

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;

- Altenburger and Schmitt 2003; Kettrup 2003; Markert et al. 2003b; Smoldis 2003; Tabors et al. 2004; Fränzle et al. 2005; Herzog 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; Stoeppeler 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 Environment¹

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

¹ Markert (1994a, b, 1996).

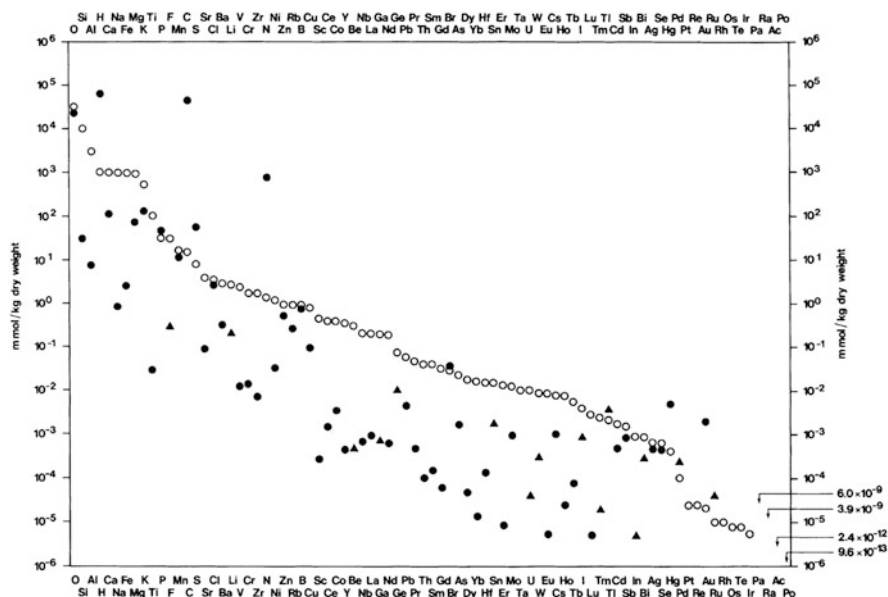


Fig. 2.1 Concentration of 82 naturally occurring elements (excluding the noble gases) in plants in the earth's crust (from Markert 1992d). The elements are listed in decreasing order based on their presence in the earth's crust. *Open circles*: concentration in the earth's crust (from Bowen 1979); *filled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

