Preface

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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

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Autumn 2014

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http://www.springer.com/978-3-319-14354-5

Chemical Evolution
The Biological System of the Elements
Markert, B.; Fränzle, S.; Wünschmann, S.
2015, XVII, 282 p. 75 illus., 48 illus. in color., Hardcover
ISBN: 978-3-319-14354-5