemical evolution, let alone make arguments on their respective likelihoods. Nor it can be estimated how the interaction of some extant biota with surface parts of a planet or large moon would (re-)shape it, possibly obstructing alternative pathways of prebiotic “synthesis” once one among them got it into biogenesis, except for a broad, as broad as possible, comparison with other celestial bodies. Even if these might not harbor local-borne life, and/or their

- local chemistry (e.g., much more reducing) or
- surface temperature (we disregard gas planets and brown dwarfs here for reasons explained before),
- similarities (e.g. presence of all HCN, HC_2CN, $(CN)_2$, CO_2 and benzene, plus NH_3 [the very molecule or its precursors, pyrolysis-GCMS] in haze droplets, on Titan) and
- differences as compared to prebiotic simulation experiments, including those run in cryogenic conditions, too,

can tell whether we forgot something in our models. The most recent and sophisticated model of Titan’s atmosphere chemistry includes 420 different reactions among a total of 83 different molecules and ions; it gives a reasonable account of all of the species hitherto detected in all troposphere, stratosphere and mesosphere of Titan.

On Earth, chemical and biological evolution almost erased (partly by metabolism itself) most of the traces of compounds formed during it; on Mars, the situation concerning chemofossils is not yet clear but there obviously is oxidative cleavage once you try to extract organics by thermal evaporation. For being very small and exposed to interplanetary cosmic radiation for substantial periods of time (which actually can be measured by its producing radionuclides inside the stones), meteorites do not either present unchanged matter as formed e.g. by FTT reactions during condensation of and inside the presolar nebula. We must look elsewhere;

Fig. 6.1 Artist impression of ESA's Rosetta approaching comet 67P/Churyumov-Gerasimenko in August 2014. The spacecraft and comet are not to scale. Image courtesy of Spacecraft: ESA/ATG medialab; Comet image: ESA/Rosetta/NAVCAM

comet nuclei are an option, and this does neither imply landing on them (Rosetta [Fig. 6.1]/Philae mission) nor even drilling deep into them: like with Saturnian satellite Enceladus, comets will deliver telling samples right into outer space, ready for gathering and subsequent analysis either on spot or on Earth, and this was already done by "Stardust" mission launched in 1996.

In comets, dust particles are shrouded by ice, and ejected once this ice does evaporate. This does not occur by simple, evenly spread sublimation from a smooth if not plane surface but rather both dust and gases (vapors) are ejected from deeper pockets far below the reach of interplanetary vacuum and UV, cosmic radiation.

Thus particles sampled right after their leaving a comet which was slowly heated up during approach to Sun—and their organic and inorganic chemical inventories—can be assumed pristine. To get this primeval matter (possible including some particles older than the Solar System embedded by the comet forming) was the objective of Stardust probe which got past Comet P/Wild 2 in 2004. In 2006, some part of the probe brought the samples down to Earth while "Stardust" mission went on until March, 2011. Analysis of retrieved particles is going on. While it was unlikely that the random sample of particles taken up by "Stardust" or similar future sampling missions would contain substantial presolar matter, some was actually identified by both isotopic data and morphology, and before Wild2 became a member of inner Solar system, it should have gathered admixtures of dust (making zodiacal light or located in the Kuiper belt) while moving through the Solar System in an eccentric track/orbit. The main content, however, was included when ices deposited on particles (at least) as old as the solar system, and the organics were preserved by deep freeze and UV shielding ever since. Arguably these are the oldest molecules we can directly put our hands and analytic gear on, and they include several amino acids, ethane diol (glycol antifreeze), glycol aldehyde (required besides inorganic catalysts to make sugars from HCHO, with template/autocatalyst $HOCH_2CHO$ recently also detected in interstellar medium) which must be major constituents. PAHs and some benzenoid hydrocarbons found (benzene, toluene, fluorene, indane) however might form by the grains impacting into carbonaceous matter as analytical artifacts.

The above compounds could be identified from single grains in picomole amounts while the total yield of 1.9 mg matter from Stardust is distributed among almost 2,000 particles trapped by the aerogel shield. This does not translate to an average weight of the particle of 1 μg, however, as there is a broad and non-uniform distribution of grain sizes in the sample. Hence one should not conclude that similar grains—the Brownlee particles surviving from shooting stars[1]—would bring in these and other organics at mM/kg levels to either Earth or Mars.

6.1 Mars Sample Return Mission

As long as Mars was considered to be similar to Earth also with respect to the presence of life, assuming large-scale springtime spreading of vegetation on Mars still in the late 1950s from spectra[2], the idea soon arose to obtain and bring back samples from Mars for more detailed analysis on Earth, including cultivation of possible extant biota in these samples. After automated sample return (although only for a few 100 g and covering a comparatively short distance) from another celestial body (the Moon) had been demonstrated in 1970–1976 (Luna [Lunik] 16, 20, and 24 probes [USSR]), soft landings on Mars were achieved in principle (Mars 3 [USSR], in late 1971) and to more success (Viking landers [USA], 1976) and experiments aiming to investigate the "life issue" or just the origins of organic matter on Mars run by ever more sophisticated robot landers remained inconclusive for decades. The idea of retrieving and returning samples from Mars—first advanced by Mars5M[3] program scheduled to take off in 1979—got pace again. Although postponed by one flight window after the other, it can now be expected that such a return mission will take place early in next decade, that is, the 2020ies. It

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[1] In the turbopause at some 85–90 km height where heavier (N_2, O_2, Ar) and lighter (H_2, H, He, Ne, O atoms) components of Earth's atmosphere start to unmix by gravitation in favor of the latter, which is the very height where most of the mass of shooting stars is evaporated (thus causing the visible emissions and radio reflections), there are enrichments of three typical compounds: CH_4, H_2O and HCN which latter is obviously derived from pyrolysis of N-containing organics in shooting-star particles (CH_4 will not make appreciable HCN in shock waves in an N_2-dominated atmosphere by the meteoroid particles being slowed down from some 25 km/s up there).

[2] Later it turned out that the IR absorptions then attributed to chlorophyll were in fact due to "semi-heavy" water HDO, and even that was located in the terrestrial atmosphere rather than somewhere on Mars!

[3] Although Mars5M was meant to place a rather huge probe on Mars, sampling was to be taken by a wire-control system just some 25 m around the site of landing. The sample return should weigh in just 8.7 kg of which some 500 g were meant to be Martian matter, planned to undergo sterilization in Earth orbit before eventually being returned to Earth. It is not known whether biological tests were to be done before sterilization. The head of the program, Kryuchkov, was finally sacked in 1978 as he could not convince authorities that the multiple automated docking procedures in both Earth and Mars orbits had any reasonable chance to succeed.
Concerning our issue of early or extraterrestrial life to be studied for comparison, avoiding contamination risks is crucial.

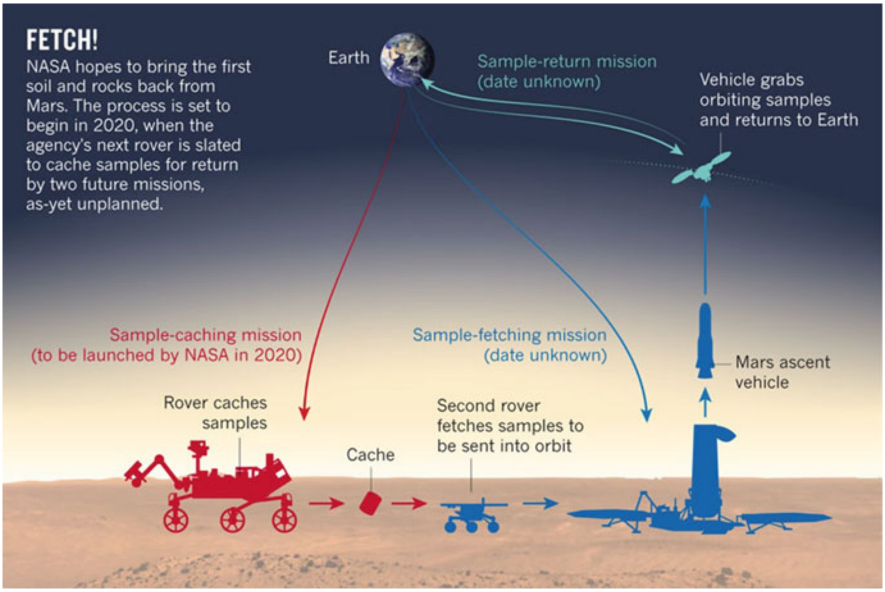

Fig. 6.2 The sample retrieval mission is meant to be organized stepwise involving several missions to Mars and 2–3 independent landing operations fairly close to each other. In the Curiosity landing mission, an adaptive hull shape was first used in a civil space mission; hitherto this technique was applied only in military reentry vehicles (to guide the warheads of ICBMs when approaching their targets) and its actual precision in reaching some point at a planetary surface as depending on density, flow of higher atmosphere(s) was a well-kept secret. While scatter radii of ICBMs are estimated to be a few 100 m judged from "energy yield" of corresponding warheads, Curiosity came down some 2 km west of the center of the landing region ellipse. With this being done just once in the Martian atmosphere, one cannot predict whether this was a typical or rather a lucky result). Samples will be stored for quite a period of time until analysis and/or biological experimentation can take place, much longer than the mere time required to bring them back to Earth. Image courtesy of Witze (2014), Nature

will consist of several probes to be independently launched, with the first rover to do the actual sampling being very similar to Curiosity. The transfer vehicle is much smaller and designed to fast cover substantial distances between sampler gatherer and—return launch vehicle, hence in a more autonomous mode (Fig. 6.2).

As a matter of fact, "date unknown" also means "as yet not included in fiscal funding plans", implying that, whatever happens on Earth, the cache with the samples might end up marooned on Mars for a very long period of time (while Viking experiments indicated changes of activity to occur within days to weeks after sampling), even disregarding the chance that either mission (2) [second rover] or (3) [Mars ascent vehicle] might fail or touch down far from the planned sites. Returning a substantial size and variety of samples (several kgs at least) does take a sizable return vehicle to be placed on Mars, and it should be placed within some 10 km distance of the original lander or the final position of rover 1. Coupling between the return stage and some orbiter in the orbit of another planet also was never done before (in manned systems, it succeeded in lunar orbit during the Apollo missions for return to Earth).

Finally, it is an open question whether the retrieved samples—if there actually is a likelihood of their containing extant, live biota—should be opened, processed and investigated at all right on Earth or elsewhere in orbiting labs or on the Moon, to avoid any risk the samples are contagious to humans or other living beings (which they might if life on either planet is derived from a common origin and mutual exchange by meteorites [which now were spotted to lie on Mars also]). By now, all people agree that samples from either Mars, Jovian moon Europa, or Saturnian satellites Titan or Enceladus should be opened and investigated in S3 labs designed for handling filaviruses like Ebola or biological warfare agents only.

6.2 Europa Drilling Project

While small Saturnian moon Enceladus gives away organics and salts dissolved in molten water right to outer space along geysers the plumes of which can be (and actually were already during the Cassini mission, Fig. 6.3) investigated by mass spectrometry, bigger Europa or Triton (where there also are prolific geysers [Fig. 6.4]) do not blast their (doubtlessly interesting) products right into space: gravity is way stronger, and propagation is limited by an atmosphere, which is very tenuous (several μPa, mainly O_2, CO_2 and SO_2) on Europa, more massive on Triton (several Pa).

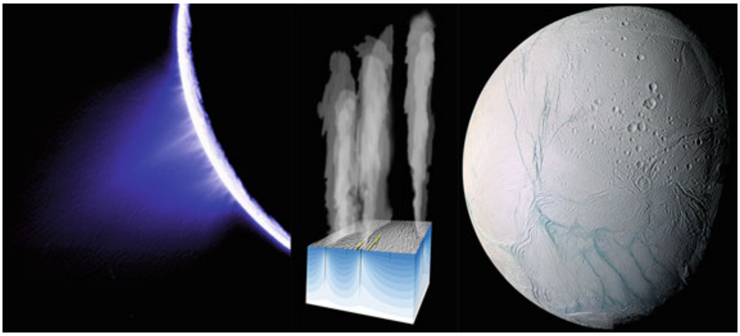

Fig. 6.3 Cassini spacecraft orbiting Saturn from 2004 to 2017 passed this region several times within 30 km of Enceladus's surface, demonstrating the degree of precision with which the probe was tracked and directed including gravitational perturbations over a distance of some 1.5 bio. km (light and radio waves take almost 90 min to cover this distance) without risking a crash. The picture demonstrates geysers ejecting from south polar region of Enceladus. Actually Cassini will be guided to impact into Saturn's atmosphere eventually to avoid contamination of either Enceladus or Titan by terrestrial microbes (the probe was not sterilized to the standards before launch which apply to landers on Mars, for example). Conditions of Enceladus allowing for chemical evolution were not known at 1997 launchtime. Image courtesy of DLR/NASA

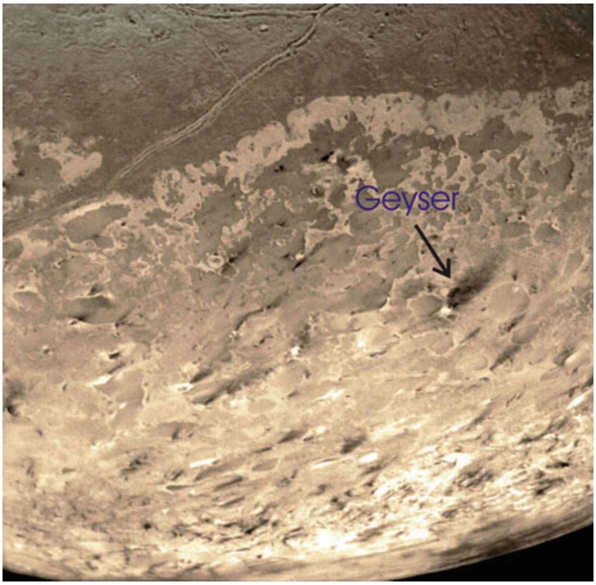

Fig. 6.4 The "geysers" on Triton which eject a dark-colored mixture of presumably liquid nitrogen (which is colorless) and disperse organic compounds up to 8–9 km height which means the primary ejection pressure must be$\geq$70 bars. This is larger than the critical pressure of liquid N_2. Deflection of the dark plumes probably takes place at some inversion layer above the troposphere. Surface pressure of the atmosphere is subject to substantial variation (at least between 1.4 and 6.5 Pa) even though the orbit of Neptune and thus also Triton around is almost circular (distance variation caused by Triton itself orbiting Neptune is $<\pm 0.01$ %). Note that the "geyser region" is the only one as far as Triton was covered by close-up photographs from Voyager 2 spacecraft (back in August, 1989) which shows the typical reddish color of degraded organic matter even though ejected and re-condensing nitrogen would "brush up" the *white* to *bluish color* of ice. Image courtesy of NASA

Although there are areas where the ice cover on Europa is <1 km thick (that is, much less than inland sheets either in Greenland or the Antarctic) ["tiger stripes"] most of the (chemical) action will be beneath the ice shield whatever energy sources might be tapped there besides of tidal heating of this moon which is a little smaller than ours (diameter = 3,067 km). Hence you must try to get into the ocean somehow, by either melting or drilling through the ice cap, to mobilize some submarine (autonomous underwater vehicle) to take photographs, take and analyze samples and so on, with a cable through the borehole permitting to send the data back to Earth directly or via a transmitter (Jovian or Europa) orbiter.

The thermal method of drilling through such an icecap was recently demonstrated in the Antarctic, all the way downward to Lake Vostok (3.8 km of ice). Although Lake Vostok does not seem to be as isolated a body of water as people used to suppose ever since its discovery ("nothing [neither microbes nor nutrients] could come in[-to Lake Vostok's waters] for millions of years[4] after the Antarctic became completely frozen") most data indicate it is completely lifeless now, that life cannot be sustained in such whereabouts even on a planet where it had ample chances to develop and evolve in more benign places. It is unknown whether there are hydrothermal sources of nutrients and energy beneath Lake Vostok now. Given this, with recently air-exposed (and surely microbe-laden) waters being pumped almost all around under the Antarctic ice-shield by the latter moving and sliding, forming a liquid water layer of about 1 m average thickness, one is left with a skeptical impression of chemical evolution going on somewhere on Europa, Enceladus or in similar locations: even for quite a number of very strange ecosystems and biocoenoses in very remote places which were discovered within the last 40 years, there are some limits life can adapt to, let alone where it can evolve. Notwithstanding this, the attempts to sample Lake Vostok without contaminating it provided most of the techniques which would be required in a similar ice penetration/submarine exploration mission on either Europa or Enceladus. Yet, there are no detailed (that is, funded) plans to do either.

6.3 Neptun/Triton Orbiter

Triton appears to be a fascinating lab of organic chemistry besides of having solid/gaseous, probably locally also liquid $N_2 + CO$ in cryogenic conditions and being a very large (2,710 km diameter, bigger than any classical KBO), reasonably accessible representative of the Kuiper belt (note that except for Pluto other KBOs are endowed with most tenuous atmospheres [$p_{tot} < 1$ nbar] at most). Many nitrogen compounds—both ring-strained organics like 2H-diazirine and inorganic radicals like nitrene NH, azidyl radical N_3—are stable to temperatures just slightly higher than they use to be on Triton. Direct experiments on behavior of such samples would not require a lander probe to heat them (bearing the risk of simply being blown up once reactions start under the lander [-vehicle]) but might be caused by either laser beams or some impactor placed from a Triton orbiter, with the fireball then accessible to spectroscopy from orbit, too. There is precedent, practical experience by causing and observing from nearby impacts of artificial objects (impactor weight some 400 kg each) on both our Moon and a comet nucleus (Temple 2).

Unfortunately, plans for a Triton orbiter did not make it on the shortlist for future top-priority (first- and soon-to-be-funded[5]) deep-space missions. The flyby

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[4] Now the turnover time of the entire water body of Lake Vostok—some 700 km (!) long and 800 m deep and up to 70 km wide (comparable to Lake Malawi, SE Africa)—is estimated to be some 10,000 years, rather than millions of years without exchange.

[5] We should be glad that Martian rovers Opportunity and Curiosity are meant to be operated (and funded) simply as long as they keep on moving on the Red Planet; both did work beyond their designed lifetimes already.

missions by New Horizons (Pluto, July 2015) cannot replace the insight possible here concerning cryogenic conditions. Neptune, by the way, is an interesting site as well, concerning its nitrogen chemistry as it might be prototypical of an entire and fairly abundant class of exoplanets which are thus called “cold-Neptunes”, including even smaller ($M_{Neptun} = 17.7$ Earth masses) and somewhat more dense ($\rho > 1.65$ g/cm^3) exoplanets than the model one.

6.4 Titan Sample Return Mission (2040s)

There are many ideas where the action is concerning chemical evolution in conditions grossly differing from those on either early Earth or early Mars, but most people would agree that Titan is among the most interesting spots we might directly (by probes rather than astrospectroscopy) investigate. Up to now, now only a single probe (Cassini-Huygens, Fig. 6.5) touched down on Titan (on January 14, 2005) and kept operating (taking photographs, analyzing volatiles evaporated from soil by the still hot heatshield which kept connected[6] to the lander probe) for about 70 min[7] (that is, less than several lander probes endured on Venus).