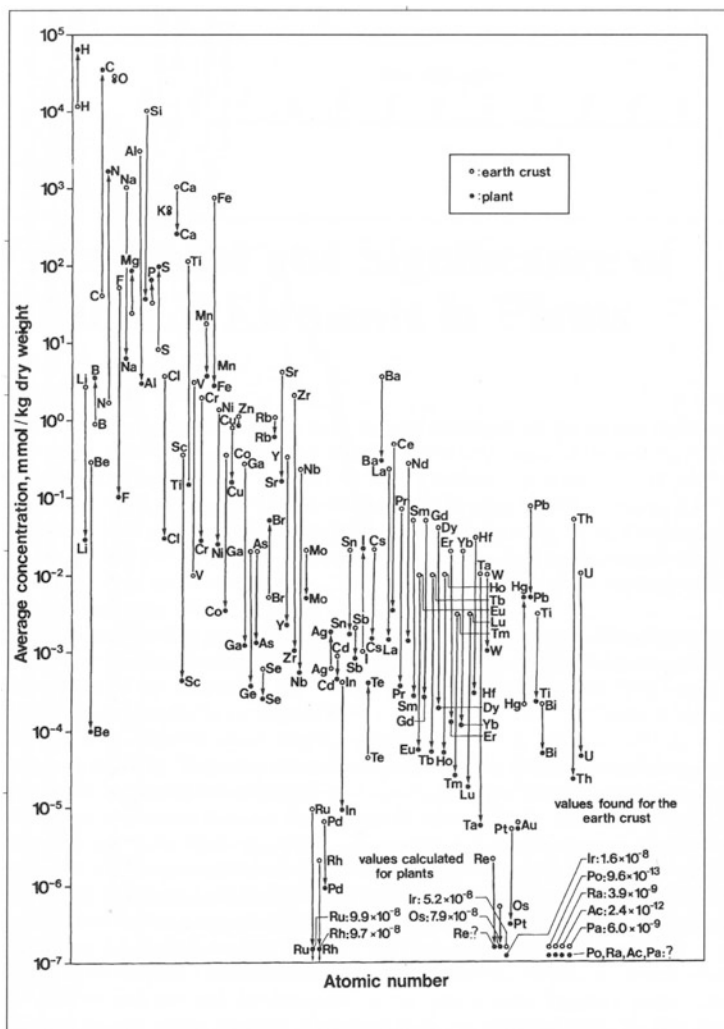


Fig. 2.2 Average concentration of 82 naturally occurring elements in plants and in the earth's crust as a function of their atomic mass (Markert 1996)

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.

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.

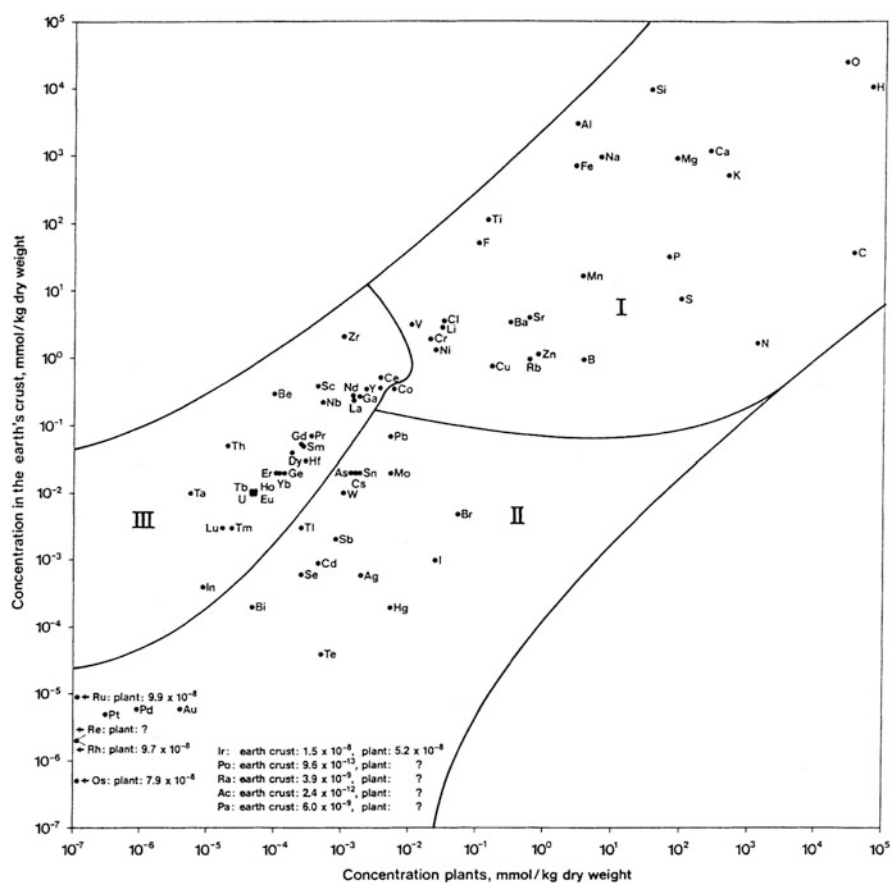


Fig. 2.4 Average concentration of chemical elements in plants in relation to the average concentration of elements in the earth's crust. All data are in mmol/kg dry weight (Markert 1996)

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 Substances²

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

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, Tl	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.

