PREBIOTIC CHEMISTRY

Is Boron a Prebiotic Element? A Mini-review of the Essentiality of Boron for the Appearance of Life on Earth

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Abstract Boron is probably a prebiotic element with special importance in the so-called "sugars world". Boron is not present on Earth in its elemental form. It is found only in compounds, e.g., borax, boric acid, kernite, ulexite, colemanite and other borates. Volcanic spring waters sometimes contain boron-based acids (e.g., boric, metaboric, tetraboric and pyroboric acid). Borates influence the formation of ribofuranose from formaldehyde that feeds the "prebiotic metabolic cycle". The importance of boron in the living world is strongly related to its implications in the prebiotic origins of genetic material; consequently, we believe that throughout the evolution of life, the primary role of boron has been to provide thermal and chemical stability in hostile environments. The complexation of boric acid and borates with organic *cis*-diols remains the most probable chemical mechanism for the role of this element in the evolution of the living world. Because borates can stabilize ribose and form borate ester nucleotides, boron may have provided an essential contribution to the "pre-RNA world".

Keywords Borates · Boric acid · Prebiotic · Boron · Essentiality · Origins of life

Introduction

Chemical species that have been involved in the appearance of life on Earth include hydrogen cyanide (Keefe and Miller 2010a) and its salts (Bermejo et al. 2009), polyphosphate and phosphate esters (Keefe and Miller 2010b), phosphoric acid (deGraaf et al. 1997), ferrous sulphide and hydrogen sulphide (Bada 2004), hydrocarbons (McKay et al. 2008), clay minerals (Brack 2006), clay crystals (Cairns-Smith 1966), and metallic and non-metallic ions (Silva et al. 2001; Strasdeit 2010). The concept of prebiotic reagent has been further developed into several different "prebiotic worlds": the "sugars world" (Weber 2007; Weber 2008), the "thioester world" (deDuve 1991), the "lipid world" (Segre et al. 2001; Bar-Even et al. 2005), the "amino

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acid and peptide world" (Kristof et al. 2005), the "pre-RNA world" (Ferris 1999; Ferris 2006; Nielsen 2007), the "RNA world" (Gilbert 1986; Raymond et al. 2005), the "hydrogen cyanide polymer world" (Clifford et al. 2006), the "iron-sulfur world" (Wächtershäuser 2000; Rossa 2008), and, more recently, the "alkaline world" (Mellersh and Smith 2010), the "basic amino acids world" (McDonald and Storrie-Lombard 2010), the "PAH world" (Bernstein et al. 1999; Ehrenfreund and Cami 2010) and the "zinc world" (Mulkidjanian and Galperin 2009).

Among prebiotic reagents, boric acid and borates, some of the most important forms of boron, are very useful in the "sugars world" (Prieur 2001; Ricardo et al. 2004; Scorei and Cimpoiasu 2006; Benner et al. 2010). They would have had a role in special temperature and pressure conditions, on a hot Earth planet, due to volcanoes and asteroid impacts (Benner et al. 2010; Sleep 2010). There is evidence that borates were essential both in the prebiotic period, as well as later in biology (Kakegawa et al. 2002; Benner et al. 2010) and it represents the core of the prebiotic chemistry because it leads to the ribose synthesis (Ricardo et al. 2004. Moreover, it has the capacity to thermostabilize the life biomolecules (Scorei and Cimpoiasu 2006; Cossetti et al. 2010) and it acts like a catalyst in many prebiotic syntheses (Saladino et al. 2011). However, boron is somewhat a rare element and it might not have been present in high concentration in the same microenvironments as the precursors of ribose have (Cleaves and Chalmers 2004).

McClendon (1976) proposed that the relative abundance of an element should be a decisive factor in the origin of its nutritional essentiality. He also suggested that the requirement for boron has been acquired over time and that there was a limited availability of boron in the primitive oceans. The fact that boron was essential for heterocystous Cyanobacteria (principally Nostocaceae), which were the predominant organisms during the Middle Precambrian Period, some two billion years ago, indicates that boron was an extremely important element during the early evolution of life, although its availability was relatively limited (Bonilla et al. 1990).

Boron has several interesting physical and chemical properties. Because of its electron structure and its position in the periodic table, adjacent to carbon, boron-containing molecules are electrophilic and adopt trigonal planar structures that are isoelectronic, neutral analogues of carbocations (Petasis 2007). The formation of additional bonds to boron produces anionic, tetrahedral compounds that behave as nucleophiles. Whereas trigonal boron compounds are extremely reactive in aqueous solution, tetrahedral species are chemically very stable and can stabilize polymer linkages or participate in chemical catalysis (Schaeffer 1964).

Even though boron chemistry is rather complex, with myriad theoretical and technological important known boron hydrides and carboranes, the reactions of boron-containing nitrogen and oxygen donors are the only biologically relevant reactions in the mildly basic aqueous milieu of seawater. The reactions of boric acid and borates with hydroxyl donors, such as alcohols, phenols, diols, polyols, or polysaccharides to produce alkoxides or "boron esters" are the most important. For example, the essentiality of boron for plants derives from a reaction of borate with carbohydrates that promotes the crosslinking and stabilization of the plant cell wall (Gonzales-Fontes et al. 2008; Carrano et al. 2009). Both mono- and diester forms are possible, and they are the most stable when derived from "chelating" dihydroxy species. The monoesters maintain a trigonal planar configuration with no net charge, while the more important diesters form anionic, tetrahedral spirocyclic compounds (Carrano et al. 2009).