Sampling beyond evaporation was not done, nor was drilling, and the lander was not mobile either. Hence the amount of data gathered right on Titan is rather limited, and it is not understood at all where the lots of ammonia came from detected during parachute descent in pyrolysis-GC/MS. An extended mission including sample retrieval and either on-site analysis or returning it to Earth (orbit) would have to cope with the extreme cold (it is a real challenge to keep wheels and sampling arms moving at <100 K over weeks or months (on Mars, problems start already at $T < 190$ K, and the same holds for devices meant to operate in the Antarctic winter). On the other hand, given the density of Titanian atmosphere and the feeble gravity (some 8 % of Earth’s gravitational acceleration) allow to fly using < 2 % the power (that is, >50 times less!) it takes with a similar system on Earth, and this holds for both airplanes and helicopters (gyrocopters might perform well in the cold, either), and boats could ship the hydrocarbon-filled basins. For returning to Earth, an impulse of some 4 km/s (much less than to leave Mars) will suffice to leave both the gravitational attraction of Titan and that of Saturn. Such a sample retrieval mission is planned to take place in the 2040s. The assembly is similar to that planned for Mars: several mobile sample gatherers which

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[6] This did not happen due to some technical failure: rather, the heatshield was completely closed covering the entire lower part of Huygens lander in order to make it float on (then only presumed, till then discovered) liquid hydrocarbon pools/lakes/oceans if it happened to land there rather than on solid ground (actually, it came down, within a river bed just recently flooded by some liquid).

[7] That connection was interrupted by horizon separating Huygens and the Cassini orbiter which acted as a telecommunications relay satellite and moved behind Titan. Broadcasting went on for several hours until lander batteries wore out but the data could not be read from terrestrial radiotelescopes directly (they just caught and tracked the non-coded signal).

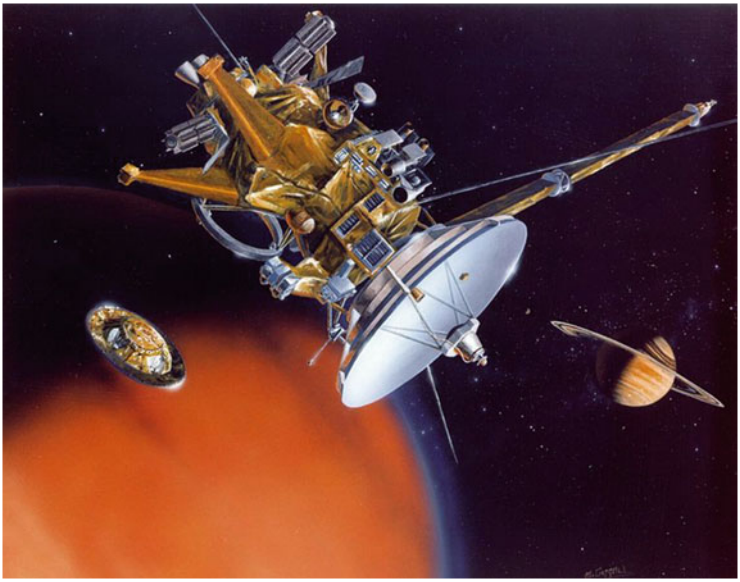

Fig. 6.5 This artist's conception of the Cassini orbiter shows the Huygens probe (*small circle on the left in the left picture*) separating to enter Titan's atmosphere (in the background Saturn, in the foreground Titan). Image courtesy of NASA/JPL/Space Science Institute

deliver their goods to the central back-stage which then takes them to Earth. Unless for electrical propulsion and rebreaking, returning the samples would take at least 7 more years. Sample conservation then is a critical issue, even disregarding the task to handle samples which at least are highly toxic.

6.5 New Horizons Heading for Pluto, Its Moons and Kuiper Belt

The probe "New Horizons", launched in early 2006 when Pluto still was considered a planet rather than dwarf-planet, gives first close-up of "cryogenic chemical evolution" in the inner Kuiper belt: except for lab simulations, the only idea of what happens in extremely cryogenic conditions ($T < 50$ K) on dwarf-planets covered by mixed ices which contain N_2, H_2O, CO, CH_4, C_2H_6 and many ill-defined photolysis- and radiation-chemical products is based on the single Triton flyby done by Voyager 2 in 1989 and a couple of poorly resolved spectra (for these objects are truly dim) of large KBOs like Eris, Haumea and Sedna. Things are going to change now: in July, 2015 NASA probe New Horizons will fly through the Pluto system with its five moons, already now (August 2014) obtaining videoframes of the largest moon, Charon (half the size of Pluto!) orbiting it (or rather the common center of gravity) and spectra of either body. Pluto's atmosphere is known to be about as dense as that of Triton but considerably warmer for unknown reasons (about same distance from Sun now).

It is conceivable that there might be super-Earths or big exomoons with stratospheric or mesospheric temperatures similar to these but an atmosphere thick enough to have ≈ 250–350 K on the surface[8]; then products trickling down from formation regions displaying cryogenic conditions might be subject to "interesting" processes at or near to the surface. Moreover, New Horizons is planned to approach one or two more KBOs after passing Pluto, maybe in 2018 or 2019, obviously increasing our knowledge of possibly prebiotic organic chemistry in such conditions even further.

6.6 Exoplanet Finding Missions

Exoplanets can be (and are, by the hundreds) spotted with several different methods but only near ones transiting their stars are actually accessible to some if rough spectroscopic investigation of the atmosphere, indicating whether there might be clouds, liquid water or some other liquid on the surface. While gas planet models are fairly easy to derive from the data, these are the ones which are least interesting. They even can be misleading: non-equilibrium compositions of atmospheres are taken to indicate life, e.g. O_2 and traces of CH_4 co-existing on Earth and—for parts of the time—on Mars also. Now methane is ubiquitous in gas planets and even brown dwarfs. If they happen to be orbited by large, water-ice covered moons (like there are many in this Solar System), UV photolysis of water will produce an oxygen atmosphere on the moon (there are tenuous ones on Europa, Kallisto and Ganymed, with the latter being much more dense in certain phases). As one cannot resolve exoplanet and exomoon over distances of many light-years (not even by spectroscopy), you might end up with a "false-positive" when looking for alien life-forms in this manner! Exomoons are better suited for maintaining extant life than most of the exoplanets so far detected, and we are on the fringe of actually pinpointing some which probably are larger than any seen in this Solar System (up to some 5,200 km diameter [41 % of Earth's], 0.025 Earth masses for both Ganymed, Titan) and hence better suited for chemical evolution and biogenesis.

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[8] Before the Pioneer 11 mission first to pass Titan in 1979, there were models predicting an even more massive N_2-dominated atmosphere of some 20–30 bar (rather than the actual 1.55 bar) surface pressure on this Saturnian moon which would permit for liquid water at some sites of the surface indeed (N_2 cannot be directly spotted by spectroscopy)! This would have been such a situation right in our backyard.

Appendix

A.1 Essentiality, Occurrence, Toxicity, and Uptake Form of Naturally Occurring Elements in the Environment

This following table (Table A.1) contains information on essentiality of chemical elements as spread over various large taxonomic groups.

Table A.1 Essentiality, occurrence, toxicity, and uptake form of naturally occurring elements in the environment (Markert 1996, modified in 2014).
The uptake of many metals as chelate complexes was not considered here. The data were obtained from Anke et al. (1989a, b), Bowen (1979), Kabata-Pendias and Pendias (1984), Markert (1986), Merian (1991) and Streit (1991); modified in 2014
Bac: essentiality for bacteria, Alg: essentiality for algae, An: essentiality for animal, Fun: Essentiality for fungi, HPl: essentiality for higher plants, +: essential, —: no essential significance so far, +/–: essentiality demonstrated only for some species, ?: essentiality is being discussed, S: average contents in soils (in mg/kg dry wt), P: average contents in plants (in mg/kg dry wt), R: average contents in the reference plant (in mg/kg dry wt), Pl: average toxicity concentration for plants, M: average toxicity concentration for man, Rat: average toxicity concentration for rats, L: lethal dose, F: examples for the function of the element, A: accumulator organism, De: deficiency symptoms if insufficient amounts of the element are available, Sp: peculiarities of the element, ?: no information available if '?' is not used in reference to essentiality of an element, rel: relatively

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Ac	Bac Alg Fun HPl An	**S**:?	Toxic	
	— — — — —	**P**:?		
		R:?		
	A: 15–1,000 Bq/kg in plants grown on thorium-rich soils (Bowen 1979). Assuming radiochemical equilibrium and a Th level of several 100 to 1,000 ppm, this does not imply "actual" bioaccumulation even though plant uptake of Ac is easier and more effective than with Th			

(continued)

B. Markert et al., *Chemical Evolution*, DOI 10.1007/978-3-319-14355-2

Table A.1 (continued)

<table>
<tr><th></th><th>Essentiality</th><th>Occurrence (mg/kg dry wt)</th><th>Toxicity</th><th>Uptake in the form of</th></tr>
<tr><td>Ag</td><td>Bac Alg Fun HPl An</td><td>S: 0.02–0.09</td><td>Toxic</td><td>Ag^+</td></tr>
<tr><td></td><td>— — — — —</td><td>P: 0.06–0.3</td><td>M: 60 mg/day</td><td>$AgCl_2^-$</td></tr>
<tr><td></td><td></td><td>R: 0.2</td><td></td><td></td></tr>
<tr><td></td><td colspan="4">A: Lycoperdales, <i>Eriogonum ovalifolium</i>
Sp: Used medically as an antibacterial ointment for burns (especially for <i>Pseudomonas aeruginosa</i>) and in dental fillings. Interaction with Cu and Se in the metabolism. Concerning grasses and their seeds, the Ag content of (wheat) flour and bran with 300 and 900 µg/kg is somewhat higher than in common soils. Fishes (at 10 µg/g) accomplish considerable enrichment with respect to either fresh- or seawater. Fungi, green algae and lichens can gather up to 200 µg/g with soils having about a thousandth of this value (i.e. BCF up to 1,000). Towards bacteria, however, silver is highly toxic</td></tr>
<tr><td>Al</td><td>Bac Alg Fun HPl An</td><td>S: 71,000</td><td>Toxic*</td><td>Al^{3+}</td></tr>
<tr><td></td><td>— — — — —</td><td>P: 90–530</td><td>Pl: 0.1–30 mg/l</td><td>$Al(OH)_4^-$</td></tr>
<tr><td></td><td></td><td>R: 80</td><td></td><td>$Al(OH)_3$</td></tr>
<tr><td></td><td colspan="4">A: Diapensiaceae, Ericaceae, Melastomaceae, Symplocaceae, Theaceae, <i>Orites excelsa</i>
F: Essentiality discussed for ferns, possibly activation of some dehydrogenases
Sp: *Aluminium is toxic for plants and fish (attachment and chemical attack to gill membranes; toxic effect depends strongly on presence of chelating ligands including ambient and synthetic (EDTA, NTA) amino- and humic acids. Possibly a component factor in novel forest damage since Al is made more readily available by acid deposition. Possible connection with Alzheimer's disease. Al is less rejected (see above) than common by grasses, ferns and tea; although not essential, Al salts are used in tea (<i>Tea sinensis</i>) plantations as fertilizers. Fairly high levels (50−80 µg/g) also in spinach, oats, lettuce, onions and potatoes but still only traces of Al soil content are absorbed</td></tr>
<tr><td>As</td><td>Bac Alg Fun HPl An*</td><td>S: 0.1–20</td><td>Toxic**</td><td>$HAsO_4^{2-}$</td></tr>
<tr><td></td><td>— — — — ?</td><td>P: 0.01–1.5</td><td>Pl: 0.02–7.5 mg/l</td><td>$H_2AsO_4^-$</td></tr>
<tr><td></td><td></td><td>R: 0.1</td><td>M: 5–50 mg/day</td><td></td></tr>
<tr><td></td><td colspan="4">F: Essential for red algae
De: *As deficiency causes a reduction in growth and affects reproduction in vertebrates and leads to cardiac death in the third generation for goats
Sp: **Toxicity increases from As(V) to As(III)
Growth inhibition in chickens and rats deprived of the element, possibly linked to arginine metabolism. High levels (up to > 100 µg/g DW) in marine vertebrates (flat fishes) and lobsters, other crustaceans; there are complete cycles of alkylated (not just methylated, but having longer-chain substituents and including trimethylarsonio- and dimethylarsine oxide groups bound to carboxylic acids, lipids, sugars etc.). There are As organic compounds which suggest co-factor roles in transferring organic groups to other molecules but not like the Wittig reaction of either phosphonium, arsonium ylides</td></tr>
<tr><td>At</td><td colspan="4">The most "stable" isotopes $^{210;211}$At are just sufficiently long-lived ($T_{1/2} \approx 8$ h) to be transferred from soils containing Th, U, Ra, Ac radiological precursors [(grand-)mother nuclides] into plants or into aquatic organisms. Organic and bioorganic chemistry do markedly differ from that of iodine analogs (it was tried to employ astatinated tyrosine locally formed by metabolism from AtO_3^- or similar precursors and laccases in thyroid cancer treatment) even though CH_3At is formed biologically by algae like with CH_3I and their lighter analogs. For environmental abundance, cp. Fr</td></tr>
</table>

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Au	Bac Alg Fun HPl An	**S**: 0.001–0.002	Slightly toxic*	$Au(OH)_3$
	— — — — —	**P**: 0.01–0.04		$AuCl_2$
		R: 0.001		
	A: Possibly Tectona grandi **Sp**: Au is administered in organic compounds as a medicinal treatment for arthritis. *Au(III) is more toxic than Au(I) Au bioaccumulation is accomplished by mustard plant *Brassica juncea*, further augmented by irrigation with thiocyanate solutions (probably via $[Au(SCN)_2]^-$), douglas fir and honeysuckle, by several orders of magnitude. Biomining of gold was demonstrated. Au^+ does attack disulfide bridges (oxidative addition), like Hg salts do			
B	Bac Alg Fun HPl An	**S**: 5–80	**Pl**: 1–5 mg/l	$B(OH)_3$
	? + — + —	**P**: 30–75	**M**: 4 g/day	$B(OH)_4^-$
		R: 40		
	A: Cruciferaceae and Leguminosae **F**: B is of significance for cell division, possibly also involved in glycometabolism and sugar transport, flavonoid and nucleic acid synthesis, and cell wall contraction; stimulates N_2 fixation by bacteria **De**: Deficiency symptoms are known worldwide (disturbance in growth, restricted root branching, phloem necrosis, fructification disturbances) **Sp**: Borates serve for water softening in detergents which involves dangers for groundwater and irrigation water Boron does not appear to be some central ion of enzyms like with metalloproteins but is required by vascular plants, algae, and some flagellates nevertheless. Essential role in animals is evident but even less understood in biochemical terms. However, B controls activities of oxidoreductases, probably by interacting with their pyridine- or flavin (-nucleotide) cofactors. Moreover, boron stabilizes certain sugars by borate H bond linking, thus increasing selectivity of Butlerov's formose reaction towards ribose formation (on expense of most stable hexose sugars glucose, fructose, and mannose). Boron accumulation in tumors followed by indirect neutron-induced radiotherapy via ^{10}B $(n, \alpha) \rightarrow {}^{7}Li$ is insignificant for physiological conditions as the active boron (cluster) compounds of general type $[B_{12}H_{12-x}Y_x]^{2-}$($x = R$, Hal (F, Cl or Br), CN, NO, NO_2, COO^-; icosahedral structure) do not naturally occur nor can be produced by living organisms, neither are emitted during technical processing of B or other elements			
Ba	Bac Alg Fun HPl An	**S**: 500	Rel. harmless	Ba^{2+}
	— +/− — — —	**P**: 10–100	**Pl**: 500 mg/l	
		R: 40	**M**: 200 mg/l	
	A: *Berthollettia excelsa*, plankton: *Chaetoceros curvisetus* and *Rhizosolenia calcaravis* **Sp:** A possible essentiality was discussed for mammals Ba is essential for desmid algae; growth rate of desmids was shown to be inversely proportional to environmental (living in acidic bog ponds) Ba levels but exact role of Ba^{2+} or proteins containing it is unknown. Brazil nuts may contain about 1 % Ba; it is a puzzle then why they are not highly toxic (the speciation form of Ba being not $BaSO_4$)			

(continued)

Table A.1 (continued)

<table>
<tr><th></th><th>Essentiality</th><th>Occurrence (mg/kg dry wt)</th><th>Toxicity</th><th>Uptake in the form of</th></tr>
<tr><td rowspan="4">Be</td><td>Bac Alg Fun HPl An</td><td>S: 0.1–5</td><td>Toxic*</td><td>$BeOH^+$</td></tr>
<tr><td>— — — — —</td><td>P: 0.001–0.4</td><td>Pl: 0.5 mg/l</td><td></td></tr>
<tr><td></td><td>R: 0.001</td><td></td><td></td></tr>
<tr><td colspan="4">A: <i>Vacciniium myrtillus</i> and <i>Vicia sylvatica</i>
Sp: *Both Be metal and Be compounds are considered to be allergenic. The carcinogenicity of Be has been demonstrated for several animal species
Be is concentrated by legumes; presence of substantial Be in hard coal possibly be related to former accumulation by plants coals originated from (large ferns). Inhalation of Be- or BeO-containing dusts causes serious lung damage</td></tr>
<tr><td rowspan="4">Bi</td><td>Bac Alg Fun HPl An</td><td>S: 0.2</td><td>Hardly toxic</td><td>BiO^+</td></tr>
<tr><td>— — — — —</td><td>P: 60 ppb</td><td>Pl: 27 mg/l</td><td>$Bi(OH)_2{}^+$</td></tr>
<tr><td></td><td>R: 0.01</td><td>Rat:160 mg/day l</td><td></td></tr>
<tr><td colspan="4">No evidence of any bioaccumulation of bismuth exists in plants (all reported levels in plants are at least one power of ten smaller than average soil concentrations) or animals but gets readily biomethylated to yield $Bi(CH_3)_3$ and reportedly even the extremely unstable hydride BiH_3 regardless of weakness of both Bi–C- and Bi–H covalent bonds. Whereas Bi is about the most benign “heavy metal” in its common inorganic speciation forms due to pronounced metallothioneine induction, biomethylation (also occurring in human liver cells) renders it neurotoxic</td></tr>
<tr><td rowspan="4">Br</td><td>Bac Alg Fun HPl An</td><td>S: 1–10</td><td>P: 15–600 mg/l</td><td>Br^-</td></tr>
<tr><td>— — — — ?</td><td>M: 15</td><td>M: 3 g/day</td><td>BrO^-</td></tr>
<tr><td></td><td>R: 4</td><td></td><td>HBrO</td></tr>
<tr><td colspan="4">A: Some red and brown algae, some Porifera, many corals, a few molluscs (Aplysia and Muricidae), fungus <i>Amanita</i>, spp.
F: Essentiality for mammals under discussion
Sp: Sources of bromide emissions are antiknock agents, fumigants for preservation purposes, insecticides, and flame-proofing agents
Substantial enrichment in aquatic plants. Br organics (CH_3Br and more complex ones) are formed and released by a couple of marine organisms. Some marine sponges produce brominated phenols and even dioxins. Ionic (salt) bromides were formerly used as tranquilizers, reducing both mental activity and sexual desire</td></tr>
<tr><td rowspan="4">C</td><td>Bac Alg Fun HPl An</td><td>S: variable*</td><td rowspan="3">Many toxic compounds in the form of CO_2**</td><td>CO_2</td></tr>
<tr><td>+ + + + +</td><td>P: 45 %</td><td>$HCO_3{}^-$</td></tr>
<tr><td></td><td>R: 44.5 %</td><td></td></tr>
<tr><td colspan="4">F: Basic structural element of all organic compounds (sugar, fats, proteins etc.)
Sp: *Very variable, depending on soil type and soil horizon. ** CO_2 and CH_4 large share of cause the greenhouse effect, the average CO_2 content of the atmosphere is 400 ppm now (2014)
Biological levels (e.g., some 45 % DW of plant leaf tissues) are much higher than concentrations of either CO_2 in atmosphere or of dissolved (hydrogen-) carbonates, so photosynthesis can be considered as a process effecting bioconcentration of carbon, too</td></tr>
</table>