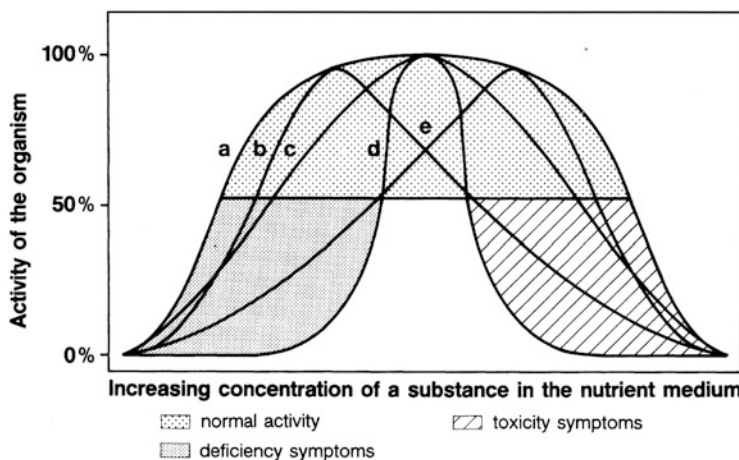


Fig. 2.5 Idealized dose-effect relations between substrate concentrations and activity of the organism (Markert 1996)

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. These 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

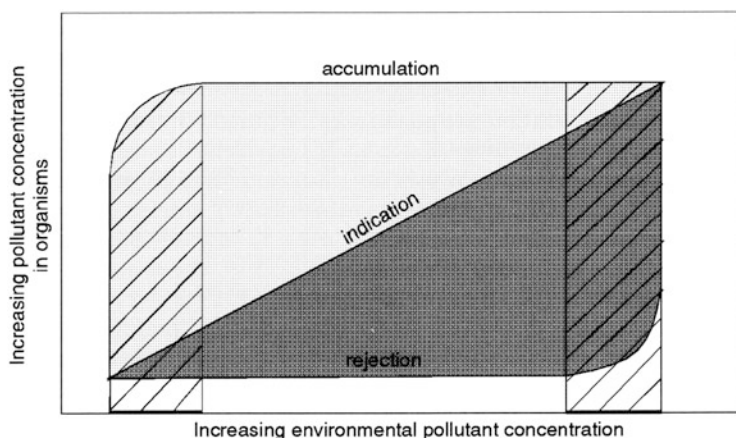


Fig. 2.6 Differing uptake activities in living organisms as a function of the substrate concentration (Markert 1996, modified after Baker 1981)

‘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

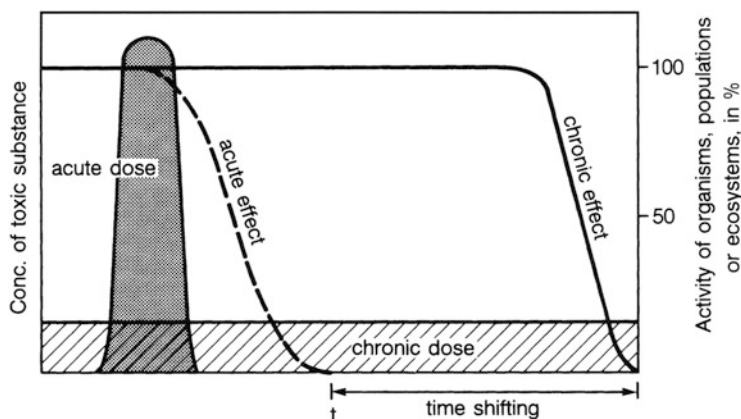


Fig. 2.7 Comparison of effect of acute and chronic doses of toxic substances on living systems (Markert 1996)

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 mucilaginous 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 Fingerprinting³