This brief review, which summarizes current knowledge concerning the prebiotic and biological roles of boron compounds, may provide guidance to research on the importance of boron as a prebiotic element. Availability of borate at the time in Earth's history, as well as

the plausibility, in terms of geological and geophysical data, that boron played a key role in the origins of life on Earth, are very well presented and discussed in a recent paper (Grew et al. 2011), so I decided not to approach these issues in the present mini-review. At the same time, most of the studies concerning boron prebiotic chemistry were realized in liquid, either water or formamide. Since the borate anion was proved to be transported into the cell (Park et al. 2004), and boric acid can penetrate across the cellular membrane (Takano et al. 2005), this mini-review will focus only on borates and boric acid. Until recently, a clear well-defined role for boron was only found in the vegetable world (Nielsen 1996).

Boron and Life

Boron and compounds containing boron have a variety of known biological functions. Boron is present in bacterial antibiotics, such as tartrolon, borophycin, boromycin and aplasmomycin (Rezanka and Sigler 2008), in the bacterial quorum sensing molecule, auto-inducer AI-2 (Chen et al. 2002), and in vibrioferrin, a boron-containing siderophore that is produced by certain marine bacteria (Amin et al. 2007). In plants, the rigidity of the cell wall depends on the formation of the rhamnogalacturonan II complex (RG-II), which is a pectic polysaccharide that is covalently linked through *cis*-diol bonds to borate esters of apiosyl residues (Ishii and Matsunaga 1996; Ishii and Matsunaga 2001). Borate crosslinking in pectic networks physically strengthens cell walls and contributes to cell adhesion (York et al. 1985).

Transporters that are responsible for efficient uptake of boron by roots, xylem loading of boron and distribution of boron among leaves have been described. These transporters are required for the efficient acquisition and utilization of boron when its availability is limited. Two types of transporters are involved in boron transport regulation in plant tissues: NIPs (nodulin-26-like intrinsic proteins) that serve as boric acid channels and boron exporters encoded by BOR1 (Miwa and Fujiwara 2010). The expression of the genes that encode these transporters is finely regulated in response to the availability of boron to ensure boron homeostasis in plant tissue. Furthermore, altering the expression of these transports generates plants with increased tolerance for high or low concentrations of boron in the environment (Tanaka and Fujiwara 2007).

Boron is an essential element not only for vascular plants but also for diatoms, Cyanobacteria and a number of marine algal flagellate species (Rezanka and Sigler 2008; Bolanos et al. 2004). Recently, an exceptional group of boron-containing compounds, the borolithochromes, has been discovered in well-preserved specimens of the Jurassic red algae, *Solenopora jurassica*, where they are responsible for its distinctive pink coloration. Borolithochromes are complicated spiroborates (boric acid esters) with two phenolic moieties as boron ligands, and they represent a unique class of fossil organic pigments (Wolkenstein et al. 2010).

The chemical structures of the above mentioned boron natural compounds are given in Table 1.

Furthermore, the high boron tolerance of *Saccharomyces Cerevisiae*, one of the most useful species of yeast that having been instrumental to baking and brewing since ancient times, has recently been shown to result from the multidrug resistance transporter encoded by ATR1, which is a gene that is widely distributed in bacteria, archaea and lower eukaryotes (Miwa and Fujiwara 2010).

Moreover, it was found that animals, such as zebra, fish, trout and frogs, also require boron (Fort et al. 1999; Rowe and Eckert 1999). This is the same for humans. Borate ions

Table 1 Chemical structures of boron natural compounds found in bacteria, algae and plants
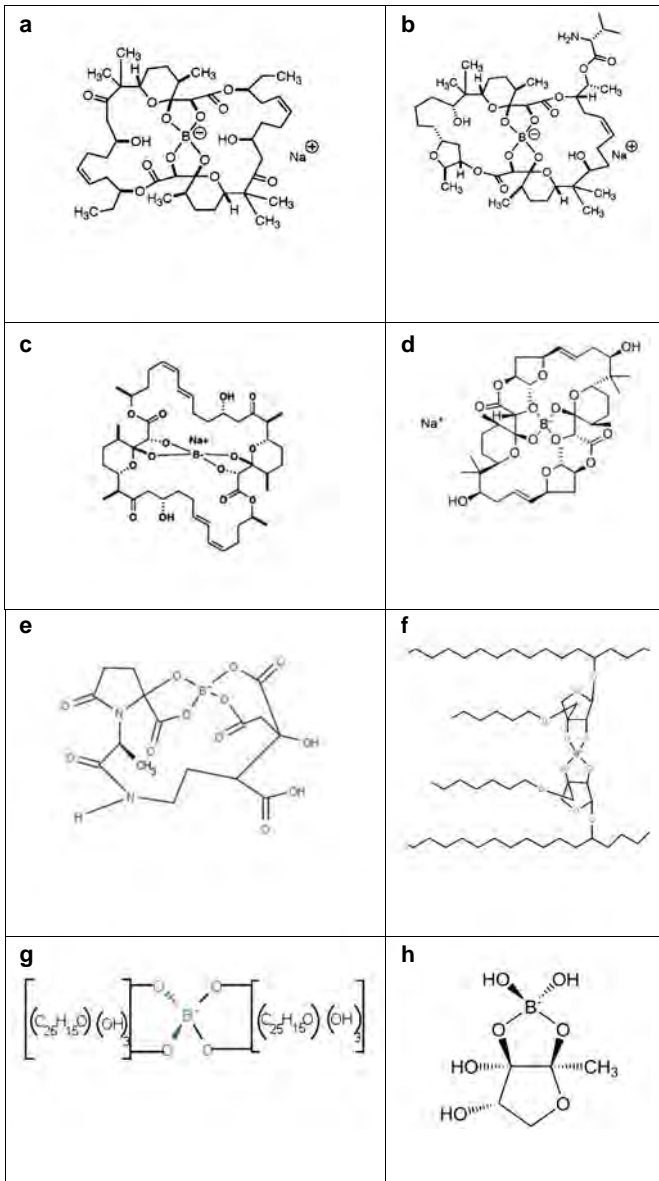
(**a**) borophycin, (**b**) boromycin, (**c**) tartrolon B, (**d**) aplasmomycin, (**e**) vibrioferrin with boron, (**f**) boron crosslinks two RG-II monomers, (**g**) main single isomeric borolithochromo ($C_{50}H_{36}O_{12}B$) and (**h**) auto-inducer AI-2