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Ca	Bac Alg Fun HPl An	**S**: 0.1–1.2 %	Hardly toxic	Ca^{2+}
	+ + — + +	**P**: 1 %		$CaOH^+$
		R: 1 %		
	A: Some algae, shells of many invertebrates, bone **F**: Structural constituent of cell walls, constituent of bone, physiological regulation function, enzyme activator, electrochemical function **De**: Deficiency in plants causes disturbed division growth small cells, drying of leaf tips, leaf deformation, restricted root growth			
Cd	Bac Alg Fun HPl An*	**S**: 0.01–3	Toxic**	Cd^{2+}
	— (+?) — — ?	**P**: 0.03–0.5	**Pl**: 0.2–9 mg/l	$CdOH^+$
		R: 0.05	**M**: 3–330 mg/day	
	A: *Agaricus* and other fungi, molluscs *Ostrea* spp. **Sp**: *Goats fed dry feed with 15 µg of Cd/kg and rats fed on a low Cd diet grew more slowly than control animals with 300 µg of Cd/kg feed. The goats with a low Cd diet had difficulty in conceiving Itai-Itai disease (Japan): the Cd content of river water from a silver mine used to irrigate rice paddies led to increased Cd content in the rice and thus to skeleton deformation and spontaneous bone fractures in man. Released from metallurgical plants, towns, refuse incineration plants, cigarette smoke, mineral fertilizers and sewage sludge. Cd distribution of radionuclide ^{109}Cd in sunflower seedlings was depicted by autoradiography; mainly Cd^{2+} keeps to vasculae. An alternative carboanhydrase (larger than the Zn-based counterpart at 43 kD [Strasdeit 2001]) was identified in marine microalga *Thalassiosira weissflogii* (catalyses establishment of equilibrium $CO_2 + 2\ H_2O \leftrightarrow HCO_3^- + H_3O^+$, this enzyme being crucial for both aerobic breathing [required for sufficiently fast removal of CO_2 from an organism during exhalation] and photosynthesis). In *T. weissflogii*, Cd- or Co-based carboanhydrases (and probably similar enzymes with other functions, like hydrolases) take over when Zn gets scarce (Price and Morel 1990)			
Ce	Bac Alg Fun HPl An	**S**: 50	Slightly toxic	Ce^{3+}
	(+?) — — — —	**P**: 0.25–0.55		$CeOH^{2+}$
		R: 0.5		
	A: *Carya* spp. (leaves), hickory trees (leaves and wood) **Sp**: See under La Ce and other REEs are used as fertilizers especially for purposes of germination and fruit-production stimulation in fruit groweries, mainly in China and Canada (the procedure is not approved in EU); typical doses are a few g/100 m^2*y as "mixed metal" salts, produced by dissolving light-REE minerals in acids. Ce is the most common and effective central ion of a methanol dehydrogenase in bacterium *Methylacidiphilum fumariolicum* (methanotrophic Verrucomicrobia). Ce can be replaced by La, Pr, or Nd in this enzyme, but not by Y or heavier REEs ($Z > 61$). Causes a direct 4e-oxidation to yield carboxylate, processing primary alcohols up to 1-butanol, probably because of co-complexation of several water molecules which distinguishes these nine- to 11-times coordinated metal ions from commonly tetracoordinate zinc which only makes aldehydes from primary alcohols			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Cl	Bac Alg Fun HPl An	**S**: 100*	Rel. non-tox.**	Cl^-
	+/– + — + +	**P**: 0.2–2 %		
		R: 0.2 %		
	A: Halophytes such as Chenopodiaceae, Frankeniaceae, Plumbaginaceae, mangroves such as Rhizophoraceae, Verbenaceae **F**: Osmolytic function, enzyme activation **De**: Wilting and root thickening **Sp**: *Very high concentrations in arid and semi-arid soils (both Cl^- and ClO_4^-) **Cl_2 and a large number of organochlorine compounds (PCBs, chlorinated dioxines) are highly toxic. Apart from the natural emission potential from the ocean, its use in de-icing salt for roads can be regarded as a potential danger for soils and waters. Chlorine is a raw material for the production of solvents and is an active substance in bleaches. It is also used for the stabilization and purification of water (Cl_2 and ClO_2)			
Co	Bac Alg Fun HPl An	**S**: 1–40	Weakly toxic (cardiotoxic)	Co^{2+}
	+/– +/– — ? +	**P**: 0.02–0.5	**Pl**: 0.1–3 mg/l	$CoCO_3$
		R: 0.2	**M**: 500 mg/day l	
	A: *Clethra barbinervis*, *Crotalaria cobaticola*, *Nyssa sylvatica* **F**: Part of vitamin $\mathbf{B}_{12}$, enzymatic **De**: Anemia, vitamin $\mathbf{B}_{12}$ deficiency, disturbance of nucleic acid synthesis **Sp**: Whether Co is essential for higher plants remains unclear, nevertheless it is required to maintain a state of symbiosis with the Leguminosae. The addition of slight quantities of Co often leads to improved yields Co is frequently employed in hydrolases in bacteria, but likewise some 95 % of human Co demand must be something else than vitamin B_{12} (= cyanocobalamine). Co^{2+} can replace Zn in many enzymes, often even increasing activity (Vallee and Williams 1968), and in alga *T. weissflogii*. No role in dioxygen transport although polyamine- and amino acid complexes of Co(II) do reversibly bind O_2			
Cr	Bac Alg Fun HPl An	**S**: 2–100	Toxic*	$Cr(OH)_3$
	— — — — (+?)	**P**: 0.2–1	**Pl**: 1 mg of Cr(VI)/l	CrO_4^{2-}
		R: 1.5	**M**: 3 g/day l	
	A: *Leptospermum*, *scoparium*, *Pimelia suteri* **F**: Insulin intensification, glucose tolerance function **De**: Diabetes, increased serum lipids **Sp**: *Cr(VI) is about 1,000 times more toxic than Cr(III) (basically only Cr(VI) is capable of passing through the cell membrane). In cells Cr(III) is preferentially found in the walls and Cr(VI) in the cell sap, whereas the concentration in mitochondria and the cell nuclei is comparatively low Cr interference with insulin and glucose metabolism is evident but poorly understood, probably not indicating Cr essentiality but rather associated with its being administered as nicotinate complex (other pyridine-3-carboxylatocomplexes, e.g. of Zn or V(IV), likewise act as insulin replacements). Chromate (Cr(VI)) is readily absorbed by mangroves (and reduced in the rhizosphere), whereas Chlorella algae take up Cr too, thereby increasing photosynthetic rates if administered together with essential metal Cu, Ni			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Cs	Bac Alg Fun HPl An	**S**: 1–20	Rel. harmless	Cs^+
	— — — — —	**P**: 0.03–0.44		
		R: 0.2		
	Sp: Cs^{137} released during nuclear fission; radioacitve ^{134}Cs cannot be produced directly by fission but just by neutron capture in natural cesium			
Cu	Bac Alg Fun HPl An	**S**: 1–80	Toxic*	$CuOH^+$
	+ + + + +	**P**: 2–20 mg/l	**Pl**: 0.5–8 mg/l	$CuC0_3$
		R: 10	**M**: 250 mg/day l	
	A: *Aeolanthus biformifolus*, *Becium homblei*, *Cryptosepalum maraviense*, *Elsholtzia haichowensis*, *Gypsophila patrinii*, *Lychnis alpnia*, *Polycarpaea spirostylis*, *Silene dioica*, *Silene vulgaris*, *Triumfetta welwitschi*, *Upaca* spp., *Veronica glaberrima* **F**: Energy metabolism, N metabolism, oxidizing systems, elastin cross-linkage, catalytic function in many redox reactions **De**: For example, grey speck disease of cereals, drying of leaf tips, wilting, spot chlorosis of young leaves, blocking of oxidation (respiration), anemia, changes in bone formation **Sp**: *Released into drinking water form copper pipes Cu (animals): as might be expected, animals whose oxygen transport relies upon hemocyanin display particularly high levels of Cu in tissues, much as with Fe in whale or (elephant) seal meat. These “Cu-enriched” food animals include arthropods (lobsters, crabs, roasted locusts), cephalopods (e.g. octopuses) and certain mussels like oysters			
Dy	Bac Alg Fun HPl An	**S**: 5	Slightly toxic	Dy^{3+}
	— — — — —	**P**: 0.025–0.05		$DyOH^{2+}$
		R: 0.03		
	A: *Carya* spp. **Sp**: See under La			
Er	Bac Alg Fun HPl An	**S**: 2	Slightly toxic	Er^{3+}
	— — — — —	**P**: 0.015–0.030		$ErOH^{2+}$
		R: 0.02		
	A: *Carya* spp. **Sp**: See under La			
Eu	Bac Alg Fun HPl An	**S**: 1	Slightly toxic	Eu^{3+}
	— — — — —	**P**: 0.005–0.015		$EuOH^{2+}$
		R: 0.008		
	A: *Carya* spp. **Sp**: See under La Bioaccumulation in yeast biomass, selectively extracting it from mixtures with Cs and Co (Roy et al. 2008). In plant leaves, photochemical reduction to yield Eu^{2+} (on expense of sugars, amino acids) is likely; that is why Eu, unlike all the other REEs, is bioconcentrated much like heavy alkaline earths Sr, Ba			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
F	Bac Alg Fun HPl An	**S**: 10–1,000	Toxic*	F^-
	— — — — +	**P**: 2–20	**Pl**: 5 mg/l	HF
		R: 2	**M**: 20 mg/day	
	A: *Acacia georginae*, *Dichapetalum* spp., *Gastrolobium grandiflorum*, Porifere *Dysidea crawshayi*, human teeth **F**: In mammals fluorine strengthens the teeth during development. An excess of fluorine can lead to fluorosis as known from grazing animals in Northern Africa **Sp**: * Fluorine is released from the ceramic, cement, and brick-making industries. The resulting dusts and gases containing fluoride can lead to agricultural and forestry damage			
Fe	Bac Alg Fun HPl An	**S**: 0.7–42 %	Hardly toxic	Fe^{2+}
	+ + + + +	**P**: 5–200	**Pl**: 10–200 mg/l	$Fe(OH)_2^+$
		R: 150	**M**: 200 mg/day	
	A: Iron bacteria, lichen *Acarospora smaragdula*, red blood corpuscles **F**: Chlorophyll synthesis, many iron enzymes, ferritin as the storage and transport form, hemoglobin **De**: Straw-colored intercostal chloroses or whitening of young leaves, apical buds suppressed, anemia, growth reduction, hemolysis Fe levels in plant tissues are **massively lower than in soils** (some 100–1,000 µg/g vs. several % up to making the main constituent in tropical oxysols, yet nanoparticles of magnetite Fe_3O_4 do form in leaves and needles and can be used for estimating heavy-element burdens, in addition giving proof that—regardless of water photooxidation in PS II producing O_2 locally—conditions inside photosynthetic organs are slightly reducing. Distribution in tomato-plant seedlings investigated by autoradiography: there, Fe does enrich along leaf edges. In landfills, there is biosynthesis and venting of homoleptic carbonyl $[Fe(CO)_5]$ (Feldmann 1999) while the organisms which accomplish this are unknown			
Fr	Gets fractionated among rat tissues within minutes (half-life of "most stable" isotopes ^{212}Fr and $^{223}Fr \approx 20$ min) although hardly binding to ligands (cp. chemical properties of Cs^+). Otherwise it is so short-lived that—although present in soils and oceans due to the ^{235}U decay chain—hardly any atom of it will make its way into living tissues (cp. At) [the total amount of either element in crust + oceans of Earth is a few grams!)			
Ga	Bac Alg Fun HP1 An	**S**: 0.1–10	**Rat**: 10 mg/day	$Ga(OH)_4^-$
	— — — — —	**P**: 0.01–0.23		
		R: 0.1		
	Sp: Used for antitumorogenic purposes, various medical applications Ga does generally undergo neither bioaccumulation nor pronounced depletion in plants, unlike Al (cp. there), with maximum values of some 5 µg/g DW, somewhat lower levels observed in vegetables. Ga^{3+} salts dissolved in water completely suppress larva hatching from carp eggs. Affinity of Ga (intermediately bound to transferrin) to tumors is used in ^{67}Ga-radiotherapy. Tea-leaf waste efficiently absorbs and retains Ga, while Al is rather readily leached upon tea-making (Chou et al. 2010). In rats, inhaled GaAs dust (from semiconductor processing) gets activated (and toxified) by As biomethylation while Ga^{3+} is bound to tissues, causing damage beyond lung membranes			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Gd	Bac Alg Fun HPl An	**S**:4	Slightly toxic	Gd^{3+}
	— — — — —	**P**: 0.03–0.06		$GdOH^{2+}$
		R: 0.04		
	A: *Carya* spp. **Sp**: See under La			
Ge	Bac Alg Fun HPl An	**S**: 1	Hardly toxic	$Ge(OH)_4$
	— — — — —	**P**: 1–2.4	(apart from GeH_4)	
		R: 0.01		
	Sp: Germanium organic compounds are used as chemotherapeutic agents for bacteria. Spiro-germanium (4,4-dialkyl-4-germacyclohexanone and 8,8-dialkyl-8-germaazaspiro (4,5)decane) are used for antitumorogenic purposes Ge (cp. Ga vs. Al): less excluded (though not actually enriched with respect to soil) by plants than Si (not all plants do contain it but there are appreciable levels in garlic and ginseng). $H_xGeO_4^{n-}$ does bind to the silicate transporter, but stronger than Si. Accordingly, < 25 mg/l (some 350 μM) Ge disrupt spicule formation in freshwater sponges, and organisms relying upon silification are generally damaged by ambient Ge			
H	Bac Alg Fun HPl An	**S**: variable	As D_2O	H_2O
	+ + + + +	**P**: 4.1–7.2 %		
		R: 6.5 %		
	F: Participates in the structure of a large number of organic compounds, supplies reduction equivalents in physiological processes			
Hf	Bac Alg Fun HPl An	**S**: 6	Hardly toxic	
	— — — — —	**P**: 0.001–1		
		R: 0.05		
Hg	Bac Alg Fun HPl An	**S**: 0.01–1	Toxic*	$Hg(OH)_2$
	— — — — —	**P**: 0.005–0.2	M: 0.4 mg/day	HgOHCL
		R: 0.1		
	A: *Minuartia setacea*, *Betual papyrifera* **Sp**: *Toxicity increases from elemental mercury, mono-divalent ionic mercury to organomercury compounds. Amalgam dental fillings may lead to allergies. Minamata disease: disease that occurred from 1953–1960 in Minamata Bay, Japan and some other Hg-exposed sites where Hg biomethylation could occur, like in Sweden. Water containing methyl mercury had contaminated the food fish. In humans, the disease took the form of serious kidney damage and damage to the immunological system also leading to fatalities			

(continued)

Table A.1 (continued)

<table>
<tr><th></th><th>Essentiality</th><th>Occurrence (mg/kg dry wt)</th><th>Toxicity</th><th>Uptake in the form of</th></tr>
<tr><td rowspan="4">Ho</td><td>Bac Alg Fun HPl An</td><td>**S**: 0.6</td><td>Slightly toxic</td><td>Ho^{3+}</td></tr>
<tr><td>— — — — —</td><td>**P**: 0.005–0.015</td><td></td><td>$HoOH^{2+}$</td></tr>
<tr><td></td><td>**R**: 0.008</td><td></td><td></td></tr>
<tr><td colspan="4">**A**: *Carya* spp.
Sp: See under La</td></tr>
<tr><td rowspan="4">I</td><td>Bac Alg Fun HPl An</td><td>**S**: 1–5</td><td>Rel. non tox.*</td><td>I^-</td></tr>
<tr><td>— +/– — — (+)**</td><td>**P**: 0.07–10</td><td>**Pl**: 1 mg/l</td><td>IO_3^-</td></tr>
<tr><td></td><td>**R**: 3</td><td>**M**: 2 mg/day</td><td></td></tr>
<tr><td colspan="4">**A**: Red and brown algae, many Porifera, some Coelenterata, *Feijoa sellowiana*
F: The thyroid gland hormone tyrosine
De: Goitre formation, cretinism
Sp: *Various iodine isotopes are released during nuclear weapons tests and reactor accidents ($^{129;131}$I) which may become dangerous due to the accumulation of iodine in the thyroid glands of mammals and humans
In humans and other higher vertebrates iodine uptake is compromised by certain plant foods, including cassava, maize, bamboo shoots, batatas (sweet potatoes) and by presence of certain large monoanions like SCN^-, N_3^- or ReO_4^- which compete for the carrier. Nitrate reductase (Mo-dependent) does process (reduce) iodate as well, that is, O atom transfer to Mo occurs although the first intermediate iodite IO_2^- is way less stable than nitrite** for vertebrates</td></tr>
<tr><td rowspan="3">In</td><td>Bac Alg Fun HPl An</td><td>**S**: 0.2–0.5</td><td>**Rat**: 200 mg/day l</td><td>$In(OH)_4^-$</td></tr>
<tr><td>— — — — —</td><td>**P**: 0.0005–0.002</td><td></td><td></td></tr>
<tr><td></td><td>**R**: 0.001</td><td></td><td></td></tr>
<tr><td rowspan="4">Ir</td><td>Bac Alg Fun HPl An</td><td>**S**: ?</td><td></td><td></td></tr>
<tr><td>— — — — —</td><td>**P**: ?</td><td></td><td></td></tr>
<tr><td></td><td>**R**: 0.00001</td><td></td><td></td></tr>
<tr><td colspan="4">**Sp**: See under Pt
Ir bioaccumulation takes place in egg shells of both birds and crocodiles (though the latter are not calcified) much beyond soil, water, food background levels; associated to KT (Cretaceous-Tertiary boundary, 66.04 mio. years BP) boundary event (probable ≈ 10-km-diameter asteroid impact at Yucatan Peninsula). Levels in land plants can be up to 20 ng/g (ppb), several orders of magnitude above soil levels), indicating sizable accumulation which is also observed in experiments with phytoplankton and marine macroalgae exposed to solutions of PGM chlorocomplex salts including $[IrCl_6]^{2-}$ (not all the PGMs are absorbed or even accumulated in these tests but Ir does). Ir maxima in late(-st) dinosaur eggs are closely correlated in time/stratigraphy with the (six in total) Ir concentration maxima shortly before, at and after the KT event 66.04 mio. years BP. Iridium is emitted by Otto-engine-driven cars along the common 3 PGMs Pd, Pt, and Rh to be deposited on street-near vegetation, including lichens (it apparently is released from spark plugs which are covered by Ir)</td></tr>
</table>