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

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

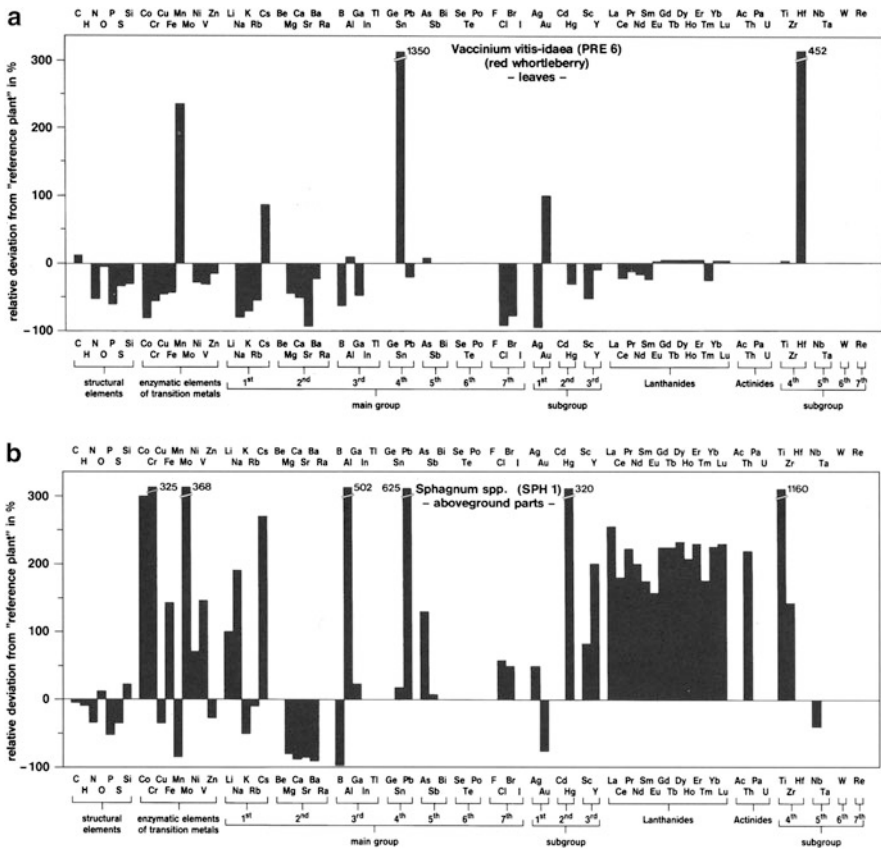


Fig. 2.8 Chemical fingerprints of (a) *Vaccinium vitis-idaea* (red Whortleberry, leaves) grown on a podsolized sanddune in the Grasmoor near Osnabrück after normalization against ‘Reference Plant’ and (b) different *Sphagnum* species (mosses, aboveground parts) grown in the Grasmoor near Osnabrück after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

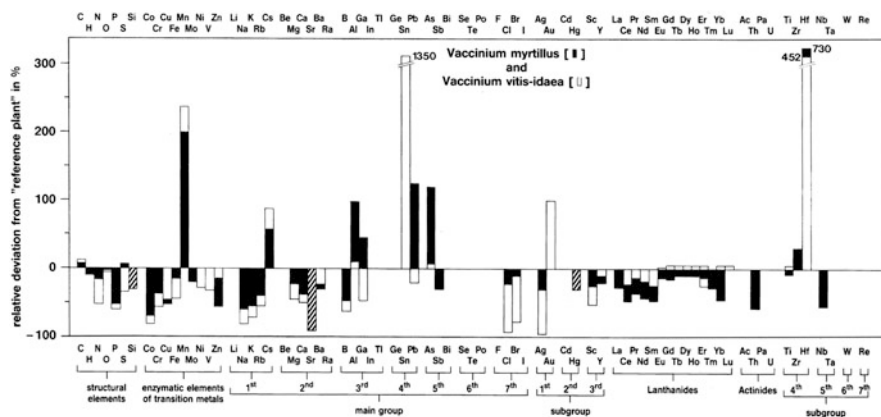


Fig. 2.9 Comparison of single fingerprints of *Vaccinium vitis-idaea* and *Vaccinium myrtillus* both grown in the Grasmoor near Osnabrück on sanddunes (Markert 1996)

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 Processes⁴

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 : 0.095 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

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 form 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–6th 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 Elements⁵

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

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-idaea* (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).