activate the mitogen-activated protein kinases pathway and stimulate the growth and the proliferation of human embryonic kidney 293 cells (Park et al. 2005). The boron transporter in living organisms, NaBCl, controls plasma borate levels in human kidney cells (Park et al. 2004). It has been shown that cell proliferation depends on the concentration of boron in the cell. At concentrations between 0.1 and 0.5 mM, borate was strongly mitogenic, and at concentrations above 1 mM, it inhibited the cell growth (Park et al. 2004; Park et al. 2005).

Prebiotic Chemistry of Boron

Four billion years ago, prebiotic chemistry on Earth led to the appearance of life.

Pentose sugars are one of the key building blocks of nucleic acids. Other sugars, including hexoses, play important roles throughout metabolic and structural biochemistry. Sugars are thus logical targets for prebiotic chemistry experiments. The formose reaction, a chain-condensation of formaldehyde under basic conditions, produces a mixture of sugars, including ribose. Ribose is a component of ribonucleic acid (RNA), which is theoretically capable of prebiotic self-replication, but it is chemically unstable (Larralde et al. 1995). Cyanamide conveys unique properties upon ribose compared with other sugars; both through the preferential formation of ribose-cyanamide and the stabilization of ribose as a cyanamide adduct (Springsteen and Joyce 2004). Aqueous silicate has also been suggested as an alternative stabilizer (Lambert et al. 2010a, b), although it has given rise to some discussion (Kim and Benner 2010). Thus, borate remains the most studied stabilizer of the furanose form of ribose.

Mechanisms by which ribose can be stabilized by boron have recently been discovered (Prieur 2001; Ricardo et al. 2004; Scorei and Cimpoiasu 2006; Cossetti et al. 2010) and may occur under special conditions in the formose reaction (Benner et al. 2010). Ribose and other pentoses have been prepared by the formose reaction from formaldehyde and glycolalde-hyde, compounds that are found in interstellar space (Hollis et al. 2000). Borate minerals were probably present in the solar system and on early Earth and the presence of boron in rocks older than 3600 Ma remains to be demonstrated (Grew et al. 2011). If the continental crust had been as enriched in lithium in the Early Archaean as it has been since, then it is reasonable to assume that boron was also enriched to a comparable degree and the boron flux from land to sea could have approached modern levels (Grew et al. 2011). It has also been suggested that ribose, together with purine bases, could have been synthesized in hydrothermal environments on the sea floor, conditions which may favour the formose reaction and may also be enriched in borate (Holm et al. 2006). A "prebiotic metabolic cycle", fed by formaldehyde and controlled by borates, has been described (Ricardo et al. 2004), leading to the preferential formation of aldopentoses.

Another relevant question raised by prebiotic studies is the selection of the beta-furanose form of ribose as a building block of RNA. Is there an underlying physical and/or chemical property of beta-ribofuranose that makes it more reactive than the competing alpha anomer? Two very stable bi-dentate complexes of ribose with borates have recently been reported (Sponer et al. 2008; Cossetti et al. 2010). The first complex involves 1,2-alpha-ribofuranose and the second involves 2,3-beta-ribofuranose; in both complexes, the borate species interact with vicinal OH groups (Chapelle and Verchere 1988). Beta-ribofuranoses can be observed in biological systems in complex with calcium (Kolb and Zhu 2004). In aqueous solution, sugars mainly adopt the six-member-ring pyranose configuration. In the presence of borate, this configuration is forced into the five-member borate-furanose form. Significantly, it was proven that complexes between sugars and boron use the furanose form exclusively when the temperature is higher than 60°C (Pelmore and Symons 1986). At limited amounts of borate, the formation of diester complexes is preferred over the monoester complex (Sponer et al. 2008).

Table 2 presents the chemical structures of boron compounds, supposed as prebiotic reagents.