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
K	Bac Alg Fun HPl An	**S**: 0.2–2.2 %	Rel. harmless	K^+
	+ + + + +	**P**: 0.5–3.4 %		
		R: 1.9 %		
	F: Electrochemical, catalytic enzyme activation **De**: Deficiency disturbs the water balance (drying of leaf tips), leaf curling (wilting) on older leaves, root rot			
Kr	Biochemically inert but readily dissolving in lipids; acts as a narcotic which actually is employed in inhalative narcosis (thus, like Ar and Xe, Kr cannot be used as a ballast gas diluting O_2 and N_2 in diving activities)			
La	Bac Alg Fun HPl An	**S**: 40	Slightly toxic	La^{3+}
	— — — — —	**P**: 0.15–0.25	**Rat**: 720 mg/day	$LaOH^{2+}$
		R: 0.2		
	A: *Carya* spp. **Sp**: The lanthanides are not considered to be essential and are only slightly toxic. In environmental specimens they obey the Harkins rule which says that a lanthanide with an odd atomic number occurs in a lower concentration than the directly adjacent lanthanide element with an even atomic number La, other REEs: distribution of ^{141}Ce among tissues of a horseradish plant was investigated by autoradiography. Ions bind to cerebral receptors, causing REE^{3+} salts to be as effective analgetics as morphin when directly introduced into the brain, in addition, Ce^{3+} (administered orally) acts against kinetoses such as sea sickness. Does kill malign bacteria on fish gills as well as in human wounds (antiseptic creams also preventing inflammation). Substantial differences in partition among the REEs concerning uptake by plants and animals			
Li	Bac Alg Fun HPl An	**S**: 1–100	Slightly toxic	Li^+
	— — — — ?	**P**: 0.01–3.1	**Pl**: 30 mg/l	
		R: 0.2	**M**: 200 mg/day	
	A: Solanaceae in arid climates **Sp**: Lithium compounds are used to treat manic depressives. Possible essentiality for mammals under discussion Li gets “really” bioaccumulated by certain Solanaceae while common levels are much below that of soil. Does cause withhold of uric acid excretion in humans and guinea pigs (mechanism unknown). Strong association of Li^+ (counterion does not matter) to polysaccharides, permitting to dissolve chitin in many different carboxamides, lactams (with LiSCN even in water) and cellulose in DMA. Accordingly Li should be associated with plant or tunicate (the only animals to produce substantial cellulose) **cell walls** while the above dissolution at very high Li^+ levels does not prevent attachment of certain other (both main group- and transition-) metal ions to a chitin strand in solution. Neurological activity is thought to be related to complexation of inositol phosphate (messenger molecule/anion). Li is possibly essential in goat kid development. A relationship (negative correlation) was noted between drinking water, diet Li contents and incidence of suicides and suicide attempts, indicating that the medical use of Li salts for treating or preventing depression in humans can be extrapolated to common food/water levels			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Lu	Bac Alg Fun HPl An	**S**: 0.4	Slightly toxic	Lu^{3+}
	— — — — —	**P**: 0.0025–0.005		$LuOH^{2+}$
		R: 0.003		
	A: *Carya* spp. **Sp**: See under La			
Mg	Bac Alg Fun HPl An	**S**: 500–5,000*	Hardly toxic	Mg^{2+}
	+ + + + +	**P**: 1,000–9,000		$MgOH^{+}$
		R: 2,000		
	A: Marine algae accumulate 6,000–20,000 mg/kg dry weight **F**: Enzyme component and chlorophyll structure, electrochemical and catalytic functions **De**: Deficiency causes stunted growth and intercostal chlorosis on older leaves **Sp**: *Higher Mg contents in the soil arise in the case of rock containing $MgCO_3$ Until recently, every living being was assumed to rely upon Mg, but then the anaerobic breeds of Loricifera living down in a Mg-rich (!) brine in Mediterranian Sea were found to contain no Mg			
Mn	Bac Alg Fun HPl An	**S**: 20–3,000	Slightly toxic	Mn^{2+}
	+ + + + +	**P**: 1–700	**Pl**: 1–100 mg/l	
		R: 200	**Rat**: 10–20 mg/day	
	A: Ericaceae and Theaceae, Diatomeae *Coscinodiscus*, Porifera *Terpios zeteki*, *Annelida hermione*, Ascidiae *Didemnum* and *Halocynthia* **F**: Nucleic acid synthesis, photolysis of water during the light reaction of photosynthesis, stabilizes chloroplast structure, metabolism of the mucopolysaccharides, superoxide dismutase, arginase, pyruvate carboxylase, malate enzyme **De**: Chloroses and necroses on young leaves, defoliation, bone deformation, anemia, reduced growth Diatoms, mollusks, and sponges are reported to accumulate Mn, but, given the extremely low marine level of Mn (20 ng/kg ≈ 0.35 nM/l) in seawater, this does rather mean accumulation is (even) more pronounced than in other organisms. Content in fish tissues up to some 5 μg/g (mg/kg), that is, BCF up to 250,000. Common levels in fruits, leaves of land plants correspond to BCF ≈ 0.1–0.2; that is, slight dilution from soil. Mn in animals is present in malate enzyme (linking glyoxylate to acetyl- or malonyl-CoA), urease. Most of Mn in animals is located in mitochondria			
Mo	Bac Alg Fun HPl An	**S**: 0.2–5	Slightly toxic	MoO_4^{2-}
	+ + + + +	**P**: 0.03–5	**Pl**: 0.5–2 mg/l	
		R: 0.5	**Rat**: 5 mg/day	
	A: Grindelia fastigiata **F**: N_2 fixation, P metabolism, Fe absorption and translocation, xanthine oxidase, sulfoxidase			

(continued)

Table A.1 (continued)

<table>
<tr><th></th><th>Essentiality</th><th>Occurrence (mg/kg dry wt)</th><th>Toxicity</th><th>Uptake in the form of</th></tr>
<tr><td></td><td colspan="4">**De**: Disturbed growth and shoot deformation, discoloration of leaf edges, disturbance of fatty acid formation from carbohydrates
Sp: Leguminosae require about three times as much Mo as other spermatophytes since N_2 fixation by the symbiotic rhizobia requires Mo
Mo is the key element in oxidoreductases. Xanthine oxidase cleaves xanthine rings, producing uric acid (cp. Li) and permitting to degrade alkaloids like caffeine and theobromin. Mo plant contents vary widely around BCF = 0.01–5. On alkaline soils where there is simple MoO_4^{2-}, plants can accumulate up to 500 μg/g DW (i.e., BCF > > 100). In landfills, there is biosynthesis and venting of homoleptic carbonyl $[Mo(CO)_6]$ (Feldmann 1999) while the organisms which accomplish this are unknown</td></tr>
<tr><td>N</td><td>Bac Alg Fun HPl An</td><td>**S**: 2,000</td><td>Ecotoxic*</td><td>NO_3^-</td></tr>
<tr><td></td><td>+ + + + +</td><td>**P**: 1.2–7.5 %</td><td></td><td>NH_4^+</td></tr>
<tr><td></td><td></td><td>**R**: 2.5 %</td><td></td><td>N_2</td></tr>
<tr><td></td><td colspan="4">**F**: Structure of many organic compounds, many metabolic physiological functions
De: Stunted growth or dwarfism, bulky growth and skleromorphosis, premature yellowing of older leaves
Sp: *Simple nitrogen compounds today represent an extensive ecotoxicological problem, e.g. the nitrate problem associated with large-scale livestock farming, NO_2 emissions, N_2O as a greenhouse gas in the atmosphere
N biological levels (e.g., some 1–4 % DW of plant leaf tissues) are much higher than concentrations of either N_2 in atmosphere or of dissolved nitrates, so photosynthesis and N_2 assimilation can be considered to effect bioconcentration of nitrogen, too. N levels in plant tissues respond to increased availability of odd-N in both gaseous (NH_3, NO_x) and dissolved (NO_3^-) states</td></tr>
<tr><td>Na</td><td>Bac Alg Fun HPl An</td><td>**S**: variable</td><td>Rel. harmless</td><td>Na^+</td></tr>
<tr><td></td><td>+/– +/– — +/– +</td><td>**P**: 35–1,000</td><td></td><td></td></tr>
<tr><td></td><td></td><td>**R**: 150</td><td></td><td></td></tr>
<tr><td></td><td colspan="4">**A**: Halophytes, some Chenopodiaceae, Frankeniaceae and, Plumbaginaceae, mangroves such as Avicennia, Bruguiera, and Rhizophora
F: Electrochemical enzyme activation</td></tr>
<tr><td>Nb</td><td>Bac Alg Fun HPl An</td><td>**S**: 10</td><td>Slightly toxic</td><td></td></tr>
<tr><td></td><td>— — — — —</td><td>**P**: 0.28</td><td></td><td></td></tr>
<tr><td></td><td></td><td>**R**: 0.05</td><td></td><td></td></tr>
<tr><td></td><td colspan="4">**A**: Ascidian: *Molgula manhattensis*
Nb environmental (soil, crust) levels typically are around 20 μg/g but very little of it is mobile unless in alkalinic conditions. So the maximum levels of about 0.5 μg/g observed in lichens and mosses represent considerable mobilization, probably due to Nb(V) forming very stable complexes with oxalic (lichens!) and citric acids</td></tr>
</table>

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Nd	Bac Alg Fun HPl An	**S**: 35	Slightly toxic	Nd^{3+}
	— — — — —	**P**: 0.1–0.25		$NdOH^{2+}$
		R: 0.2		
	A: *Carya* spp. **Sp**: See under La			
Ni	Bac Alg Fun HPl* An	**S**: 2–50	Toxic**	Ni^{2+}
	+/– +/– — +/– +	**P**: 0.4–4	Pl: 0.5–2 mg/l	
		R: 1.5	Rat: 50 mg/day	
	A: *Alyssum bertolinii* and *Alyssum murale*, *Dicoma* spp., *Homalium* spp., *Hybanthus floribundus*, *Pimelia suteri*, *Planchonella* spp., *Psychotria* spp. *Rinorea bengalensis*, *Sebertia* spp., Poriferae *Dysidea* **F**: Interaction with iron resorption **De**: Growth reduction **Sp**: *For some plants and microorganisms Ni is a component of urease and therefore essential. **$Ni(CO)_4$ is a highly toxic industrial product Ni is the metal which tends most frequently to display hyperaccumulation in plants. Otherwise, BCF < 1 even in plants known for high Ni contents like tea. In landfills, there is biosynthesis and venting of homoleptic carbonyl [$Ni(CO)_4$] (Feldmann 1999) while the organisms which accomplish this are unknown Ni (probably): methanol CO insertase (catalyses Monsanto-process-like formation of acetate/acetyl CoA from CH_3OH and CO) in clostridium *Moorella thermoacetica*. Urease in plants (animals use Mn for this hydrolytic transformation), CH_4 biosynthesis by way of Ni-porphyrines. Present in many hydrogenases (there are others which contain Fe only), typically combined with ligands CO, CN^- and thiolate (cysteine sidechains of the surrounding protein)			
O	Bac Alg Fun HPl An	**S**: 49 %	Toxic in the form of O_3 and peroxide	O_2
	+/– + + + +	**P**: 40–44 %		CO_2
		R: 42.5 %		
	F: Constituent of many organic compounds, provides oxidation equivalents in metabolism **Sp**: *Lethal for obligate anerobic microorganisms			
Os	Bac Alg Fun HPl An	**S**: ?	Very toxic in the form of volatile OsO_4	
	— — — — —	**P**: ?		
		R: 0.000015		
	Sp: See under Pt Concerning Os bioaccumulation from aqueous media, see iridium			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
P	Bac Alg Fun HPl An	**S**: 200–800	Ecotoxic*	HPO_4^{2-}
	+ + + + +	**P**: 120–30,000		$H_2PO_4^-$
		R: 2,000		
	F: Hydroxyapatite for mammals during bone and teeth formation, energy metabolism, phosphorylation, DNA and ATP structure **De**: Disturbance of reproductive processes (flowering inhibition), bulky growth, dry tips in the case of conifer needles **Sp**: *Eutrophication of waters; phosphate esters which enter the water as insecticides have a toxic effect on many hinds of aquatic life: phosphates are relatively harmless while phosphonic acid esters and PH_3 are very toxic P contents of biomass are closely related to average metabolic activity (requirements for ATP/volume) and to reproduction/cell budding rates (nucleic acids contain P and control reproduction of cells and entire organisms) [ecological stoichiometry] but generally much above soil P contents. Water can be depleted from inorganic P by phytoplankton levels residual levels down to $<<$ 1 nM/kg			
Pa	Bac Alg Fun HPl An	**S**: ?		
	— — — — —	**P**: ?		
		R: ?		
Pb	Bac Alg Fun HPl An*	**S**: 0.1–200	Toxic	$PbCO_3$
	— — — — ?	**P**: 0.1–5	**Pl**: 2–3 mg/l	
		R: 1	**M**: 1 mg/day	
	A: *Amorpha canescens*, *Minuartia verna*, lichen *Stereocaulan pileatum* **F**: *Essentiality for vertebrates under discussion. Pb enters the environment (currently to a decreasing extent) particularly from the use of tetraethyl lead as an antiknock agent for petrol engines Pb levels in plant tissues and fruits are generally much below that of soil. Some relative enrichment occurs along Ca in bones and in animal kidneys			
Pd	Bac Alg Fun HPl An	**S**: ?	Toxic	
	— — — — —	**P**: ?		
		R: 0.0001		
	Sp: See under Pt Pd shows some (unspecified [400 ng/g *fresh* weight vs. soil levels usually being < 10 ng/g]) enrichment in tree leaves. Carcinogenic in rats but not towards humans (cp. applications in dentistry). Transfer factors using simulated catalyst loss dust gave BCFs up to 0.3 for land plants like Phacelia, Urticaria (Eckhardt and Schäfer 1999), that is, substantial mobilization but not "real" accumulation. Pronounced bioaccumulation from 3-way-catalyst converter-ejected particles attacked by humic acids into zebra mussel *Dreissena polymorpha* (also holds for Pt, Rh)			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Po	Bac Alg Fun HPl An	**S**: 8–220 Bq/kg	Highly toxic for vertebrates	
	— — — — —	**P**: 8–12 Bq/kg		
		R: 0.05		
	A: *Carya* spp. **Sp**: See under La			
Pr	Bac Alg Fun HPl An	**S**: 3–12	Slightly toxic	Pr^{3+}
	— — — — —	**P**: 0.03–0.06		$PrOH^{2+}$
		R: 0.05		
	A: *Carya* spp. **Sp**: See under La, Ce			
Pt	Bac Alg Fun HPl An	**S**: ?	Slightly toxic	
	— — — — —	**P**:?		
		R: 0.00005		
	Sp: 0.9–2.3 g of Pt are contained in older three-way catalytic converters. Pt metal and its salts cause allergic contact eczema. *Cis*-Dichloroplatinum(II)complexes are used in cancer therapy. Pt and its family enter into the environment due to natural wear from exhaust catalytic converters in cars. Together with aluminium oxide as the carrier material, these compounds are released into the air in a highly dispersed metallic form as suspended matter and subsequently deposited. The consequences of this are still unclear, particularly since the concentrations of platinum metal naturally occurring in the environment are very low and often cannot be determined exactly (please have a look to Table A.2 where some research results of platinum metal concentrations in the environment are listed) Pt uptake of plants is notable near heavy-traffic-loaded roads from 3-way catalytic converters and in larger areas from particles eluted from Pt/Rh NH_3 oxidation catalysts (making nitric acid which ends up in nitrate fertilizers) ending up in nitrogen (nitrate) fertilizers. Bioaccumulation in plants mainly is restricted to the rhizosphere. See Pd. Pronounced bioaccumulation from 3-way-catalyst particles attacked by humic acids into zebra mussel *Dreissena polymorpha* (also holds for Pd, Rh). Unlike other PGMs which remain oxidized and form complexes interacting with biomass, Pt soon gets reduced into nanocluster particles and hence is way less bioavailable than all the other five PGMs			
Ra	Bac Alg Fun HPl An	**S**: ?	Radioactive*	Ra^{2+}
	— — — — —	**P**: 0.03–1.6 ppt		
		R: ?		
	A: *Bertholletia excelsa* **Sp**: *Similar chemical behaviour to Ba and Ca, therefore incorporation into the bone substance. 10–20 µg is sufficient to cause bone-marrow depression and myelosarcomas Ra undergoes slight enrichment in plants beyond soil background (radioactivity levels (the latter being about 30 Bq/kg = 0.8 ng/kg [corresponds to ^{226}Ra])			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Rb	Bac Alg Fun HPl An	**S**: 10–100	Slightly toxic	Rb^+
	— — — — —	**P**: 1–50	**Rat**: 10 mg/day	
		R: 50		
	Sp: Similarity to K, may replace K at bonding locations, however not in terms of its neurophysiological effect Otherwise, Rb can fully and reversibly replace K in many organisms, including multicellular ones like marine algae. β^-decay of ^{87}Rb is main source of internal radioactive body burden in humans. Rb levels found in soy beans and apples (220 and 50 µg/g, respectively) are somewhat above the common ones in soil, indicating bioaccumulation throughout the plant body, while levels of K in plant fruits are < 0.5 times that in soil, meaning there is some fractionation even though in many plants and bacteria K and Rb can mutually and reversibly replace each other			
Re	Bac Alg Fun HPl An	**S**: ?		ReO_4^-
	— — — — —	**P**: ?		
		R: ?		
	Re is accumulated by various flowers, and by quite different Black Sea organisms below chemokline, perhaps via ReS_4^- formation and its uptake along Mo. Little reports on biochemical behavior although ^{188}Re complexes are used in palliative radiotherapy, indicating effective retention by human tissues			
Rh	Bac Alg Fun HPl An	**S**: ?		
	— — — — —	**P**: ?		
		R: 0.00001		
	Sp: See under Pt There are Rh inputs from 3-way exhaust gas converters (formerly Pt/Rh-, now Pd/Rh alloys spread on ceria/ZrO_2) and agrarian nitrogen fertilizers (cp. Pt) are likely. Levels detected in NIST citrus leaves SRM suggest sizable depletion with respect to that estimated in average soil. For other (ectropical) land plants cp. Pd. Pronounced bioaccumulation from 3-way-catalyst particles attacked by humic acids into zebra mussel *Dreissena polymorpha* (also holds for Pt, Pd)			
Ru	Bac Alg Fun HPl An	**S**: ?		
	— — — — —	**P**: ?		
		R: 0.00001		
	Sp: See under Pt Ru bioaccumulation does take place in edible alga *Porphyra* spp. noted by enrichment of fissiogenic (then emitted from Windscale/Sellafield [UK] nuclear reprocessing plant) $^{103;106}$Ru in this seafood. Ru complexes are capable of catalyzing many hydrogenation/dehydrogenation processes which likely interfere with biochemistry			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
S	Bac Alg Fun HPl An	**S**: 200–2,000*	Ecotoxic**	SO_4^{2-}
	+ + + + +	**P**: 600–10,000		HSO_4^-
		R: 3,000		
	A: Individual plants of the Cruciferae, *Allium* spp., sulphur bacteria, vertebrate hair, feathers **F**: Constituent of amino acids (cysteine and methionine), of coenzymes, acid mucopolysaccharides, and sulphuric acid esters **De**: Very similar to N deficiency, intercostal chloroses of young leaves, premature yellowing of leaves and needles **Sp**: *Considerably higher contents on gypsum soils. **Influence of anthropogenic SO_2 emissions in 'new' forest damage, soil acidification Almost all organisms are capable of reducing sulfate into SH^- and organics derived thereof; many even base their redox metabolism on SO_4^{2-} as terminal electron acceptor (SRBs). In both soil and ocean water typical levels are several hundred mg/kg, and commonly about the same in freshwaters, the S content of common living beings do represent substantial bioaccumulation, even neglecting sulfate reducers (which get rid of excess S by venting H_2S)			
Sb	Bac Alg Fun HPl An	**S**: 0.01–1	Toxic*	$Sb(OH)_6^-$
	— — — — —	**P**: 0.1–200 ppb	**M**: 100 mg/day	
		R: 0.1	**Rat**: 10–75 mg/day l	
	Sp: *Sb(III) is more toxic than Sb(V) Antimony does undergo ready biomethylation but will not end up in organoelement cycles like As does			
Sc	Bac Alg Fun HPl An	S: 0.5–45	Slightly toxic	$Sc(OH)_3$
	— — — — —	P: 0.01–0.2		
		R: 0.02		
	There is no bioaccumulation of scandium; all levels in plants or animal tissues $\ll$ soil levels (the latter being several μg/g)			
Se	Bac Alg Fun HPl An	**S**: 0.01	Toxic*	SeO_3^{2-}
	— — — +/– +	**P**: 0.01–2	**Pl**: 1–2 mg of Se (IV)/l	
		R: 0.02	**M**: 5 mg/day	
			Rat: 1–2 mg/day l	
	A: Fungus Boletus *edulis*, individual species from the families of the Compositae, Lecythidaceae, the Leguminosae (e.g. *Astragalus*), and the Rubiaceae **F**: Component of glutathione peroxidise **De**: Deficiency causes lipid peroxidation, endemic cardiomyopathy, and hemolysis in animals and man **Sp**: *Selenite and selenates are very toxic. The toxicity of As, Hg, Cd, Tl, and NO_3^- is reduced if Se is taken up at the same time. The toxic effect results from the replacement of sulphur by Se in amino acids			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Si	Bac Alg Fun HPl An	**S**: 33 %*	Physically, e.g. in the forms of asbestos	$Si(OH)_4$
	+ — — +/– —	**P**: 2,000–8,000		
		R: 1,000		
	A: Diatoms, radiolarians and siliceous sponges, Sphenopsida, Cypercaes, Gramineae, Junacae **F**: Structural component of siliceous skeletons, calcification **De**: Growth disturbances, bone deformation **Sp**: *Clearly lower contents on particular soils, e.g. limestone. Organic Si compounds may be highly toxic. Some Si compounds such as Si halogen compounds are corrosive. Si is essential for bone development in young chickens, other vertebrates. SiO_2 needles fortify stems of many plants. Given the very high level in soils (cp. Ca, Al), there can be no "real" bioaccumulation in land plants. However, there is bioaccumulation in the oceans given the local concentration of dissolved silicates in ocean water (depleted near the surface), especially with organisms making most of their skeletons or supporting backbones from SiO_2, such as sponges and certain diatoms, that is, in both animals and plants			
Sm	Bac Alg Fun HPl An	**S**: 4.5	Slightly toxic	Sm^{3+}
	— — — — —	**P**: 0.02–0.04		$SmOH^{2+}$
		R: 0.04		
	A: *Carya* spp. **Sp**: See under La Sm^{3+} does insert into chlorophyll, removing Mg to produce a bis-porphyrin sandwich complex which reaches substantial concentrations in chlorophyll stacks of chloroplasts and can there be detected owing to its typical fluorescence (extent of Mg replacement up to ≈ 0.5 %, much more than with other REEs, probably due to differences in complex chemistry while Gd, Yb can be detected in the same manner, but less readily)			
Sn	Bac Alg Fun HPl An*	**S**: 1–20	Hardly	$SnO(OH)_3^-$
	— — — — —	**P**: 0.8–7	**M**: 2 g/day	
		R: 0.2		
	A: *Silene vulgaris*, Poriferae *Terpios zeteki* **F***: Sn may possibly be essential for vertebrates **De**: Growth disturbance occur in vertebrates, furthermore digestive enzymes are not secreted **Sp**: Organotin compounds (e.g. triphenyltin) were used as fungicides, insecticides and bactericides Growth depression was observed in young rats deprived of Sn supply; could be reversed by giving them tin compounds again. Sn is enriched in cereal grains including corn. Sugar beet and other plants reach very high levels (0.1 % DW) and more if grown on Sn-rich soils, e.g. near tin smelters.			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Sr	Bac Alg Fun HPl An	**S**: 20–3,500	In the form of Sr^{90*}	Sr^{2+}
	— — — — —	**P**: 3–400		
		R: 50		
	A: Protozoa *Acanthometra*, brown algae **Sp**: Sr seems to be essential for some organisms. However, this requires further investigation. Sr is required for growth, reproduction of stony corals (aquarium experiments). Certain vegetables, like onions, lettuce, and cabbage have Sr levels near to, but smaller than in average soils. Otherwise, there is depletion rather than bioaccumulation *Sr^{90} is a decay product from nuclear explosions and as a consequence of its similarity to Ca is incorporated into bone structure			
Ta	Bac Alg Fun HPl An	**S**: 0.5 < 4	Slightly toxic	
	— — — — —	**P**: < 0.001	**Rat**: 300 mg/day l	
		R: 0.001		
	A: Ascidia *Stylea plicata* Ta cannot be bioaccumulated for the same reasons than with Nb, but rejection tendency is even stronger (whereas Nb does form a couple of soluble complexes with biogenic ligands, Ta rapidly turns into the pentoxide even in alkaline pH conditions). While there are usually several hundred μg/kg soil, levels in plants do not exceed 5 μg/kg, in food plants at most 1/10th of this value			
Tb	Bac Alg Fun HPl An	**S**: 0.7	Much more toxic than other REEs	Tb^{3+}
	— — — — —	**P**: 0.005–0.015		$TbOH_2^+$
		R: 0.008		
	A: *Carya* spp. **Sp**: See under La			
Te	Bac Alg Fun HPl An	**S**: ?	Toxic	$HTeO_3^-$
	— — — — —	**P**: 0.01–0.35	**Pl**: 6 mg/l	
		R: 0.05	**Rat**: 1–9 mg/day l	
	Te levels in coal are perhaps related to former bioaccumulation by tree ferns. Now, it is vented after organismic uptake due to rapid formation of (truly nasty-smelling) volatile $(CH_3)_2Te$ by biomethylation (can be controlled by administering ascorbic acid and other radical scavengers). Thus, there is no evidence for recent bioaccumulation effected by anybody			
Th	Bac Alg Fun HPl An	**S**: 9	Toxic	$Th(OH)_4{}^{4-n}$
	— — — — —	**P**: 0.03–1.3		
		R: 0.005		
	There is no bioconcentration of thorium due to same reasons like with Nb and Ta			