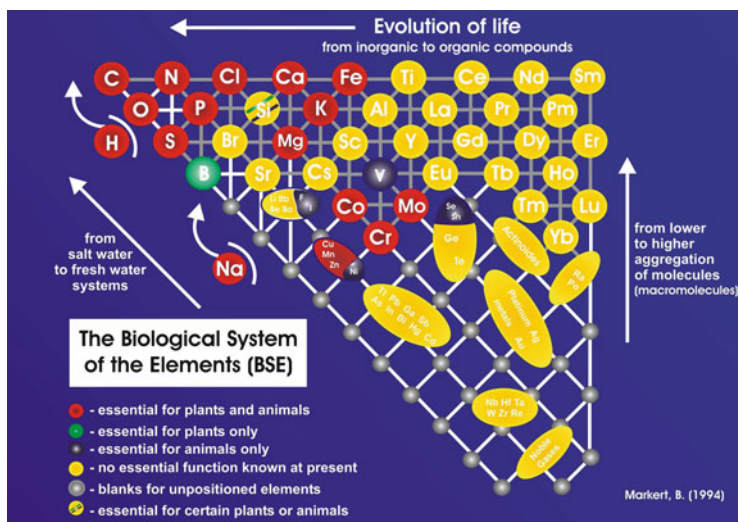


Fig. 2.10 The Biological System of the Elements (BSE) for terrestrial plants (glycophytes) (Markert 1994a). The diagram shows relationships among the elements together with their corresponding essential functions (colours), extent of biochemical functions and the corresponding capacity to form macromolecules 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 (NIST, 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 role⁶:

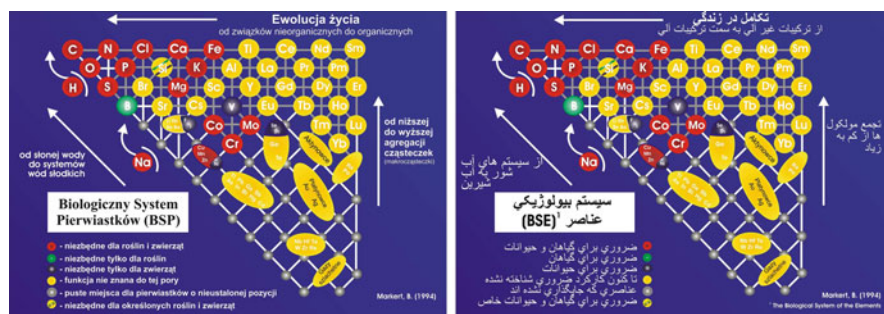


Fig. 2.11 The Biological System of the Elements (BSE) after Markert (1994a, b) was already published in several languages like in French, Spanish, Chinese, Persian (Farsi), Latvian, Lithuanian, Polish (Markert et al. 2010, 2012a, b, 2013a, b, c, 2014) with Russian, Arabic, Hindi versions and others soon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

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

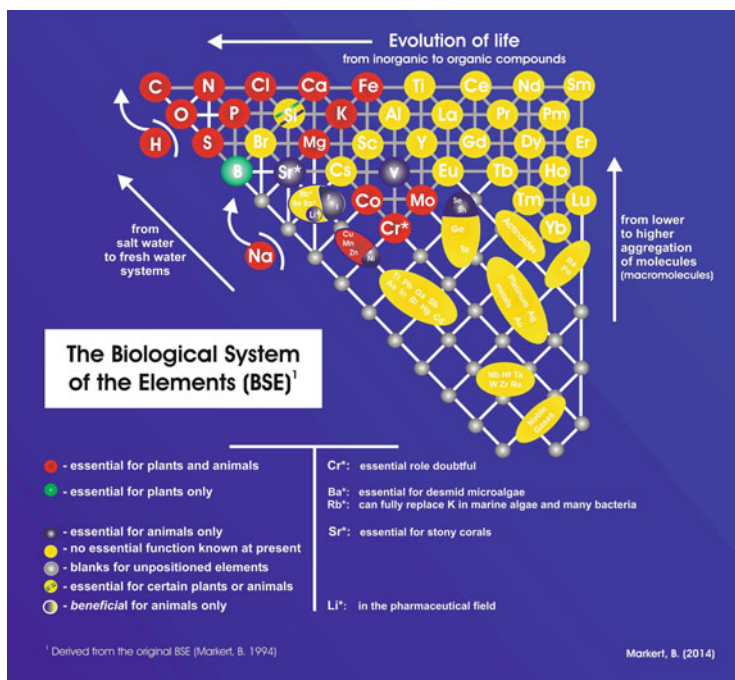


Fig. 2.12 Extended Biological System of the Elements after Markert (1994a, b) showing exceptions of the role of certain elements to specific animals/plants