At the 12th International Conference on the Origin of Life (San Diego, California 1999), we presented, for the first time, our hypothesis that boron thermally stabilized the genetic material of the first living cells, based on the observations of stable ribosyl borate esters

Table 2 Chemical structures of boron compounds, supposed as prebiotic reagents
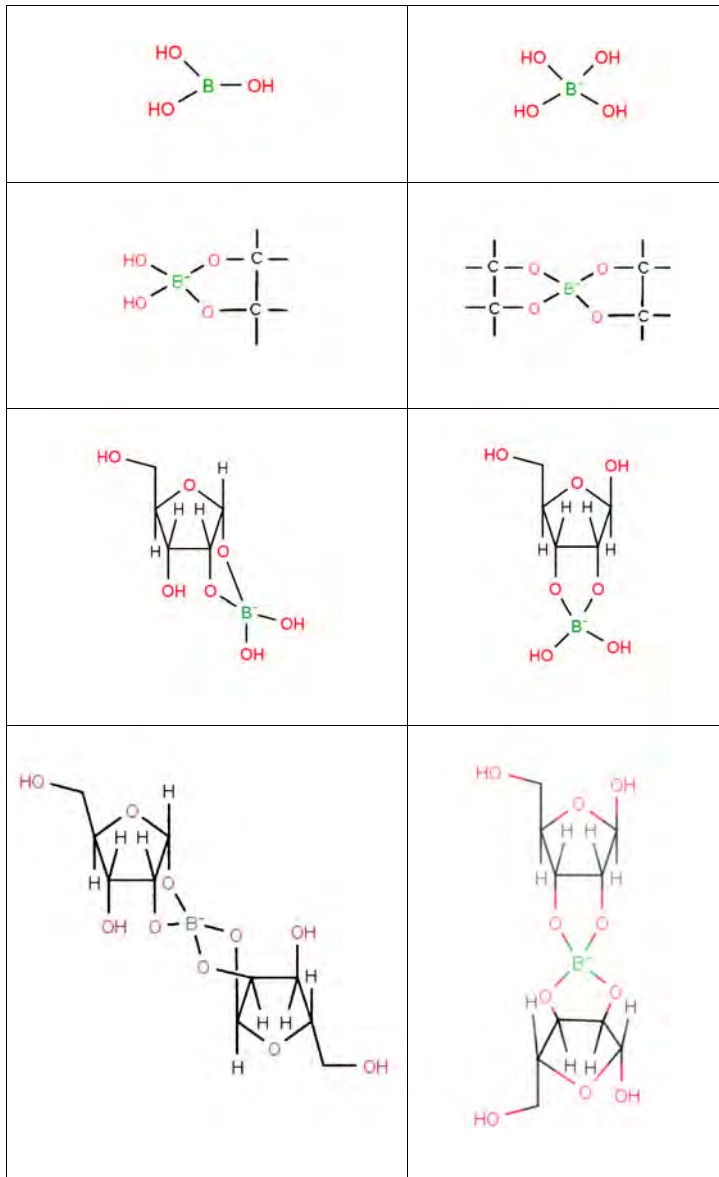
(**a**) boric acid, (**b**) borate anion, (**c**) and (**d**) their diol mono- and di-esters, (**e**) 1,2-α-ribofuranose boron monoester, (**f**) 2,3-β-ribofuranose boron monoester, (**g**) 1,2-α-ribofuranose boron diester and (**h**) 2,3-β-ribofuranose boron diester

(Scorei and Cimpoiasu 2006). Because boron has opposite effects on the relative thermal stabilities of ribose and glucose under acidic and basic conditions, these two sugars and their associated biological roles may have developed in different environments.

A "pre-RNA world" type of chemistry could exist at high temperatures and low pH, which allows the formation of borate diesters of ribofuranose, whereas a "pre-metabolic

world" type of glucose-based chemistry would be favoured by high temperatures and high pH and be rich in glucosyl borates and anionic borates. Initially, these two different chemical worlds could have evolved separately; later, they could have associated into more complex biochemical systems (Scorei and Cimpoiasu 2006).

The transition from the "pre-RNA world" to "RNA world" is one of the most important questions of prebiotic evolution and may be the key of understanding the appearance of biological life on Earth. Because borates can stabilize ribose and form borate ester nucleotides, boric acid may have provided an essential contribution to the "pre-RNA world" of carbohydrates

Boron and Phosphorus

In biological systems, purine nucleotides are synthesized by construction of the purine base on a pre-existing ribose-5′-phosphate. However, adenosine-5′-triphosphate can be synthesized directly from adenosine and trimetaphosphate if the 2′- and 3′- OH groups of adenosine are blocked by borate (Etaix and Orgel 1978), and trimetaphosphate and boric acid have been found in the fumaroles of Japan (Yamagata et al. 1991; Kanzaki et al. 1979).

The complex formed between ribose and boron is particularly interesting because the borate occupies the C2 and C3 OH groups, leaving the C5 OH available for reactions, such as phosphorylation (Zubay and Mui 2001; Li et al. 2005).

One of those reactions with prebiotic potential may have been the capacity of borate ester dinucleotides to polymerize and to form oligonucleotides in the presence of active phosphorylation agents. It is well known that aqueous phosphate readily reacts with calcium to precipitate as an insoluble apatite. In a sterile seawater medium at 25°C and pH≥9, apatite (Ca-orthophosphate) forms a single phase. At pH values between 7 and 9, however, the mineral whitlockite ($Ca_{18}Mg_2H_2$ $(PO_4)_{14}$) is primarily formed (Gedulin and Arrhenius 1994). The mechanism by which phosphorus could have been available for prebiotic reactions is still unknown. It has been suggested that phosphorus-containing compounds might have accumulated in a hydrophobic medium in which the absence of calcium ions would have prevented them from precipitating as apatite (Morchio and Traverso 2005; Holm et al. 2006; Costanzo et al. 2007). Pyrophosphates could have been formed during early subduction of oceanic lithosphere by dehydration of protonated orthophosphates. A key to pyrophosphates formation in these geological environments is a low local activity of water (Holm and Baltscheffsky 2011). The interest for phosphite as a possible prebiotic phosphorus source is not only due to the higher solubility of its calcium salt compared to apatite (approximately 1000 times higher), but also to its greater reactivity as a phosphorylating agent. It has been established that ammonium phosphite, for example, readily reacts with nucleosides to give nucleoside-phosphites (nucleoside H-phosphonates), under conditions in which ammonium phosphate cannot react (Schwartz 2006).