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Ti	Bac Alg Fun HPl* An	**S**: 1,500–5,000**	Hardly toxic***	$Ti(OH)_4$
	— — — — —	**P**: 0.02–56		
		R: 5		
	F:*Although it is not regarded as essential for plants it may nevertheless play a positive role in cereal growth and for N_2 fixation by Leguminosae ** 15 % in the upper layers of lateritic soils. The measured Ti content during plant analysis may be used as an indicator of contamination by soil particles *** Due to its grain size of 20 µm, the titanium dioxide pigment is classified as dust pollution There are very high soil levels of Ti, yet it is low in plants, no bioaccumulation (a maximum of 80 µg/g in nettle compares to some 0.3 % in average soils). Does not provoke adverse body reactions but apparently increases carbohydrate production rates in plants (hormesis)			
Tl	Bac Alg Fun HPl An	**S**: 0.01–0.5	Toxic	Tl^+
	— — — — —	**P**: 0.03–0.3	**Pl**: 1 mg/l	
		R: 0.05	**M**: 600 mg/day	
	Sp: Particularly high environmental concentrations in the vicinity of cement factories Tl bioaccumulation takes place in green rape leaves, feasibility of biomining was demonstrated. Pine trees and certain flowers also enrich to high levels. In ocean water, up to 45 % of Tl (i.e. some 1 ng/l) are present as (formed by biomethylation, than chemically rugged) $(CH_3)_2Tl^+$, which should increase uptake by being somewhat lipophilic			
Tm	Bac Alg Fun HPl An	**S**: 0.6	Slightly toxic	Tm^{3+}
	— — — — —	**P**: 0.0025–0.005		$TmOH^{2+}$
		R: 0.004		
	A: *Carya* spp. **Sp**: See under La			
U	Bac Alg Fun HPl An	**S**: 0.01–1	Highly toxic	$UO_2(CO_3)_3^{4-}$
	— — — — —	**P**: 0.005–0.06	**Rat**: 36 mg/day l	
		R: 0.01		
	A: *Coprosma arborea*, *Uncinia leptostachya*, some corals Ash from burnt wood contains U beyond environmental (soil) levels, and there are some organisms which effect UO_2 or $USiO_4$ precipitation by reducing uranyl compounds which latter are exceptionally lipophilic (readily dissolve in esters including lipids, ethers, alcohols, or aldehydes, organophosphates) and are adsorbed right through human and animal (amphibian!) skin. Bioaccumulation in some yeast species and lichen *Trapelia involuta*			

(continued)

Table A.1 (continued)

<table>
<tr><th></th><th>Essentiality</th><th>Occurrence (mg/kg dry wt)</th><th>Toxicity</th><th>Uptake in the form of</th></tr>
<tr><td>V</td><td>Bac Alg Fun HPl An</td><td>S: 10–100</td><td>Toxic</td><td>$H_2VO_4^-$</td></tr>
<tr><td></td><td>— +/– — +/– +/–</td><td>P: 0.001–10</td><td>P: 10–40 mg/l</td><td>HVO_4</td></tr>
<tr><td></td><td></td><td>R: 0.5</td><td>Rat: 0.25 mg/day</td><td></td></tr>
<tr><td></td><td colspan="4">A: Fungi: <i>Amanita muscaria</i>, <i>Astragalus confertiflorus</i>, ascidians
F: Inhibitation of cholesterol synthesis
De: Growth reduction, changes in lipid metabolism, fertility disturbances
Sp: Some sea cucumbers, in isolated cases molluscs and generally ascidians contain high V concentrations. Some species of ascidians have a vanadium complex in their blood and other species a pyrrole complex in the green blood corpuscles, the vanadocytes.
There is pronounced V bioaccumulation in <i>Amanita muscaria</i> and other toadstools, using a V(IV)-specific ligand “amavadine”. Extreme bioconcentration from seawater in tunicates like <i>Ascidia nigra</i>. Though there V is associated with blood cells, it has no function in oxygen transport though there are V-dependent haloperoxidases. Typical enzymes are haloperoxidases which make OCl^- or OBr^- from the halide and H_2O_2 and an isoform of nitrogenase which, while binding N_2 to bridge 2 Fe atoms and reduce it there like in Mo nitrogenase, is formed in deprivation of Mo and formation does rely on another gene. Enzymatic phosphorylation and ribonuclease activity can be blocked by (pentavalent) vanadium</td></tr>
<tr><td>W</td><td>Bac Alg Fun HPl An</td><td>S: 1.5</td><td>Slightly toxic</td><td>WO_4^{2-}</td></tr>
<tr><td></td><td>— — — — —</td><td>P: 0.0005–0.15</td><td>Pl: 10 mg/l</td><td></td></tr>
<tr><td></td><td></td><td>R: 0.2</td><td>Rat: 30–50 mg/day l</td><td></td></tr>
<tr><td></td><td colspan="4">A: <i>Pinus cembra</i>
Sp: The physiological effect of tungsten is as an antagonist to molybdenum where the replacement of Mo by W in the corresponding enzymes (e.g. xanthine oxidase) generally leads to a drop in activity
W replaces Mo in certain oxidoreductases of Archaea, and more so of clostridia (catalysis works best in the neighborhood of some point where their different states of the redox catalyst do co-exist, and the conditions when this applies to Mo and W are obviously and expectably different. Hence one or the other element may be more effective depending on local conditions, especially pH and temperature). Like in modified ferrothioredoxines, in which one Fe ion out of the Fe_4S_4 cluster (distorted CsCl structure, binding more co-ligands [e.g. citrate, amino acids and proteins via thiolate (cysteine)] is mobile and exchangeable by other ions of different oxidation states to yield $M'Fe_3S_4$ structures which have many functions in biology (e.g. nitrogenase, Mo-based oxidoreductases), W is/gets associated with iron thioclusters. In archaean aldehyde oxidoreductases (which are highly selective towards substrates; there are different ones processing HCHO, higher R-CHO, and glycol aldehyde in <i>Pyrococcus furiosus</i>, growing fastest at 100 °C), W cannot be replaced by either Mo or V even in high excess while W is scarce (Mukund and Adams 1996). While average W soils levels are about 1–2 µg/g, there may be up to 100 µg/g in trees growing in Rocky Mountains. Massively absorbed from solutions by barley, probably as simple WO_4^{2-} ion (by way of sulphate carrier?). In landfills, there is biosynthesis and venting of homoleptic carbonyl $[W(CO)_6]$ (Feldmann 1999) while the organisms which accomplish this are unknown</td></tr>
</table>

(continued)

Table A.1 (continued)

	Essentiality	Occurrence (mg/kg dry wt)	Toxicity	Uptake in the form of
Xe	Bac Alg Fun HPl An	**S**: will adsorb to clay or peat but does not undergo chemical reactions	Toxicity: see below	
	— — — — —	**P**: no data		
		R: no data		
	Xenon is biochemically probably fully inert, yet lipophilic and neurotoxic at partial pressures >10 kPa (lesser amounts can, like Kr, be applied as an inhalable narcotic agent)			
Y	Bac Alg Fun HPl An	**S**: 40	Slightly toxic	$Y(OH)_3$
	— — — — —	**P**: 0.15–0.77		
		R: 0.2		
	A: Poriferae *Melithoca* spp., *Carya* spp. Y is accumulated by apple fruits to extents which vary widely by sort. Substantial enrichments in cabbage and seeds of woody plants. Significant reduction of soil Y contents due to agrarial cultivation which indicates kind of "phytoremediation". Y is associated with nucleic acids in vivo and thus, like PGM-based cytostatics, might influence reproduction			
Yb	Bac Alg Fun HPl An	**S**: 3	Slightly toxic	Yb^{3+}
	— — — — —	**P**: 0.015–0.030		$YbOH^{2+}$
		R: 0.02		
	A: *Carya* spp. **Sp**: See under La Yb levels in some lichens ≥ those of supporting soil or bedrock			
Zn	Bac Alg Fun HPl An	**S**: 3–300	Toxic	Zn^{2+}
	+ + + + +	**P**: 15–150	**Pl**: 60–400 mg/l	$ZnOH^+$
		R: 50	**M**: 150–600 mg/l	$ZnCO_3$
	A: *Armeria maritima* subsp. *halleri*, *Minuartia verna*, *Silene vulgaris*, *Thlaspi alpestre*, *Viola tricolor* var. *calaminaria* **F**: Chlorophyll formation, enzyme activator, energy metabolism (dehydrogenases), protein degradation, formation of growth substance (IES), transcription **De**: Growth inhibition, whitish-green discoloration of older leaves, fructification disturbances **Sp**: Toxic symptoms in humans are sexual immaturity, skin lesions, and grey hair. Soils rich in Zn are termed 'calamine soils' and support 'calamine flora' Zn ions are the most common constituent of metalloproteins, yet levels in plant or animal tissues as a rule do not surpass those in soils, rather, are somewhat lower. When lacking aerosol supply, mosses might absorb a 35 μg/g minimum for their demands from bedrock by means of delivering amino acids (which they also do under drought stress)			
Zr	Bac Alg Fun HPl An	**S**: 1–300	Slightly toxic	$Zr(OH)_n{}^{4-n}$
	— — — — —	**P**: 0.3–2	**Rat**: 250 mg/day	
		R: 0.1		
	Zr gets bioaccumulated up to some 500 μg/g in leaves of certain deciduous trees (Hf behaves differently). Rapid absorption by aquatic plants; in humans, you will not find Zr given away in either urine or sweat, rather, there is irreversible accumulation in both bones and soft tissues.			

Commonly, it is assumed that all organisms on Earth, including the Archaea, can be traced back to one single common precursor (one **l**ast **u**niversal **c**ommon **a**ncestor, LUCA) although there are more than slight differences among organisms in e.g. genetic code and cell wall chemistry. Nevertheless this assumption—whether it does hold or not (which we probably will never know for sure)—has some implications for the problem we deal with: if LUCA existed, the set of chemical elements it had happened to absorb and contain were likely to make their way onward into functions and thus enzymes—and hence probably were related to some superposition of the chemical composition of the site where LUCA happened to assemble (which we do not know) and of metal complexation properties as changing during chemical evolution (which we understand rather well). The latter in turn depend on the key intermediates transforming into one another. Hence there should just be a bias towards metal ions undergoing fairly strong retention. The energy of retention to polyamide polymers (mimicking peptides and their typical linkages) of course is not identical to binding strengths to possible protoenzyme substrates as the donor sites of the latter use to differ from carboxamide moieties.

Concerning **accumulation**, we deal with single "steps" here as it is obvious that pronounced toxicity in low(er) trophic levels, such as Cu, La, Pd inhibiting phytoplankton growth or the extreme toxicity of Be, Tl, U for herbivorous animals will limit bioaccumulation throughout an entire trophic ladder or—network regardless of the chemical properties of an element or its respective speciation form. A biocatalytic function does not entail enrichment to significant levels. There are elements devoid of any biological function despite of being both a) highly abundant in nature and b) known to be effective in experimental prebiotic catalysis, such as Al and Ti. Unlike its homolog Ga, Al is effectively kept out of living tissues; even the cases we use to consider as representing "bioaccumulation" of Al, e.g. in grasses, ferns or black tea leaves, do show Al concentrations which are several orders of magnitude lower than in an average or even clayey soil. For aquatic organisms, there are sets of "expected" or "predicted" (rather than measured) BCF and BAF values throughout the Periodic System, mostly for freshwater.

These lists were made for estimating particularly large radionuclide exposition risks. Nevertheless a comparison with actual behavior of certain heavy-metal radionuclides, including ^{90}Y, ^{110}Ag, ^{106}Ru, $^{141;144}$Ce, and ^{147}Pm, shows that the real potential for bioconcentration/bioaccumulation from freshwater as well as ocean (consider the pH difference!) uses to be **under**estimated. These values thus are of doubtful use and should be replaced with a more rigorous formal treatment which relies upon pieces of empirical information on partitioning thermodynamics.

If there was no LUCA but life on Earth originated twice or more often at more or less mutually remote sites (possibly to merge into one more sophisticated being afterwards [thus giving rise to endosymbiosis]), chemical conditions at these different sites were most likely to differ, too, with unlike prebiotic catalysts operating. Then elements, including such with hardly any or no contemporary "positive" (other than toxic) biological function, like Al, Ba, Ti, Pb, probably were spread unevenly which implies different "prebiotic intermediates" would accumulate at different sites. Then there should be variations in composition among the different precursors of earliest living beings. These variations of composition in turn reflect differences in affinities towards certain metal ions which eventually would make their way into chemical basics of certain cell organelles (C/N ratios, contents of amino acids, lipids, metal ion inventories). Especially archaea, with lots of "deviations" (as compared to all other organisms) from cell wall chemistry (long-chained ethers rather than lipids or cellulose) over details of genetic code to peculiar redox biochemistry pathways then should thoroughly differ in essential trace element patterns from other living beings.

Actually there is nothing in (enzymatic, catalytic) use of metal-forming elements or "uncommon" non-metals (like Se) which would not be likewise or for somewhat different purposes applied by other organisms, too. There is not a single element used by Archaea which all other organisms would omit or avoid to use while not living in such extreme conditions of all temperature (>93–121 °C), pH (strongly acidic, sometimes $\text{pH} < 0$) and redox potentials. This statement even holds for W (Mukund and Adams 1996), which also is used by clostridia and other bacteria dwelling in strongly reducing environments. Probably it is significant that there almost inevitably is pronounced organotropy in multicellular life on Earth regardless of trophic level (the only known exception concerning a non-essential element in an omnivorous animal [Ti in rats; Wünschmann et al. 2001]) allowing to determine different binding is even holds for properties in different parts (organs) of a single organism. Some of these differences make obvious sense while others are related to climate etc. factors, requiring further research.