- 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

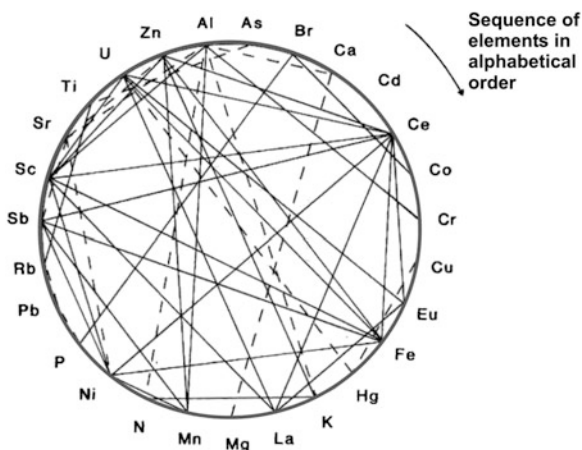


Fig. 2.13 Highly positive (*straight connection lines*) and highly negative (*broken connection lines*) abundance correlations among pairs of chemical elements in 13 species of plants (Markert 1996)

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 be extended using correlations analysis 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 macro-nutrients 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

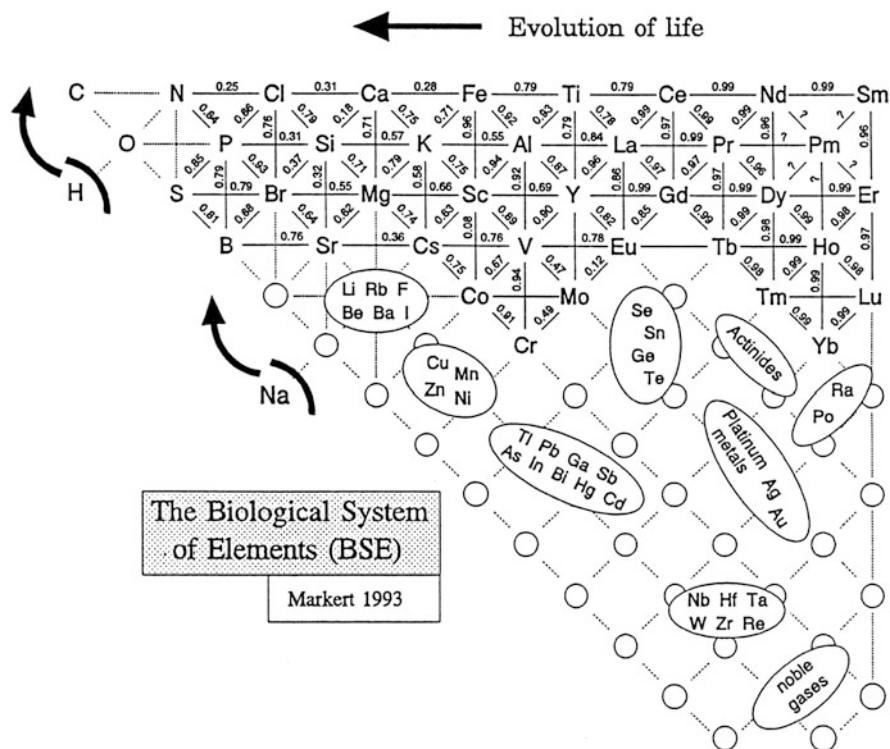


Fig. 2.14 The Biological System of the Elements (BSE) with correlation data from linear regression analysis (Markert 1996)

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 form 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 for 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 $\text{B}(\text{OH})_4^-$) are similarly taken up anionically. All other elements, if they do not occur in a chelated form 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 (Döbereiner’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). Döbereiner’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