Returning to borates, the boron-containing nucleotide analogues have recently been synthesized. These compounds dimerize via a borate ester bond, rather than the phosphate linkage of their natural counterparts. This result reveals a new perspective on the role of boron in the prebiotic chemistry and it could represent the basis of an artificial genetic code (Martin et al. 2009). A new dynamic, programmable ligation system based on the reversible DNA templated formation of a boronate internucleosidic linkage has recently been developed. The systems have several significant features: 1) DNA-templated dynamic self-organization, 2) adaptive behaviour in response to external triggers (temperature, pH value, diol concentration or cyanide ions), and 3) dynamic selection of the optimal building blocks (Martin et al. 2011).

Summing up, boric acid/borate anions may have acted as prebiotic reagents by stabilizing the furanose form of ribose (Ricardo et al. 2004) and by catalyzing the formation of several prebiotic chemical units, such as amino acids polyesters and polypeptides (Commeyras et al. 2002; Kolitz et al. 2009). Recently reported data show the role of borates in the prebiotic synthesis of biomolecules, other than sugars (Saladino et al. 2011). These data, in connection with the recent use of H_3BO_3 as a catalyst for the polymerization of amino acids (Kolitz et al. 2009), further enhance the major role of borate minerals in the prebiotic processes. The reported data show that formamide oligomerizes in the presence of borate minerals leading to nucleobases and biogenic carboxylic acids. Moreover, the ability of boric acid to form reversible 1:2 mixed-ligand borates has been used to induce glycoside transport through a bulk liquid membrane (Riggs et al. 1996). Boronic acids were found to facilitate the transport of various ribonucleosides in and out of liposomes, artificial cells (Westmark and Smith 1996; Smith et al. 1998; Westmark et al. 1996). Borate esters, the main precursors for boronic acid derivatives, result by simple dehydration of boric acid with alcohols (Hall 2005).

Is Boric Acid an Essential Molecule for Life?

The results reviewed in this paper are consistent with the theory that boron is an essential element for the living world. Regarding the bonds strength, an important difference exists between boron and carbon: the energy of C-C linkage is around 335–377 KJ mol^{-1}, whereas the B-B linkage is much weaker, 297±21 KJ mol^{-1}, which makes it very unstable. On the other hand, the B-O is very strong (515 KJ mol^{-1}), therefore the molecular architectures are very stable. This kind of structure is so stable, almost "static", to be inadequate for living organisms which require compounds that are more "dynamic" (Krogh-Moe 1963). By hydration, the strength of the oxygen boron bond decreases to 398 KJ mol^{-1} (for example in hydrated boric acid), but no enzymatic systems have been found yet, capable to degrade it. Boron is ubiquitous in the environment with an average concentration of 4600 μg/L (430 μmol/L) in seawater, a much higher concentration compared to seawater content of molybdenum [9.6 μg (0.1 μmol)/L], iron [5.6 μg (0.1 μmol)/L], zinc [4.9 μg (0.075 μmol)/L], copper [3.2 μg (0.05 μmol)/L], or manganese [2.0 μg (0.036 μmol)/L] (McClendon 1976). At typical physiological boron concentrations (between 0.006 and approximately 9.0 μmol/L) in plants, animals or humans, inorganic boron is essentially present only as mononuclear specie of boric acid $B(OH)_3$ and as borate $B(OH)_4^-$ (Weser 1967). Undissociated (and uncharged) boric acid is very soluble in water [$B(OH)_3$-saturate solution at 20°C=0.75 mol/L] and its permeability coefficient for transport across the lipid bi-layer is several orders of magnitude higher than that of ions (Takano et al. 2005), on the same order as urea (Raven 1980). The similarity between the molecular radii of boron (2.57 Å) and water (2.82 Å) suggests that boron can replace the water molecules that hydrate the polar head groups of lipids (Verstraeten et al. 2005).

Experimental data from plants and animals show that boron plays a critical role in membranes and/or extracellular matrix (Blevins and Lukaszewski 1998; Brown et al. 2002). The importance of borate as a crosslinking molecule is revealed by the discovery of a variety of borate-dependent molecules: rhamnogalacturonan II (RG-II) in plant cell walls (Ishii and Matsunaga 1996; Kobayashi et al. 1996), boron-polyhydric alcohol complexes isolated from phloem extracts (Hu et al. 1997), bacterial signalling molecules and their receptors (Chen et al. 2002), and several antibiotics (Hunt 2003). Current understanding of boron physiology suggests that boron functions as a crosslinking molecule in plants