More information on *relative* binding to sediment (which approximately goes along $\log k_{OW}$ for neutral species, allowing for e.g. U(VI) lipophilic behavior) and binding to biomass (averaged over different organisms of a biocoenosis) can be obtained by closer scrutiny on radioactive decay chains provided some of the radionuclides are preferentially absorbed by organisms: once decay equilibria, e.g. in the series ([fallout] $^{239}\text{Pu}) \rightarrow {}^{235}\text{U} \rightarrow {}^{231}\text{Pa} \rightarrow {}^{227}\text{Ac}$, or (better understood) $^{238}\text{U} \rightarrow \ldots \rightarrow {}^{234}\text{U} \rightarrow {}^{230}\text{Th} \rightarrow {}^{226}\text{Ra} \rightarrow \ldots \rightarrow {}^{210}\text{Pb}$ have established, specific activities of the single nuclide interconnected per mass or volume of sample should be identical (that is the definition of radioactive equilibrium, provided the last [lightest] nuclide still is radioactive, as in the two above cases which terminate at ^{207}Pb and ^{206}Pb, respectively), unless for bioaccumulation (consider the biomass share of soils, aquatic sediments!). Next to and downstream of (now abandoned) French uranium mine at Les Bois Noirs, the aquatic moss *Fontinalis antipyretica* was investigated which for quite a period of time binds metal ions just to its surface, only later, while still growing, relocating them into the tissues. *Fontinalis* tends to bind alkaline earths, thus specific activities of ^{226}Ra are >40 times (inside discharge pipe), about ten times (from a few m to 1.5 km downstream) and even much more distant twice to three times those for ^{238}U and some 60 times the decay rates for ^{210}Pb at 1 (1.5) km, and 5–10 times at 9–30 km. Similar phenomena were seen among mother/daughter isobars $^{210}\text{Pb/Bi/Po}$ in various organisms of the Black Sea while levels in water column (oxic part) and sediment (showing sulphate reduction) were close to radiological equilibrium.

Likewise, one can expect, since apple fruits do readily accumulate yttrium (see below) but have low levels of Sr that from an equilibrium mixture ^{90}Sr/Y in soil ^{90}Y will be absorbed in particular and thus display larger activity than ^{90}Sr in apples.

A.2 Additional Information for Pt (Platinum Metals in "Unpolluted" Plant Samples)

Since the 1990s progress in analytical methods enabled a fairly precise routine determination of levels of various PGMs in biological samples. One difficulty was the fact that there was no analytical procedure for quantitatively determining platinum levels at 50 ppt in plants. Zeisler and Greenberg (1982), as well as Zeisler (1988) only came close to these levels in NIST reference materials for plants by using a radioanalytical procedure (Fig. A.1). These data are still too isolated to enable confident statements to be made about their accuracy. Not even by using ICP/MS or graphite tube AAS after reducing Pt(IV) to Pt(II) with tin(II) chloride and extraction as a dithizone complex with isobutyl ketone was it possible to make the platinum metals analytically accessible for 'normal concentrations' in plant samples, contrary to citations in the literature (e.g. Alt et al. 1988, 1993; Beinrohr et al. 1993). At best the detection limits lie in the lower ppb range. Since the platinum metals cannot be reliably determined analytically in unpolluted plant material, their natural occurrence can only be estimated after standardization with the levels in the earth's crust, as is shown in Fig. A.1. As a whole, the calculated concentrations of platinum metals lie in the middle and lower ppt range. With an average emission of 2 μg of platinum per km traveled, and with levels of 0.7 μg/g of platinum and 0.3 μg/g of palladium in the dust along roadways (Rosner and Hertel 1986; Alt 1988), one can plan on the natural concentrations cited above being rapidly exceeded, with results that cannot be estimated. Biological samples here include both CRMs (certified reference material) obtained from either animals [bovine liver, mussel meat] or plants [e.g., orchard leaves, green tea] and "ordinary" environmental samples, taken far from possible PGM emissions by traffic [Pt, Pd, Rh and Ir] or nitrate fertilizers [Pt + Rh (Ostwald catalyst for ammonia oxidation)]. Methods used for these ppt-level (ng/kg) analyses include voltammetry, photometry of intensely colored complexes or ICP-MS (requiring high-resolution for interferences among Pt and HfO, etc.) rather than INAA which is little[1] sensitive for these elements, e.g. for the exceptionally large lifetime of an excited state of ^{192}Ir formed during activation which effectively precludes detection of typical γ radiation. For some reason, levels of PGMs are exceptionally large in salad (composition of which was not revealed in terms of plant species, possible admixtures of cheese, feta or the like). Reported values are listed in Table A.2.

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[1] „little" with respect to the analytic criteria to be met here: for most other elements, you would never try/be challenged to determine ng/kg amounts, not even with lighter actinoids or rarest REEs Ho, Tm, Lu. The lowest value we were ever concerned with in our analytical work was about 70 ppt Th in mother's milk (Wünschmann et al. 2008).

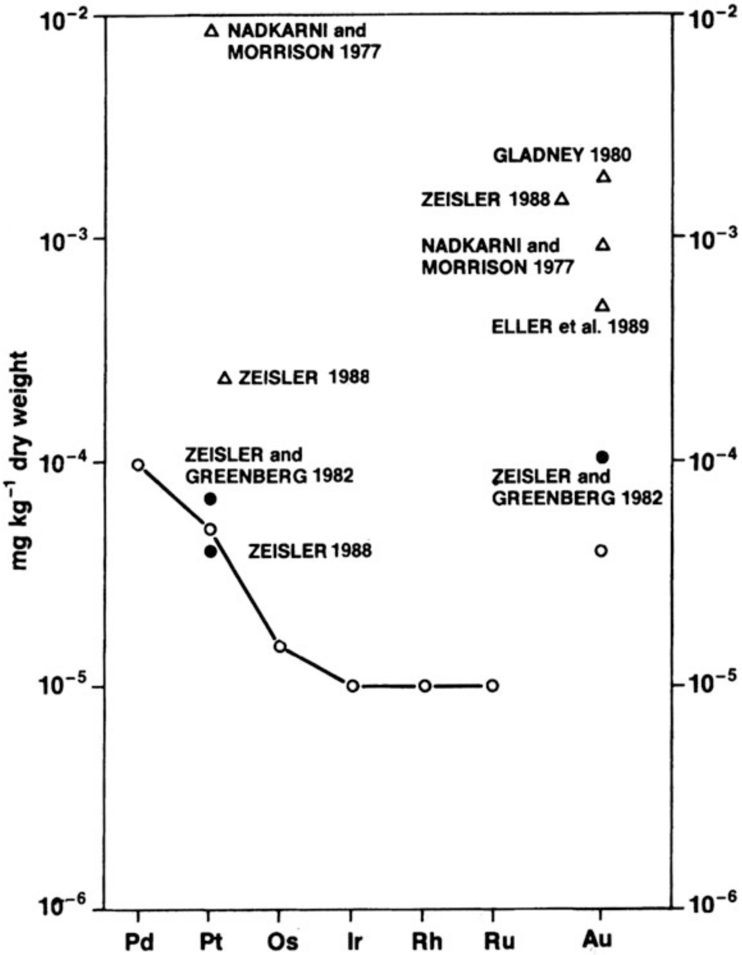

Fig. A.1 Calculated 'normal concentrations' of platinum metals and gold in plants (open circles) from levels in the earth's crust in comparison with concentrations measured by different laboratories in NIST citrus leaves (filled circles) and NIST orchard leaves (open triangles). Data are in mg/kg dry weight (Markert 1996)

In normal conditions, platinum itself turns up in grass (*Lolium perenne*) in a fairly large protein fraction (160–200 kDa) mainly, whereas if there is PGM stress (additional inputs, like next to heavy-traffic roads) >90 % get bound to peptides of <10 kDa, however. For osmium, there are no data on biota concentration levels whatsoever, except a general 10 ppt statement for green plant photosynthetic organs (Markert 1996). Ru enrichment by algae from marine sources should involve redox cycling at MnO_2 interfaces and subsequent reduction/trapping by biogenic ligands, switching between hepta- and trivalent Ru, with the latter absorbed by *Porphyra edulis*.

Table A.2 Platinum concentrations in unpolluted plant samples

Element	Source	Level (ng/kg DM)	Remarks, authors
Ru	*Porphyra* algae	Several hundred	Does enrich in edible algae; marine background about 50 fM/l, radionuclide ^{106}Ru similarly abundant in Welsh part of Irish Channel
Rh	Spruce twigs	20	Leon et al. (1997)
	salad	210	Alt et al. (1997)
Ir	Egg shells (birds, crocodiles)	10–1,000	Higher levels only seen if test animals were exposed to Ir; Yang et al. (2001)
	Human tissue	About 20	Emsley (2001)
	Land plants	≤20,000	
Pd	Mammalian tissues	2,000	Emsley (2001)
	Tree leaves	Enrichment up to some 30,000	0.4 ppm in fresh leaves; assumed water content 92.5 %; Emsley 2001, apparently unrelated to Pd-rich soils
	Plants	Several 100–1,000	Most plants tolerate substantial Pd in water but it is highly toxic to water hyacinth
Pt	BCR pig kidney	40	
	Mammalian muscles	About 200	Emsley (2001)
	Orchard leaves (NIST 1571)	Below reliable determination	
	Spruce twigs	100–550	Voltammetry; Leon et al. (1997)
	Peeled potatoes	100	Alt et al. (1997)
	Salad	2,100	
	Flour	≤40	
	Wine	Up to 2.4 ng/l	

Starting with elemental Pt colloids (but taken from heavy traffic tunnels and Pt sponge catalysts), dissolution was attempted using aqueous-oxygenic conditions and various ambient (e.g. triphosphate) and biogenic (humic acids, adenosine, amino acids histidine and methionine). Polyphosphates reduced dissolution while the other compounds essentially had no effect, except for methionine. This probably is why Pt is taken up from the environment (where it would undergo fairly fast reduction into the nanocolloidal element, unlike with other PGMs, especially Pd) to an extent far lower than the other PGMs.

Glossary

Abiogenesis Formation of living beings/reproducing entities from organic matter by mere energy input and catalytic processing rather than metabolism, that is, not involving life-forms which are already around.

Ahrland B-type behavior In the 1950s, Swedish chemist Sten Ahrland made a quite simple distinction among different metal ions: those fluorocomplexes of which would be more stable than iodocomplexes (e.g. Al^{3+}, Ti^{4+}), or nitrile, pyridine complexes/solvates are more stable/do not undergo solvolysis in S, Se donor solvents like dimethyl sulfoxide, selenophene and others which behave the other way round: while fluorides of Ag^{+} or Pb^{2+} readily dissolve in water, the iodides are most hardly soluble, and thiophene etc. complexes of these ions remain unchanged upon dissolution in either acetonitrile, methanol or even water. The first group is called class A, the second class B. Of course there are intermediate cases between A- and B-types which then bring about isolable linkage isomers with ligands like thiocyanate SCN^{-} or cysteinate.

Asteroids Literally “small stars”, actually small planets (diameter range: about 1 m up to dwarf-planets, that is $<$1,000 km).

Autocatalysis A kind of catalyzed chemical reactions where the catalyst itself is among the range of reaction products, meaning the reaction kinetics is bound to speed up with time going on (→ “clock reactions”). When there are additional reactions interfering with autocatalyst, even more strange things may happen, like chemical oscillations.

Baudisch, Oskar (1881–1950) Austrian (Hapsburg monarchy)-American organic photochemist, radiation chemist and marine researcher. Did research on how and from which precursors nitrogen might be introduced into organic compounds upon UV irradiation (trying to understand the biochemistry of green plants), thereby making oximes, hydroxamic and nitronic acids from HCHO, higher aldehydes, sugars or alcohols by illumination. During these experiments on a mixture containing iron salts, nitrite, and CO gas, a product giving a positive ninhydrine test (red to pink colour) was obtained and assumed to be glycine, but keep in mind that ammonia, simple primary amines and oximes give the same test.

B. Markert et al., *Chemical Evolution*, DOI 10.1007/978-3-319-14355-2

Belousov-Zhabotinsky oscillator A chemical oscillator first described in 1951 by Russian chemist and biophysicist Boris Pavlovich Belousov (1893–1970). In 1960s, doubts that such reactions could exist at all were decreasing for theoretical reasons, prompting Russian physicist Anatoli M Zhabotinsky (1938–2008) to re-investigate this oxidation process in more details. Citric acid or similar CH-acidic compounds (malonic acid, cyanoacetic acid, 2,4-pentanedione, and others) are oxidized by bromate in mineral acid solutions to eventually yield brominated hydrocarbons, -carboxylic acids, HCOOH and CO_2. Oscillating redox conditions are indicated by color changes of the 1e-redox relay catalyst.[2] Zhabotinsky not only reproduced Belousov's little-recognized work but discovered chemical waves and optical as well as chemical excitability (e.g. by a silver wire put somewhere into the oscillating system which cleaves bromine-containing intermediates) and made a first mechanistic and mathematical model of the events.

Big Bang The event in which the Universe, and spacetime itself got started from a state of almost infinite density and temperature. The situation before cannot be known for sure as causality is suspended "before" and during this event.

Biogenesis The event(s) of spontaneous formation of life from inanimate matter on some planet or moon. → abiogenesis.

Biogenetic law The rule that morphological features of larvae of animals resemble earlier stages in evolution, with young embryos of humans (or dogs, or birds) first looking like a fish larva or tadpole, to become more specific in appearance only much later.

Biological System of the Elements (BSE) A grouping of elements according to biological function and abundance correlations in a set of given organisms (originally, green plants).

Biomethylation Transformation of inorganic binding forms of either non-metals (Ge, As, Sb, Se, Te) or metals (Tl, Sn, Bi, Cd, Hg, Pt, and others) by different organisms and pathways (organocobalt complexes or sulfonium salts [S-adenosyl methionin]) to produce neutral (then volatile) or cationic (Tl, Ge, Cd, Hg) lipophilic organic species. Large risk of damaging central nervous system, especially with CH_3Hg^+. Toxicity of products does vary widely but neutral volatile non-metal oligomethyls tend to be very short-lived in daytime air (which contains OH radicals).

Biomineralization Mostly multicellular[3] living beings can produce certain minerals which then fortify their bodies against mechanical strain or fulfil other

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[2] In Belousov's original experiment, this was cerium (Ce(III) being colorless while Ce(IV) is orange-yellow), later Mn(II)/phosphate- or ferroin $[Fe(bipy)_3]^{2+}$ (red or blue) or the analogous ruthenium complex $[Ru(bipy)_3]^{2+}$ (which is an effective photosensitizer capable of inducing chemical waves also) were applied for providing more conspicuous color changes during oscillations.

[3] Some foraminifers produce exoskeletons of either silica or strontium sulfate. Deposition of iron oxides or ZnS by iron-oxidizing bacteria or archaeans does not occur in a spatially controlled manner and thus is not considered biomineralization.

mechanical functions, e.g. in teeth. Typical products are hydroxyl apatite (vertebrate teeth), calcium carbonate (calcite in vertebrate bones, aragonite in mollusc—reinforcing structures [snail or clam shells]), needle-shaped silica (in many kinds of plants).

Bruno, Giordano [congregational name, originally Filippo B.] (1548–1600) Dominican monk (active 1565–1576) and Renaissance scholar. Worked on topics in biology, astronomy (shortly before invention of refractor telescope) and philosophy. Arrived at the conclusion that stars are objects similar to Sun, probably surrounded by planets also and there is a very large to infinite number of other worlds inhabited by living beings. As this rose questions by (also Lutheran, Calvinist[4]) Churches whether these beings would also require (additional, independent from Christ's stay on Earth) measures of salvation, he got sued by Inquisition. Finally, he was incarcerated and tortured at Florence and assassinated (burned on the stake) for his views in 1600. One of only two scholars of natural sciences (rather than humanities, political sciences or philosophy) agreed to have actually martyred for maintaining a scientific position (the other being Soviet geneticist Nikolai Vavilov [1884–1943] who was killed in Gulag for his constantly opposing Mitchurin-Lyssenko party (i.e. CPUSSR) genetics).

Calvin, Melvin (1911–1997) American biochemist who detected the pathway by which CO_2 is connected to precursors of sugars (glyceric acid-, ribulose phosphates) in photosynthesis by means of ^{14}C labelling and autoradiography of chromatograms. Nobel Laureate (chemistry, 1961). Later (in 1959) coined the term "chemical evolution" in the sense we use it throughout this book. Besides, he did pioneering work (Garrison and Calvin 1951) on radiation-chemical formation of "interesting" organics from CO_2 using $Fe(II)_{aq}$ as an internal electron and proton source. Also took part in first → SETI-conference in 1961.

Catalysis Enhancing kinetics of a chemical reaction by adding some agent which does not remain bound in the final product(s), decreasing activation barriers of this reaction. If several functional groups are present in a more complicated substrate molecule or ion, catalysis by a given agent will enhance just one or few of the pathways then possible, increasing selectivity of a transformation. Catalysts can be homogeneous (i.e. gaseous or dissolved in some fluid) or heterogeneous (exhibiting solid or liquid (immiscible) active surfaces, and have any degree of internal chemical complexity (from hydrated proton [acid catalysis] over simple complexes, molecules [e.g. 2-hydroxinitriles] up to macromolecules [enzymes]). They cannot change position of a chemical equilibrium, hence always promote forward and backward reaction (microscopic reversibility) → autocatalysis.

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[4] In trying to escape Inquisition for his views, he spent some time teaching and preaching at London, Wittenberg, Geneva, Zurich and various sites in pro-reformation France also but did not earn effective protection there.

Celestial body Objects existing and moving in the skies, far off Earth's atmosphere. Includes all stars, planets, moons and associations thereof (galaxies, stellar clusters) but meteorites (former small asteroids) do no longer consist to this category of objects for being trapped by and on Earth.

Chemofossil Chemical compounds trapped and preserved in sediments which are of doubtlessly biological origins, indicating the former presence of living organisms at the site. Whereas e.g. many amino acids, porphyrines with no or little substituents might be formed abiotically (in chemical evolution) or/and come in with meteorites, there are other compounds, e.g. phytol, phytane (a periodically methyl-branched long-chain hydrocarbon and the respective alcohol produced by removing the side-chain of chlorophyll) which were never seen in simulation experiments but are produced by green plants, algae, photobacteria in tremendous amounts. Thus phytane in sediments more than 3 bio. years old offers the best indication of a rather advanced, "modern" way of doing photosynthesis. Of course, such compounds must be rather stable towards degradation or isomerization while fairly complicated. Thus they are almost involatile, requiring liquid extraction rather than evaporation for isolation if one would look for chemofossils e.g. on Mars (this is actually planned) or in Martian-origin or other meteorites presumed to contain traces of an extinct local biota.

Clock reaction An autocatalytic reaction where first one reactant (usually, a reductant, like sulfite HSO_3^- or thiosulfate) is completely consumed only then to permit a second reaction between the by-product (reduced oxidizer, in Landolt's [1886[5]] classical iodate-based system iodide ion) and remaining oxidant. This latter reaction then is rapid and causes distinctive changes of color (production of elemental iodine by comproportionation of iodate and iodide being indicated by starch becoming blue) or rapid precipitation (of As sulfides when thiosulfate is oxidized by As(V), first producing $As(OH)_3$ and tetrathionate, then decomposing the latter). The delay depends on concentrations of the reactants, starting pH, temperature and was given in a formula by Landolt in 1887 which holds provided sulfite concentration is less than 1/3 of that of iodate. Clock reactions sometimes can be modified to become oscillators by adding another (competing) reductant.

Comets Small objects (some 100 m–30 km nucleus diameter) consisting of ices mainly which did condense from the protosolar nebula at the very outskirts of the Solar System. After being redirected into highly eccentric orbits by the large planets, having perihelia at least within the Jovian orbit, these ices and included dust start evaporating every time the comet approaches Sun, making it increase its brightness dramatically until all volatiles have removed. Then it either falls into small pieces or keeps on its previous eccentric orbit as an Apollo-Amor- or Aten-group asteroid, eventually hitting any of the terrestrial planets or the Moon.

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[5] Hans-Heinrich Landolt (1831–1910), Swiss chemist. Original author/editor of the physicochemical tables Landolt-Börnstein, (1st ed. published in 1883).

By such impacts before being completely stripped of volatiles, comets brought most of water to both Earth and Mars.