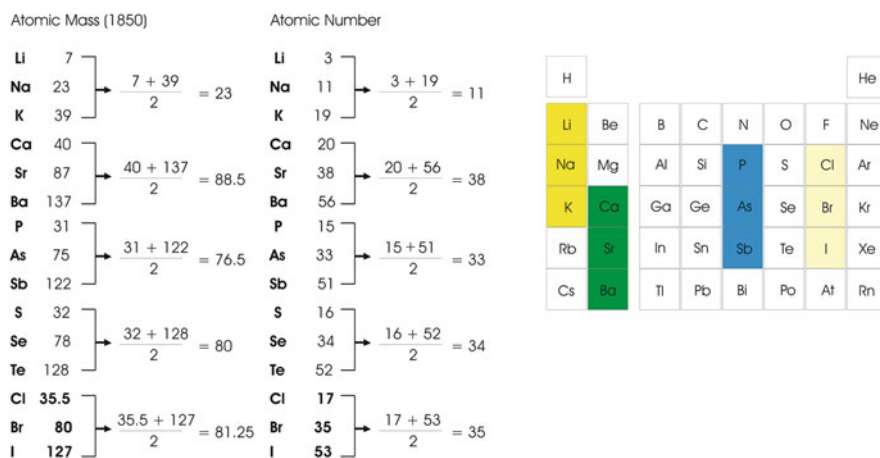


Fig. 2.15 Döbereiner’s triads (Döbereiner 1819) as corresponding to modern PSE representations

Group →	1	2	3	4	5	6	7	8	9	10	11	12	13	14	15	16	17	18
↓ Period																		
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 Mendeleev 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 actinoids⁷ [$Z = 90$ [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 complete⁸ (Fig. 2.16).

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 ($> 0.2 \mu\text{s}$) 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 Mendeleev 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-pairing⁹ 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 salts¹⁰ 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 Ahrlund B-type behavior.

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. Dobzhansky]).

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 $\text{HCHO}/\text{HOCH}_2\text{—CHO}$ 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 spontaneously¹¹ 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 alkaline pH it does form upon reduction of permanganate MnO_4^- readily. Hence in these conditions ($\text{pH} > 6$) oxidations by permanganate become **autocatalytic** and exhibit strange, sometimes even oscillating¹² 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

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 $T < 250^\circ\text{C}$) 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, $-\text{OPO}_3^{2-}$, $-\text{COOR}$, $-\text{COSR}$) 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). Generally 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 states¹⁴).

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

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!

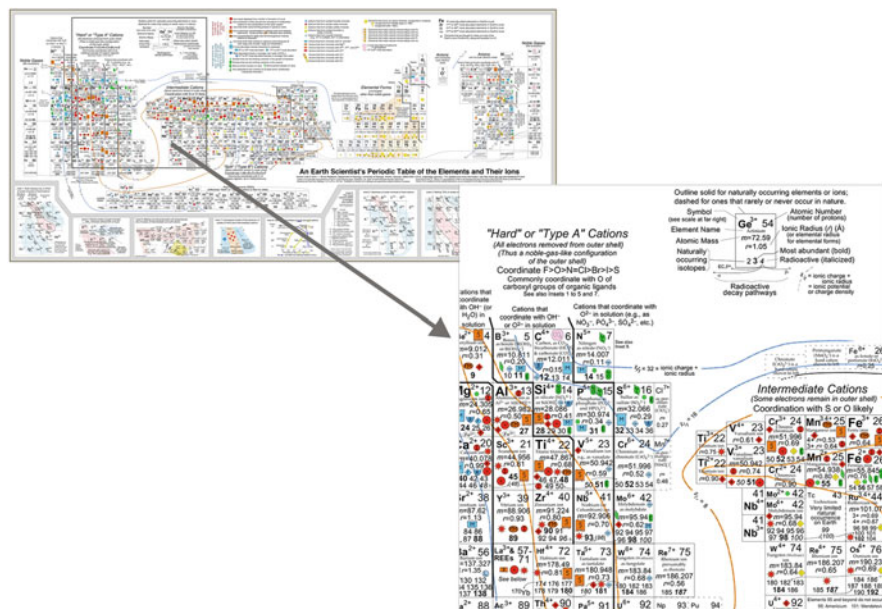


Fig. 2.17 Railsback's 'Earth Scientist's Periodic Table of the Elements and Their Ions' alias 'Geochemical System of the Elements' (GSE) shows physical properties and abundances of elements and their ions and isotopes of importance to Earth scientists (Railsback 2003). These trends in mineralogy, aqueous 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 $\text{\AA} = 0.1 \text{ nm} = 100 \text{ pm}$). 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 $[\text{Mn}^{\text{III}}(\text{OH})]^{2+}$ 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 $T < 110\text{ }^{\circ}\text{C}$). 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.

Chemical Evolution

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