(Loomis and Durst 1992; Brown et al. 2002). Borates can crosslink molecules because they contain two pairs of hydroxyl moieties that can reversibly form diester bonds with molecules that present *cis*-diols in a favourable configuration. Biologically interesting *cis*-diol-containing molecules primarily react with borate, rather than boric acid (Zittle 1951), because borate linkages have a greater stability (Gerrard 1961), whereas trigonal boron esters are easily hydrolyzed (Otsuka et al. 2003). Borate diester complexes and free boric acid have been found in a number of plant species (Bassil et al. 2004). Compounds with a configuration where *cis*-diols exist on a pyranose ring (e.g., the pyranose form of alpha-D-glucose) form weaker complexes with boron than those compounds configured to have predominately *cis*-diols on a furanose ring (e.g., apiose and ribose). Thus, in early plants, boron may have driven the selection of sucrose as the mobile storage carbohydrate, because other algae sugars form a tight complex with boron (Bonilla et al. 1990). The low concentration of an alpha-furanose form of D-glucose in aqueous solutions (Zubay 1988) suggests that glucose was selected as the aldose component for general energy metabolism, due to its low reactivity with boric acid.

The stability of borate-diol esters is strongly dependent on the specific structure of the diol, and the concentrations and ionization constants of the participating molecules (Bergold and Scouten 1983; Springsteen and Wang 2002). At a given pH, a lower pKa will favour ionization and a strong complex will be obtained (Power and Woods 1997).

In animal cells, a molecule containing two boronic acid residues, [N,N′-bis-3(dihydroxylborylbenzene)-adipamide], causes the agglutination of suspended red blood cells, suggesting that borate linkages can function in cell-to-cell adhesion (Burnett et al. 1980). Boron also stabilizes the structure of the heme proteins under oxidative stress in vitro conditions, and it has been suggested that heme proteins possess sites that can bind to borate ions (Shakir et al. 2010).

Moreover, it has been shown that borate has a significant stabilizing effect on both molecular architecture and catalytic function of the bone alkaline phosphatase. The observed stabilizing effect of borate may be attributed to borate bridging between the carbohydrate residues of alkaline phosphatase (Weser and Kaup 2002). Recent reports reveal the in situ formation of borate esters that mimic the corresponding phosphate esters supports enzyme catalysis. The structural homology of the borate anion with phosphate, combined with its ability of spontaneous esterification of the hydroxyl groups, suggested that phosphate ester recognition sites on proteins might exhibit significant affinity for non-enzymatic formed borate esters (Gabel and London 2008).

Furthermore, theoretical and experimental data support the involvement of boron in cytoskeleton function, probably by its participation in the cytoskeleton-dependent structural organization of the cell. The function could either be direct, by affecting the organization or stability of cytoskeleton components, or indirect, through interaction with other cytoskeleton binding or anchoring molecules, such as glycoproteins and/or glycolipids. In animal cells for example, the membrane-to-cytoskeleton adhesion occurs through bonds between cytoskeleton proteins and glycoproteins/lipids in the membrane (Bassil et al. 2004). Literature data convincingly show that boron is required for the incorporation and presumably for the crosslinking of hydroxyl proline-rich structural glycoproteins into the cell wall (Bonilla et al. 1997; Redondo-Nieto et al. 2008).

In addition, there are scientific data showing that the proteasome, a multi-subunit enzyme complex that plays a central role in the regulation of proteins that control the cell cycle, and degrades proteins (Voges et al. 1999), needs boron for its functionality. Low and high concentrations of boron will inhibit this extremely important enzymatic system, but an adequate concentration of boron is beneficial (Goldbach et al. 2001; Çolak et al. 2011).

Boron has been shown to possess the following features in large parts of biology: i) to be a cell signalling molecule, ii) to be a co-factor of the enzymes it regulates, iii) to be a non-enzymatic co-factor, iv) to play both structural and functional roles, including electron transfer, redox sensing and structural modules, and v) to play a role in the cytoskeleton structure. Although boron has not yet been shown to be an essential nutrient in animal cells, more data will probably support such a role in the future.

The complexation of borate with organic *cis*-diols remains the most probable chemical mechanism for the involvement of this element in the evolution of the living world. Because animal and plant cells actively transport borate anions when the boron concentration in the environment is low, yet boric acid can diffuse directly through cell membranes at high environmental concentrations, the scientific community regards boron as an enigmatic element (Carrano et al. 2009).

Boron and Life on other Planets

Boron should not be neglected when searching for life on other planets (Benner et al. 2010).

While the cosmic abundance of boron is one of the least known of the 92 natural elements (Cameron et al. 1973), its abundance in the solar system is well known (Palme and Jones 2005; Lodders 2010). Boron is potentially a useful indicator of the possible presence of life on other planets, but it is a challenge to recognize boron using available technology for planetary atmosphere analysis. It has been shown that boron is highly volatile under appropriate conditions. The property of boron to sublime was used to separate it from an organic matrix (Gaillardet et al. 2001). A few papers suggest the presence of boron on Moon, Mars, Jupiter and Titan (Shaw 1995; Spivak-Birndorf et al. 2008a, b; Beer 1976; Abbas and Schulze-Makuch 2007; Green 2009).

Fifty-eight lunar rocks have been analysed by prompt gamma neutron activation for boron, gadolinium and samarium. In lunar rocks, boron behaves similarly to samarium, gadolinium, lithium and other incompatible LIL (Large Ion Lithophile) and HFS (High Field Strength) elements, collectively known as the KREEP component. According to Shaw (1995), distribution of boron on the moon can be understood in terms of a mixture of KREEP and boron-poor lunar rocks. By correlation with other KREEP elements, the lunar boron abundance is estimated to 0.14 ppm (Shaw 1995).