Complex formation constant In solutions, metal ions or atoms and → ligands combine to form associates in which the solvent is replaced by the ligands; these associates are distinguished by specific chemical formulae, that is, they are daltonide compounds, e.g. $[Fe(CN)_6]^{3-}$ with a stoichiometric ratio iron:cyanide = 1:6. At low (er) ligand concentrations (or in solvents which are strongly coordinating themselves, like water, or nitriles) only one or some solvent molecules might be replaced by the ligands, giving rise to a series of equilibria[6] which connect different complexes containing different numbers of the same ligand bound to the same cation. As always, these equilibria can be described by an equilibrium constant (or, in fact, several ones which may be multiplied to determine a "gross" or "total" one) which is best determined by electrochemical methods. It can be predicted by an equation containing the → electrochemical ligand parameter. Among divalent ions bound to bidentate → ligands, complex formation constants usually behave like $M = Ba \approx Sr < Ca < Mg \approx Mn < Fe < Co < Ni < Cu > Zn \approx Cd$ (Irving-Williams[7] series) which is why Cu^{2+} can remove all other divalent ions from their complexes, the main reason of Cu toxicity in uncontrolled situations → Wilson-Menkes syndrome

Curiosity The nickname of rover Mars Science Laboratory. Being equipped with six wheels and almost as big as a common car, it was deployed on Mars in August, 2012. Driving autonomously (unlike former rovers which required detailed instruction from Earth), it can sample and analyze both fine-grained martian materials and solid rocks (drilling, laser ablation) and do quite a range of modern analytical chemistry as well as taking photographs and obtaining a wealth of other data → rover.

Doebereiner, Johann Wolfgang (1780–1849) German chemist, pioneer of applied catalysis (flame lighter), who did arrange most of the elements then (in 1829) known in a precursor of the Periodic System of Elements ("rule of triads"), thus predicting the atomic weight of bromine just after it being discovered.

Dwarf-planets Big asteroids which use to be almost spherical for their own gravity but the latter is too weak to clean orbits near to them. Except for Ceres, all D's are located in the → Kuiper belt, → planet.

Earth ***Early***: The planet between its formation and beginning of the enrichment of the atmosphere with free oxygen or other oxidants, that is, 4.5 to some 2.4 bio. years BP.

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[6] This is the more common case; sometimes the fully coordinated species is so stable as to preclude isolation of any intermediate which still retains solvent molecules, like hexacyanoferrates and some other cyanometallates in water or $ZnCl_4^{2-}$ in dimethyl formamide (DMF): you will neither isolate (as whatever salt) nor even find by spectroscopy any appreciable amount of cyanoiron cations in water or $ZnCl^+$, solvated neutral $ZnCl_2$ (like it would be with other metal ions) in DMF, it rather is going to be the fully solvated cation besides of hexacyanoferrate or $ZnCl_4^{2-}$.

[7] Robert J.P. Williams (born in 1926), now considered nestor and mastermind of bioinorganic chemistry.

Super: High-density terrestrial-like exoplanet consisting of rocks and metals. Mass >1 up to some 10 Earth masses, diameter about one to twice that of Earth or Venus. Similarity to Earth and habitability for living beings doubtful as these bodies should retain very massive atmospheres, with results perhaps similar to conditions on Venus even when the stratosphere is cold.

Ecological niche An ecological niche is a kind of "function" or resource a certain species makes use of in an ecosystem; f.e., passive or semipassive filtration of phyto- and zooplankton in the ocean may be effected by either sponges, gorgonia, jellyfishes or plankton-eating fishes (as a rule, fish larvae or, quite on the contrary, very big ones, which however do rather active filtration). These species, if present next to each in comparable conditions (not all of them will stand faster water currents), thus will compete with each other for the resource, and by evolution, succession or migration, either replace each other or switch to another resource (if only partly) sooner or later. Hence the number of coexisting species in the same ecological niche is small at best. In a newly formed biotope, evolutionary radiation to occupy lots of different niches can be very fast, e.g. with cichlid fishes in Lake Malawi. Metabolic pathways opened during late chemical and biological evolution also correspond to ecological niches while conditions or "fitness" for the above competition also can (in principle) be estimated by → SNA arguments, analyzing the effects of different feeding strategies (depending on food items) on matter flow.

Electrochemical ligand parameter Different complexes of the same transition metal ion may differ in colour although their formal composition is identical and LMCT bands (which often are located far in UV) can be neglected in these cases. This does indicate that excitation of electrons from the metal ion to higher levels (dd band excitation) or passover to/from some reaction partner depends on which ligands are linked to the central ion. Besides of optical spectroscopy ("ligand spectrochemical series") the interorbital energy differences can be measured by determining energetic aspects of direct electron transfer from or into the upper orbital, exchanging electrons with anodes (rarely, cathodes) or oxidants. This is done e.g. by using an anode which adsorbs the complex, thereby oxidizing or reducing it by electrochemical means, or applying an oxidant which is selected as to change oxidation state of the center rather than exchanging ligands in an oxidative manner, say, chlorate or PbO_2/acid acting on fluoro complexes. Except for some complexes of osmium, the effect turns out to be additive, that is, redox potential changes caused by replacing (e.g.) three ligands with three (among them identical) others are three times as large as for replacement of one ligand only. Thus, if considering turning one homoleptic complex into another, you can divide the total redox potential change (in octahedral complexes) simply by six (or by three, if bidentate ligands are concerned) to obtain the redox potential change from one such ligand exchange. Therefore people started in the 1970s to construct tables on this effect which closely resemble the colloquial electrochemical series, and were duly called "ligand electrochemical series", using various standard transformations like Cr

(0/+I) in pentacarbonylchromium complexes, Mo(0/+I) in bis-diphosphane-mono-dinitrogen Mo complexes, Mn(I/II) in mixed carbonyl/isocyanide complex cations of manganese, and eventually (Lever 1990) Ru(II/III) in quite diverse ruthenium complexes. While—of course—the exact size of the ligand exchange-caused electrochemical effect does depend on the very system (all these tables mentioned before are based on d^6/d^5 redox transitions in octahedral complexes), and also on solvent, all these scales are linearly correlated to each other, and that by Lever is the one comprising the largest number of different kinds of ligands, moreover includes the largest number of biochemically relevant ligand (-kind)s. Thus the latter Lever Ru-based scale (which in fact was already "extended" by correlations using data of the above-mentioned other plus some osmium or pentacyanoferrate complexes linked by linear correlation) was selected to predict complex stabilities.

Elements ***Beneficial***: An element which enhances vitality or reproduction, growth rates of organisms exposed to it, e.g. with using REE salts for better germination and fruit-production performance of trees.

Essential: An element which cannot be removed from (supply to) an organism without keeping it from either survival, reproduction or growth, or (with animals) changes of its behavior. Resupply of the element will remove the above symptoms. In certain cases, some elements are required during certain parts of the life-cycle (e.g. metamorphosis in amphibians) only while others are needed by almost all living beings.

Evolution ***Biological:*** Change of living beings by mutation of nucleic acids and selection among thus slightly different phenotypes responding in a random process towards ambient and changing environmental conditions and challenges.

Chemical: Transformation of organic and other chemical compounds by absorption of energy and condensation processes to afford both monomers relevant for biological processes (like amino acids or sugars) and polymers which might eventually (arrange into an entity) capable to reproduce (→ biogenesis, → LUCA).

Cosmic: Gradual transformation of matter during expansion and aging of the universe. In quantitative terms this process still is rather in its beginnings even though the rate at which new (especially massive) stars are produced did massively decrease billions of years ago. Therefore cosmic evolution in terms of transformation of elements from Big Bang (H, He, traces of Li) and back-release into → interstellar medium almost did come to a halt.

Mineral: Response of solid and dissolved chemical compounds to chemical effects by the biota insofar as they cause formation and precipitation of minerals (mainly, oxidized ones, like sulfates and arsenates) which did not exist before. A "fast-forward" version of M.E. occurs when air-filled caves are driven by miners into reducing phases (like coal, sulfide- or arsenide minerals).

Equilibrium The final state of a process which can occur both in the given and reverse direction. At equilibrium, no more free energy can be obtained from the system (be it chemical or other), and there can be no more features of irreversible thermodynamics like coupling effects or chemical oscillations while, e.g. isotopic exchange keeps on occurring.

Frasnian-Famennian transition A series of two or more mass extinction episodes in upper Devon ages, the Kellwasser and Hangenberg events some 374 and 360 mio. years BP the latter of which also hit terrestrial organisms. In the ocean, large amounts of anoxic shales are formed, indicating sulfate reduction after oxygen depletion up to close to the ocean's surfaces, particularly in warm rather than cold(er) waters. Near the surface, there were also thorough changes: between both events, first tetrapods evolved while placoderm armoured fishes and the majority of jawless ones got extinct. Trilobites and ammonites were also hit severely, the general effect being much more massive than it was in the KT event. The triggering reasons of the FF transition(s) are unknown but possibly linked to CO_2 and nutrient depletion by plants covering most of solid land now.

Fischer-Tropsch-type (FTT) In 1925, Franz J.E. Fischer (1877–1947) and Hans Tropsch (1889–1935) developed a method to catalytically convert a CO/H_2 mixture into long-chained hydrocarbons, alcohols, fats etc. by means of heterogeneous catalysis based on Co, Fe, Ni, or Ru, each supported on porous oxides like kieselguhr, alumina, or zeolithes.

GC-MS Gas chromatography combined with (subsequent) mass spectrometry (a "hyphenated method" of chemical analysis). A powerful means of chemical analysis which also permits to identify unknown products only requiring they are (a) volatile below 400 °C and (b) do not chemically react with the cladding of the capillary adsorbing the vapors. Now even applied in outer space as an automated system (on Mars).

Golden Age of Earth exploration The era of discoveries from about 1480 to mid of seventeenth century (Americas, S Africa, Australia, etc.).

Helmont, Jan Baptista van (1580 [or 1577]–1644) Flemish physiologist, chemist and physician. The first to do quantitative experiments on plant growth, weighing a seedling and the willow tree and the soil mass 5 years after. Established an enhancement of both carbon and water within the plant in the process but did not account for possible sources of the former even though he himself had introduced the term "gas" and the existence of gases other than air, water vapour into scientific literature. First to discuss activity of chemical agents (equivalent to modern enzymes) in digestion of food in poikilothermic animals (translated into English in 1662) and discovered "gas sylvestre" from various sources (fermenting must, beer and burning charcoal) to be identical (CO_2) and obstructive of breathing. Refuted old teaching of four elements, retaining just air and water besides some also nowadays considered elements.

Herrera's sulphobes In early twentieth century, Mexican chemist Alfonso Luis Herrera (1868–1942) started investigating the reaction between aq. HCHO (already then known to give sugars in certain conditions) and ammonium thiocyanate (known to be separated by volcano exhalations). Besides of several amino acids and other organic products, colorful hollow structures arise (similar to microspheres or lumispheres prepared from amino acids by thermal treatment) which are excitable to some extent, although not alive. Recent repetitions of this work gave several amino acids while the structure of the polymers still is not known.

Hurwitz method Eigenvalues of a matrix describing operations which convert something into something else are calculated and investigated whether they are real or complex numbers. In "classical" matrix stability analysis, the individual terms of a matrix can have continuously changing values, necessitating the full-scale mathematical apparatus to be used. If there is stoichiometry however, like in chemical or nuclear reactions, the single values in the matrix must be integer, permitting to replace analysis of entire event space with considering a discrete grid of points located in it. Then quite a number of theorems apply which in term allow for discussing (and predicting!) behavior of some stoichiometric system; these theorems were deduced by Bruce Clarke in 1974/1975 and form the backbone of → stoichiometric network analysis, allowing to predict the behavior of a metabolic pathway, its persistence in evolution (→3F-rule) or that of an entire ecosystem with more or less pronounced coupling to matter sources and sinks across its ecotones.

Intermediates Chemical reactions often occur in several steps which connect/transform the educts mixed up to the products eventually isolated. F.e., if thiocyanate is reacted with iodate according to $IO_3^- + SCN^- + 2H_2O \rightarrow I^- + SO_4^{2-} + HCN + H_3O^+$ (irreversible reaction), formally three oxygen atoms and six electrons are transferred between I and S atoms, finally yielding sulphate, iodide, and HCN, plus acid but this does not happen in one step, rather HO-SCN and cyanosulfate $NC\text{-}SO_3^-$ can be pinpointed as intermediates (more details can be learned by using isotopically labelled [^{18}O-enriched] iodate or water).

Interstellar Medium (ISM) The vast volume in between the stars (within galaxies or globular star clusters), but not between galaxies. There is a small yet relevant concentration of atoms and molecules and molecular ions several orders of magnitude higher than in the intergalactic medium. Main component of ISM matter is hydrogen (either ionized or atomic **or** completely as H_2/H_3^+).

Kuiper-belt dwarf-planets The largest members of the Kuiper belt, namely Pluto, Eris, Sedna and Haumea with their respective satellite systems (Pluto has at least five moons, Haumea two). While not necessarily sphere-shaped (e.g. Haumea) because these objects are so cold as to preclude creeping of material, they follow "well-cleaned" orbits–cleaned by their gravitation (most of their satellites are likely to be captured also. Diameters range from some 1,300 to 2,300 (Pluto, Eris) km, with Pluto being the biggest while Eris is little smaller yet more massive, indicating it contains a larger nucleus of minerals and possibly metals. Pluto is the only one among these dwarf-planets which has a substantial atmosphere. Off the Kuiper belt, there is only one other dwarf-planet in the Solar System: Ceres.

Ligand Binding (Latin ligare = binding something to...) partner of a metal ion or—atom in some complex, normally providing two or more electrons for binding via inert electron pairs or (side-on π-binding) double or triple bonds of alkenes, alkynes, arenes (toadstool- or sandwich complexes) and their heteroatomic derivatives. In metalloproteins, an entire protein macromolecule acts as a ligand, with the actual binding caused by side-chains of amino acids in the protein. Ligands can be anions (from atomic ones like halides or sulfide over small molecular ions [CN^-, SR^-, PhO^-, $H_2NCHR'COO^-$ {bidentate}, $C_2O_4{}^{2-}$ {bidentate}, SCN^-, $NO_2{}^-$ {both capable of either bridging between metal ions or forming linkage isomers}] to macromolecular ions like humic acids) or neutrals (e.g., CO, PF_3, phosphanes, arsanes, pyridine, nitriles), rarely—as they "should" donate electron (-pair)s to the metal center—cations.[8] Of course, cations in larger molecules might readily behave as ligands using other neutral or anionic sites; e.g. the essential proteinogenic amino acid arginine contains a cation (guanidinium ion) in the side chain but will bind to metal ions—also in quantitative terms of → complex formation constants—much like glycin(at)e or other simple amino acids do.

Lotka kinetics A theoretical (Lotka[9] 1910) model which brings about abundance oscillations of the species/intermediates involved by invoking consumption of one by another which increases abundances of the latter (higher rate of reproduction in predators if there is plenty of food [prey] in one season).

LUCA Last universal common ancestor, a being postulated to have existed just before → biogenesis provided there was just one "successful" way into biogenesis. Then LUCA would be the common precursor of whatever lives on Earth now or became extinct during the last >3.5 bio. years.

Leucine-zipper A common structural motif in proteins containing zinc. First described self-replicating peptides were derived from leucine-zipper sequences in 1996, and autocatalysis in replication was shown to involve the peptide (consisting of 32 amino acid residues) as a template.

Maastricht-times The latest phase of Cretaceous, some 69–66 mio. years BP, just before extinction of dinosaurs and ammonites. This was the time when both *Tyrannosaurus rex*, the biggest land-dwelling predator ever, and huge (wing span > 11 m) pterosaurs *Quetzalcoatlus ingens* and *Hatzegopteryx* evolved.[10]

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[8] Exceptions concerning stably binding cations include trimethyl sulfonium ion (analogous in electronic structure and binding mode to phosphanes) bound via the formally cationic sulfur atoms (which still has a vacant electron pair) to low- or zerovalent Mn or Cr or acyl ligands the "actual" charge of which is as doubtful as in the case of NO but probably closer to neutral than representing bound RCO^+ or NO^+.

[9] Alfred Lotka (1860–1940), American mathematician and biologist.

[10] Some people take these giant forms, and similar ones of ammonites forming oddly-shaped hulls, as a symptom of crisis predicting a catastrophe. But how should dinosaurs or ammonites "preview" something to happen over a million years or so? Small dinosaurs (other than birds) went extinct also, and the biggest sauropods lived in upper Jurassic and earliest Cretaceous (of Argentina).

Maillard polycondensation A crosswise reaction between sugars, including polysaccharides (starch, pectin) and amino acids or peptides which can be induced by either heat (then it is simply baking) or pressure[11] (the system loses volume in the process), thereby limiting the range of pressures where life as we know is possible. Produces brownish, insoluble polymers (baking!) which degrade into acrylic amide etc. upon further pyrolysis. Can be inhibited by amine oxides (in deep water fishes, trimethyl amine N-oxide [TMAO]), the latter keeping them from being fried at local temperature (+2 °C) already. TMAO toxicity becomes intolerable below 8,200 m depth for these fishes which are best adapted to extreme depths, limiting the range where vertebrates can live while there are worms, holothurians, jellyfishes, shrimps etc. down to $>$10,000 m.

Mantle The layer in between crust and core of a (terrestrial) planet or dwarf-planet big enough to have seen differentiation. Earth's mantle mainly consists of high-pressure Mg, Fe silicates like olivine. Though being solid rather than "really" liquid, it has to transport more heat than possible by conduction, causing convection which is the cause of Earth's magnetic field: convection of a medium which conducts electricity (normally, olivine is an isolator but under such large pressures it becomes first a semiconductor and then a metal).

Meerwein[12]-Ponndorf-Verley reduction Hydride transfer from a secondary alcohol (commonly the simplest one, 2-propanol[13] which is also used as solvent) to ketones or aldehydes, catalyzed by Al(III)- or Ti(IV)-alcoholates to produce the respective reduction products, primary or secondary alcohols. The reaction does not occur with readily enolizable ketones, e.g. cycloketones or 2,4-pentanedione, and it is reversible (Oppenauer oxidation, done by heating an alcohol dissolved in acetone which contains $AlCl_3$ or $TiCl_4$).

Meyer, von, Julius Lothar (1830–1895) German physician and chemist. Starting in toxicology (PhD thesis on effects of CO on blood), he switched to chemistry. Pioneering the periodical system elements (along with Mendeleyew with whom he cooperated) and structural chemistry, i.a. discussing a cyclic structure of benzene already in 1865. Founder of the Zeitschrift für Physikalische Chemie (the first on this topic) in 1887, together with Mendeleyev and W. Ramsay (who was later-on, discoverer of most noble gases).

Mendeleyev, Dimitry Ivanovich (1834–1907) Russian chemist, pioneer of spectroscory and applied petrochemistry, crude oil technology. Co-author of the periodic system of elements (with → J. Lothar Meyer) who predicted

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[11] In a series of classical experiments, the pioneer of high-pressure physics and -chemistry Percy Howard Bridgman (Nobel Price in 1946) exposed slices of meat and raw, thermally untreated yolk/ sugar mixtures to pressures of several up to 30 kbars, obtaining "grilled" meat and baked foods though working well below ambient temperature.

[12] Hans Leberecht Meerwein (1879–1965), German organic chemist. Also worked on carbenes, rearrangement reactions and introduced diazoalkanes, tertiary oxonium salts like $(CH_3)_3O^+(BF_4)^-$ as powerful alkylation agents into the method list of preparative organic chemistry.

[13] 2-propanol is cheapest by far, and its oxidation product, acetone, is highly volatile, hence can be readily removed from the reaction mixture by reduced pressure, allowing completion of this reaction in conditions which protect also very labile reaction partners (ketones, aldehydes)

chemical and physical properties of elements then "still missing" in the PSE framework, like Ga, Sc, Ge. Admitted women to his lectures already in the 1870s.