Rocks ejected from Mars by asteroid impacts can be transferred to Earth on low-temperature trajectories. Laboratory studies of the acceleration forces that rocks experience during the ejection and re-entry processes provide clear evidence that the surfaces of both Mars and Earth are potential candidates for the cradle of terrestrial life (Kirschvink and Weiss 2001). The nakhlites are the most altered Martian meteorites. They contain a relatively abundant secondary mineral assemblage known as iddingsite that is believed to have been deposited by low-temperature aqueous fluids on Mars. Boron isotopes can be useful tracers for fluid-rock interactions and the boron isotopes system of Martian meteorites helps to constrain the compositions of aqueous crusted fluids on Mars. Boron concentrations of pyroxenes in both meteorites are low (below 0.5 ppm). Nakhla mesostasis crystals is enriched in boron (approximately 4–7 ppm), compared to pyroxenes, but it has an average of $\delta^{11}B$ (–7.3±1.8‰) that is indistinguishable, within errors, from the value in the pyroxenes (Spivak-Birndorf et al. 2008a, b). It would be necessary a higher amount of boron on Mars that borate could have an important role in this planet "pre-RNA world". It is suggested that Jupiter might be a suitable place for searching for boron because it forms numerous stable, volatile compounds with hydrogen and other elements that are present in sufficient abundance to be sought either spectroscopically or by entry devices (Beer 1976).

In the periodic table of elements, boron precedes carbon and the high abundance of carbon in the Titan's atmosphere and surface environment suggests the presence of some boron in the surface environment (Abbas and Schulze-Makuch 2007). Boron has another interesting characteristic, as the basis for a living organism. In addition, the bonds between boron and nitrogen, which is located on the right of carbon in the periodic table, are able to mimic carbon-carbon bonds when present in the same molecule. The boron/nitrogen compounds are able to form aromatic structures, enabling the possibility of DNA analogs (Schulze-Makuch and Irwin 2008). Numerous gaseous, liquid and solid hydrocarbon species contain alkyl groups and this will make possible the encounter between such groups and boron, so that a hindered dialkyl or trialkyl borane is produced (Abbas and Schulze-Makuch 2007).

Conclusions

Borates are important prebiotic reagents that could have contributed to the evolution of prebiotic structures. Initially, they would have protected and stabilized particular chemical conformers. Later, they became an important chemical messengers in the establishment of the structure of cell membranes and the cytoskeleton.

An important event in the prebiotic chemical evolution is the selection of molecules that can evolve chemically and survive in hostile planetary environments. It is argued here that favourable interactions with borates selected the furanose forms of ribose, a chemical structure with evolutionary potential, to lead to the appearance of the first genetic material on Earth. The ribose furanosyl borate ester remains probably the most important borate-sugar in the building process of the "RNA world", which is a bridge toward the modern "biological world". The selectivity of boron carriers for the sugars and nucleoside transport in the primordial lipidic vesicles is a big challenge for future studies in the boron prebiotic chemistry.

References

Abbas SH, Schulze-Makuch D (2007) Synthesis of biologically important precursors on Titan. J Sci Expl 21 (4):673–687

Amin SA, Kupper FC, Green DH, Harris WR, Carrano CJ (2007) Boron binding by a siderophore isolated from marine bacteria associated with the toxic dinoflagellate gymnodinium catenatum. J Am Chem Soc 129:478–479

Bada JL (2004) How life began on earth: a status report. Earth Planet Sci Lett 226:1–15

Bar-Even A, Shenhav B, Kafri R, Lancet D (2005) The lipid world: from catalytic and informational headgroups to micelle replication and evolution without nucleic acids. In: J. Seckbach, J. Chela-Flores, T. Owen, F. Raulin (eds) Life in the universe: from the miller experiment to the search for life on other worlds. Springer, Berlin, ISBN 1-4020-2371-5 (HB); ISBN 1-4020-2372-3 (e-book) pp 111

Bassil E, Hu H, Brown PH (2004) Use of phenylboronic acids to investigate boron function in plants. Possible role of boron in transvacuolar cytoplasmic strands and cell-to-wall adhesion. Plant Physiol 136(2):3383–3395

Beer R (1976) Jupiter and the boron problem. Icarus 29(2):193–199

Benner SA, Kim HJ, Kim MJ, Ricardo A (2010) Planetary organic chemistry and the origins of biomolecules. Cold Spring Harb Perspect Biol 2:a003467

Bergold A, Scouten WH (1983) Borate chromatography. In: Scouten WH (ed) Solid phase biochemistry. Wiley, New York, pp 149–187

Bermejo MR, Rogero C, Salván CM, Esteban SO, Martín-Gago JA, Veintemillas-Verdaguer S (2009) Thermal wet decomposition of prussian blue: implications for prebiotic chemistry. Chem Biodivers 6(9):1309–1322

Bernstein MP, Sanford SA, Allamandola L, Gillette JS, Clemett SJ, Zare RN (1999) UV irradiation of polycyclic aromatic hydrocarbons in ices: production of alcohols, quinones and ethers. Science 283 (5405):1135

Blevins DG, Lukaszewski KM (1998) Boron in plant structure and function. Annu Rev Plant Physiol Plant Mol Biol 49:481–500

Bolanos L, Lukaszewski K, Bonilla I, Blevins D (2004) Why boron? Plant Physiol Biochem 42:907–912

Bonilla I, Garcia-Gonzalez M, Mateo P (1990) Boron requirement in cyanobacterial. Its possible role in the early evolution of photosynthetic organisms. Plant Physiol 94:1554–1560

Bonilla I, Mergold-Villaseñor C, Campos ME, Sánchez N, Pérez H, López L, Castrejón L, Sánchez F, Cassab GI (1997) The aberrant cell walls of boron-deficient bean root nodules have no covalently bound hydroxyprolin-/proline-rich proteins. Plant Physiol 115:1329–1340

Brack A (2006) Clay minerals and the origin of life. In Handbook of clay science, edited by F. Bergaya, B.K. Theng, G. Lagaly, Amsterdam, Elsevier pp 379–391.