Meteorite An asteroid which was captured and fell down onto the surface of some planet (so far, m's were detected on both Earth and Mars), thereby losing most of its mass by atmospheric ablation. If it burns completely, with nothing but microdust to reach the ground, it is called a shooting star.

Miller and Urey in their seminal 1953 experiment Stanley Miller (1930–2007) and his PhD supervisor, Nobel Laureate (1934, for discovery and working out applications of hydrogen isotope deuterium) Harold C. Urey (1893–1981), jointly designed the first experiment in 1953 to investigate organic products from putting energy (here, a spark discharge) to a mixture of reduced (hydrogenated) gases, detected glycine, more complex amino acids and several other compounds. Miller became the principal researcher in chemical evolution for the rest of his lifetime, renowned for rigorous experimental demonstration what will or will not happen in favor of—however chemically plausible—speculations on pathways and products of respective organic chemistry. Urey returned to geochemistry, developing a method of determining paleotemperatures, paleoclimates by (oxygen) isotopic fractionation.

Moon The big, permanent[14] natural satellite of Earth. Diameter 3,476 km (27 % of Earth), mass 1/81 of Earth (which is an exceptionally large value and owes to its peculiar way of formation). The brightest object in nocturnal sky, yet lacking an atmos- or hydrosphere.

NASA National Aeronautics and Space Research Administration, a civilian authority founded in 1958, just after the first successful launches of satellites (which had been delayed due to rivalries among the different branches of US military who were supposed each to supply rocket hardware for some satellite launch, but would not like to see this integrated into a satellite-launch project run by somebody else).

NMR Nuclear-magnetic resonance (spectroscopy), a method to determine the interaction of nuclear spin (in nuclei which have either an odd number of protons [odd-Z nuclei, e.g. all isotopes—stable or radioactive—of Al, K, Rb, La and so on] or an odd number of neutrons [^{13}C, ^{17}O, ^{33}S, ^{43}Ca, ^{49}Ti, ^{57}Fe etc.]) which is aligned by an outer magnetic field with the electrons surrounding it. In this magnetic field (which is very strong [5–10 T]) the spin of the above nucleus can take only two or very few different orientations among which it is flipped by radio electromagnetic radiation while the electrons around "shield" it. Even though only the outermost electrons are involved in chemical binding or

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[14] Among the large number of asteroids orbits of which resemble that of Earth (some of which are locked in Lagrange points ahead [Earth Trojans]) one or another gets trapped in a temporary unstable orbit ("horseshoe orbit") around Earth, adding a second, third... natural satellite to the list. But this does last for a few to a few hundred years only, and all known objects of this kind are smaller than a car (!). From these orbits, they will return to common solar orbits, while the chance or risk of impact to Earth (or Moon) is next to zero.

removed by oxidation (except for REEs and actinoid elements), changes of electron density by altered chemical binding or oxidation/reduction will cause changes down to where the nucleus is, causing the radio frequency where the spin-flip causes an absorption to alter. This radio frequency is measured against some standard, be it the neat element or some compound (e.g. tetramethyl silane $Si(CH_3)_4$ for both ^{13}C- and ^{29}Si NMR or $CFCl_3$ for ^{19}F-NMR). Interestingly, even apart from the above cases the range of shifts which are possible for different binding forms of one element differ much more for heavy elements like molybdenum, platinum, or rhenium (frequency changes can be of order 0.5–1 % here) than with light elements for which one would assume chemistry to happen fairly close to the nucleus (although these atoms are not too much smaller than the previous ones, there are few, if any electrons "in between" the chemical bonds and the nucleus): for H, D, ^7Li, ^{13}C or ^{15}N NMR shift effects are of order 10^{-5} only. NMR can be used both to determine chemical structures (by analyzing interactions with spins of other nuclei in the same molecule or ion) and to follow chemical reactions: to give a simple example from our sphere of interest, if you mix cyanide, HCHO and aqueous ammonia, you can observe two signals of each ^{13}C and ^{15}N in the very beginning, directly after mixing while then additional ^{13}C- and ^{15}N-signals belonging to glyconitrile, aminoacetonitrile and—after hydrolysis beginning—glycin(at)e will appear for either NMR-active nuclide, possibly additional ones from iminodiacetonitrile and iminodiacetate also. Of course, frequencies for the different primary, secondary amino groups or the carboxylates will not differ too much from each other while there is a substantial distance between cyanide carbon and that of a nitrile or formaldehyde and a CH_2 group. The effect is related to both chemical kinetics and changes of chemical properties (in some cases, "umpolung") of certain (in this case, carbon and nitrogen) atoms (the difference between nitrile N and CN^- anion in terms of ^{15}N NMR will be small but on hydrolysis of glyconitrile or AAN this latter signal vanishes completely to be replaced by that of NH_4^+, of course).

Ontogeny The pathway of shaping an animal from egg or very young larva.

Oparin and Bernal (1920s) Alexander I Oparin (1894–1980), John D. Bernal (1901–1971) and John B.S. Haldane (1892–1964) described possible pathways into making organic compounds relevant in biochemistry from atmosphere and hydrosphere of early Earth in then merely theoretical studies during the 1920s, with Bernal pointing out the possible role of clays in catalysis, production of polymers.

Opportunity (→ rover)

Oscillation Periodic switching between several different states of a given system neither of which is stable but does return to the other(s) periodically as long as there is sufficient "driving force": in a pendulum, the swinging mass is fastest when at the lowest point but therefore is bound to run on until returning ($v = 0$) when all this kinetic energy was converted into potential energy (the swinging mass being elevated now). Similar considerations hold for mutual charging and uncharging of a capacitor and an induction coil in electrical resonator arrays, or transmission and absorption of radiation in matter of variable density next to the surface of high-mass variable stars (cepheids). Chemical oscillators are more difficult to understand than those physical ones. Time-scales of oscillations can vary widely.

Paracelsus Original name Theophrastus Bombastus of Hohenheim (about 1493–1541): Swiss-German medic, philosopher, theologian and alchemist. Famous for the first statement on toxicology: everything becomes toxic if only the dose is large enough. Supported rebels in German peasant's war (1525). Started teaching in German (at Basle) rather than Latin to better spread then modern medical knowledge (transcending old teaching still based on Hippocrates and Galenos). Probably died of mercury poisoning, with very high levels still present in his bones.

Pasteur rule that living beings originate from other living beings French medic and pharmacologist Louis Pasteur (1822–1895) gave proof that if one precludes access of bacteria or insects (lying eggs) to food samples, there will be neither decay by rotting nor growth of new insects on/in these samples. Invented and introduced first vaccination against rabies.

Pauli's law Austrian physicist Wolfgang Pauli (1900–1958) who also postulated existence of the neutrino showed that particles with half-integer spin (called fermions in honor of Enrico Fermi [1901–1954], another Nobel laureate in physics) behave somewhat oddly: they cannot reside in identical states (energy, spin, etc.) within a closed volume, which particles with integer spins (bosons) can well do. Therefore, ≥ 3 electrons or other fermions will (have to) spread over several energy levels, producing (a) weakly bound states of some of them and (b) an internal pressure acting against reducing the volume of the system (electron degeneracy pressure). That is why there is solid, hardly compressible matter which nevertheless readily undergoes chemical reactions. Two or 2*n fermions might combine to jointly act as a kind of super-boson, e.g. in superconductivity (Cooper pairs of electrons) or in atomic nuclei (both protons and neutrons are fermions, too).

Periodic System of the Elements (PSE) An arrangement of the chemical elements into groups according to similar chemical properties, e.g. low-melting, volatile, extremely reactive soft light (alkali) metals or (almost) inert noble gases or rare earth elements. Designed in late 1860s by → L. Meyer and → D. Mendeleyev. More recently extended to take account of similarities among very heavy elements ($Z = 89 \ldots 103$; actinoids, subgroup introduced by nuclear chemist and prolific element-maker Glenn T. Seaborg [1912–1999]), the only person ever in honor of whom an element [seaborgium, $Z = 106$, homolog of Cr, Mo, and W] was named while he was still alive. Now the PSE is complete (there are no more "voids" for missing elements after $Z = 117$ [a still nameless halogen] which was prepared by high energy ^{249}Bk+^{48}Ca collisions) until novel "super-heavies" with $Z \geq 121$ will be prepared (g-subgroups).

Photochemistry Chemical transformations, e.g. splitting of bonds, ring opening or—closures, redox reactions among different parts of a complex or molecule, brought about by visible light or UV radiation. The most significant photochemical processes in biology are photosynthesis (reduction of CO_2 by electrons usually taken from photooxidation of water) and the ring-opening of steroids turning a 1,3-cyclohexadiene into a hexatriene to afford vitamin D varieties.

Phylogeny The origins of organisms which live now or are extinct themselves in terms of their own precursors in evolution. Normally phylogeny is considered only within one kingdom of multicellular organisms (i.e. not looking back beyond the appearance of rather modern animals in Cambrian times), with the ancestors of animals, green plants and fungi having separated about 1.3 bio. years ago according to molecular (mutation rate) data.

Planets ***Gas:*** Massive (some ten to >2,000 Earth masses), low-density (<2 g/cm^3) objects which mainly consist of gases/highly compressed fluids around a small silicate rock/metal core. In solar system: Jupiter, Saturn, Uranus, Neptune. ***Terrestrial:*** Rocky planets with large metal cores, low total mass (about 0.03–10 Earth masses), density exceeding that of common rocks (3.5 to >7 g/cm^3) and fluid covers which are just a negligible part of total mass. In solar system: Mercury, Venus, Earth, Mars.

Dwarf: Very small rocky or ice-dominated planets/asteroids, spherical yet too small to control/"clean" the environments of their orbits by their gravitation. Diameter some 700–3,000 km, mass between several 10^{-4} and 10^{-2} Earth masses. In solar system: Ceres (biggest inner-zone asteroid), → Kuiper belt dwarf planets.

Popper, Karl (1902–1994) Austrian-British philosopher concerned with problems of theory of sciences: what are meaningful scientific questions and experiments (condition of possible falsification of a hypothesis)? Also involved with historical sciences, political philosophy, and neurosciences ("The Self and its Brain", with Nobel laureate Sir John C. Eccles).

Prebiotic Organic chemistry predating and possibly leading to → biogenesis.

PRX (→Pyrolytic Release Experiment)

Pyrolytic Release Experiment (PRX) One of the first experiments directly done on another planet (Mars) to look for life or (autotrophic) metabolism in soil samples from Martian surface (taken by [stationary] Viking lander probes [in 1976/1977]) labeled by ^{14}C. A two-step protocol permits to distinguish in analysis labeling gases (+methane) simply re-released by heating (e.g. of carbonates) from possible (pyrolytic remains of) organic compounds (or HCN, C_2N_2, COS…) produced in the fines with or without illumination (organic compounds or HCN, C_2N_2, COS are retained and then thermally oxidized in a CuO-loaded column giving rise to a second peak of radioactivity in analysis). Results of experiment are sensitive to addition of (excess) water, constraining possible mechanisms apart from extant biology. Results could be but partly reproduced in the lab using different iron-containing minerals or clays; they may or maynot (more likely) indicate activity of extant Martian life and are compatible with the more recent experiments done there.

REE (rare earth elements) Heavy (except for Sc, Y, Eu), very reactive, normally trivalent[15] metals which are not rare, rather ubiquitous but rarely form enriched minerals.

Reference Man A human being taken to have an average elemental chemical composition. Varieties of reference man are also used for models of pharmacokinetics, calculations of decompression tables in diving (here, the relative amounts of muscles, fat, and highly perfunded tissues are crucial) and other purposes.

Reference Plant A green plant taken to have an average elemental chemical composition.

Rover An unmanned vehicle designed to drive (rather than fly or soar [balloons deployed on Venus] in the atmosphere) and do research besides of taking photographs on another → celestial body (up to now, either on Moon [Soviet Lunokhod rovers, Yutu [PR China] or Mars [see list below]).

Curiosity (Mars Science Laboratory): Landed in August 2012 in Gale Crater, Mars, still operational. The biggest (some 900 kg) and most advanced rover so far deployed, including a full-scale chemical laboratory, sample drilling system and laser ablation spectrometer which meanwhile was used hundreds of thousands of times (range: 7 m!). Powered by an RTG (125 W) rather than solar cells like the other three rovers.

Opportunity: Landed in 2004, still operational. Total weight 160 kg. Covered more than 40 km up to now. First to directly find aqueous-shaped sediments on Mars (clays, jarosite) but not equipped to do real chemical analysis.

Spirit: Identical design to Opportunity. Operational from 2004 to March 2010 but on the other side of Mars.

***Sojourner*:** Very small prototype rover (10 kg, in fact constructed by Mattel™ toy car producer for advertising purposes rather than as a scientific device although fitted with a camera), moving around next to its lander in 1997.

Satellites In systems of celestial bodies where there is a mass hierarchy (i.e., one of the objects is most massive by far, excluding symmetrical double, triple stars or double asteroids which orbit their common center of gravity) movements around the common center of gravity dictated by dynamic systems stability are tantamount to the smaller entities orbiting the biggest one. Then the former are referred to as satellites.

Schiaparelli, Lowell after 1877 During the near approach between Mars and Earth in the 1877 opposition Giovanni Schiaparelli (1835–1910, Italian astronomer and historian of astronomy) tried to resolve optically details on the surface of Mars. His 1888 Mars map correctly gives some of the large depressions (Chryse Planitia, Argyre and Hellas basins) and Tharsis elevation (the big

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[15] Except for tetravalent Ce, Pr, Nd, Tb, and divalent, strongly reducing forms of Eu (also existing in water), Sm, Dy, Ho, Tm, Yb.

volcanoes) but in between there are lines which were soon interpreted as products or remains of a Martian civilization ("canali") while Schiaparelli would not advance this interpretation but rather thought of naturally formed valleys or rivers. The biggest such structure in his map actually exists (Vallis Marineris tectonic trough) while the others are optical illusions caused by connecting dots at the very edge of visibility. Percival Lowell (1855–1916) devoted an entire new observatory at Flagstaff (Arizona) to further investigate these purported traces of advanced life-forms on Mars in 1894. The seasonal color changes on Mars—discovered already in Antiquity and now known to be due to global dust storms—were taken by Lowell and French astronomer Camille Flammarion (1842–1925) as evidence of vegetation spreading in spring, a view which was maintained until the first space probes actually passed Mars (in the 1960s) and this idea so far appeared to be corroborated even by IR-spectroscopic investigations.

SETI campaigns SETI means Search for Extraterrestrial Intelligence. This search (systematically starting in 1960 even though the first attempts date back to 1922 at least) is done not by looking for chemical peculiarities of celestial bodies possibly bearing intelligent life-forms (which might pollute their environment by spectroscopically very distinctive compounds like we do it) but just by looking for purposeful or chance (escaping radio waves meant for local communication) emitted electromagnetic (radio or optical [laser]) signals. While SETI research led to discovery of a couple of very interesting natural radio sources in Universe, there is just a single emission captured in 1977 which never turned up again which was possibly bearing information (the famous "wow!" signal).

Sol One sol is a local (Martian) day, lasting about 24.66 (Earthly) hours.

Stefan's and Boltzmann's law of radiation Austrian (Habsburg monarchy times) physicists Josef Stefan (1835–1893) and Ludwig Boltzmann (1844–1906 [suicide], also working as a philosopher) pioneered statistical thermodynamics. Stefan found emissions (thermal energy losses) by blackbody radiation sources to increase with the fourth power of absolute temperature according to

$$P = \sigma \times a \times T^4, \text{ Where } \sigma \approx 5.60 \times 10^{-8}\ \mathrm{W\ m^{-2}\ K^{-4}}.$$

At 100 K, this means one m^2 of surface will radiate 5.6 W while at 1,000 K this does increase to 56 kW given there is no retention of radiation by greenhouse effect.

Strecker Synthesis Adolph Strecker (1822–1871), while trying to elucidate the formation of 2-hydroxy carboxylic acids from aldehydes and formic acid or the nitrile of the latter, HCN, not just succeeded in synthesizing (racemic) lactic and mandelic acids, but also (by adding ammonia) ran into the first synthesis of amino acids (in 1850). Thus he prepared alanin before it was obtained from proteins and worked out procedures to distinguish and separate Strecker synthesis products from each other and from isomers like lactamide (by preparing platinum complexes thereof). Probably died from thallium poisoning contracted during later works on organometal chemistry. Today the original Strecker synthesis of amino acids, involving aqueous hydrogen cyanide, is outdated, and was replaced by procedures which use e.g. trimethylcyanosilane. After 1953, Stanley → Miller showed that the Strecker pathway was probably involved in making substantial amounts of both 2-hydroxy- and 2-amino acids by spark discharges as both product HCN and hydroxy- or aminonitriles could be isolated from the mixtures.

Stoichiometric Network Analysis A method to analyze stability and dynamic behaviour of feedback structures which process matter. SNA is best suited to identify features of → autocatalysis. Biological reproduction with its link to metabolism and retrieving essential elements from the environment can be considered a kind of autocatalysis, too, and thus theorems of SNA apply and dictate what is feasible in both single living beings and entire ecosystems.

Tunguska event On June 30th, 1908, a small asteroid or comet fragment (some 50 m in diameter) hit the atmosphere over the valley of River Podkamennaya Tunguska in Siberia between Irkutsk and Vanavara cities. About 9 km above ground the object exploded (some 15 MT TNT equivalent) to break down more than 2,000 km^2 of trees. It is uncertain whether some part of the object left a crater. Fortunately, the region was and still is essentially uninhabited, hence the explosion mainly killed raindeer flocks and few people (reports vary, most likely four Tunguz herdsmen were killed in the blast).

Vernadsky, Volodymyr Ivanovich (1863–1945) Ukrainian chemist, who founded the discipline of biogeochemistry (in 1916). Started analyzing most of then USSR territory for possible links between human and animal diseases and geochemical peculiarities ("biogeochemical provinces"). Pointed out possible general trends on how the biota changes dealing with chemical elements during evolution: presumed to make use of the entire accessible amount of essential elements and steadily increasing turnover.

Viking Two identical stationary Mars landers deployed by USA in 1976. The first to look for traces of life or metabolic activities right on Mars (in soil samples) [→PRX]. Operational until 1982, capturing weather data only in the end.

Volcano-curve function The activity of catalysts depends on the binding energy of the substrate to the (homogeneous or heterogeneous) catalyst center. There is a maximum of activity at "middle"—rather than very low or very high—binding energies, producing a plot of binding energy vs. catalytic activity (turnovers/s) which has a distinctive summit and more or less looks like a volcano.

Wildt, Rupert (1905–1976) German-American astronomer. Did pioneering work on spectroscopy, component identification of planetary atmospheres. Detected methane and ammonia in atmospheres of inner gas planets, pointed first to extreme greenhouse effect to be expected on Venus due to CO_2 levels.

Wilson-Menkes syndrome Brain damages in humans caused by Cu accumulation due to genetic defects in Cu^{2+} transportation by chaperons. Can be treated by medication which accomplishes Cu complexation, like with penicillamine, otherwise crippling and lethal in very young children already.

Wöhler, Friedrich (1800–1882) German chemist. First (together with Liebig) to identify isomers (cyanate/fulminate), Showed ammonium cyanate to thermally rearrange to yield urea, then (1828) taken as the first synthesis of an organic compound[16] by humans. First to prepare elemental Al, Be, Ti, Y, B, mainly by electrolysis of salt melts (or clay in case of Al).

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[16] Four years earlier, in 1824, the hydrolysis of cyanogen to give oxalic acid was reported by Berzelius, but then oxalate was taken to be inorganic!

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