Brown PH, Bellaloui N, Wimmer MA, Bassil ES, Ruiz J, Hu H, Pfeffer H, Dannel F, Römheld V (2002) Boron in plant biology. Plant Biol 4(2):205–223

Burnett TJ, Peebles HC, Hageman JH (1980) Synthesis of a fluorescent boronic acid which reversibly binds to cell walls and a diboronic acid which agglutinates erythrocytes. Biochem Biophys Res Commun 96:157–162

Cairns-Smith AG (1966) The origin of life and the nature of the primitive gene. J Theor Biol 10(1):53–88

Cameron GW, Colgate SA, Grossman L (1973) Cosmic abundance of boron. Nature 243:204–207

Carrano CJ, Schellenberg S, Amin SA, Green DH, Küpper FC (2009) Boron and marine life: a new look at an enigmatic bioelement. Mar Biotechnol 11:431–440

Chapelle S, Verchere JF (1988) A boron-11 and carbon-13 NMR determination of the structures of borate complexes of pentoses and related sugars. Tetrahedron 44:4469–4482

Chen X, Schauder S, Potier N, Van Dorsselaer A, Pelezer I, Bassler BL, Hughson FM (2002) Structural identification of a bacterial quorum-sensing signal containing boron. Nature 415:545–549

Cleaves HJ, Chalmers JH (2004) Extremophiles may be irrelevant to the origin of life. Astrobiology 4(1):1–8

Clifford N, Matthews W, Minard RD (2006) Hydrogen cyanide polymers, comets and the origin of life. Faraday Discuss 133:393–401

Çolak S, Geyikoglu F, Keles ON, Türkez H, Topal A, Unal B (2011) The neuroprotective role of boric acid on aluminium chloride-induced neurotoxicity. Toxicol Ind Health, published online 4 May 2011, doi:10.1177/0748233710395349.

Commeyras A, Collet H, Boiteau L, Taillades J, Vandenabeele-Trambouze O, Cottet H, Biron JP, Plasson R, Mion L, Lagrille O, Martin H, Selsis F, Dobrijevic M (2002) Prebiotic synthesis of sequential peptides on the hadean beach by a molecular engine working with nitrogen oxides as energy sources. Polym Internat 51:661–665

Costanzo G, Saladino R, Crestini C, Ciciriello F, Di Mauro E (2007) Nucleoside phosphorylation by phosphate minerals. J Biol Chem 282:16729–16735

Cossetti C, Crestini C, Saladino R, Mauro ED (2010) Borate minerals and RNA stability. Polymers 2:211–228. doi:10.3390/polym2030211

deGraaf RM, Visscher J, Schwartz AW (1997) Reactive phosphonic acids as prebiotic carriers of phosphorus. J Molec Evol 44:237–241

deDuve C (1991) Blueprint for a cell: the nature and origin of life. In: Neil Patterson Publishers, Burlington, North Carolina, pp 275

Ehrenfreund P, Cami J (2010) Cosmic carbon chemistry: from the interstellar medium to the early earth. Cold Spring Harb Perspect Biol 2:2097

Etaix E, Orgel LE (1978) Phosphorylation of nucleosides in aqueous solution using trimetaphosphate: formation of nucleoside triphosphates. J Carbohydr Nucleos 5:91–110

Ferris JP (1999) Prebiotic synthesis on minerals: bridging the prebiotic and RNA worlds. Biol Bull 196:311–314

Ferris JP (2006) Montmorillonite-catalysed formation of RNA oligomers: the possible role of catalysis in the origins of life. Philosoph Trans Royal Soc B 361:1777–1786

Fort DJ, Stover EL, Strong PL, Murray FJ, Keen CL (1999) Chronic feeding of a low boron diet affects reproduction and development in Xenopus laevis. Biol Tr Elem Res 129:2055–2060

Gabel SA, London RE (2008) Ternary borate-nucleoside complex stabilization by Ribonuclease A demonstrates phosphate mimicry. J Biol Inorg Chem 13(2):207–217

Gaillardet J, Lemarchand D, Göpel C, Manhès G (2001) Evaporation and sublimation of boric acid: application for boron purification from organic rich solutions. Geostandards Newslett 25:67–75

Gedulin B, Arrhenius G (1994) Sources and geochemical evolution of RNA precursor molecules: the role of phosphate. In Early life on Earth, edited by S. Bengston, Nobel Symposium no. 84, New York, Columbia University Press, pp. 91–106.

Gerrard W (1961) The organic chemistry of boron. Academic, New York, p 308

Gilbert W (1986) The RNA World Nature 319:618

Goldbach HE, Yu Q, Wingender R, Schulz M, Wimmer M, Finderklee P, Baluska F (2001) Rapid response reactions of roots to boron deprivation. J Plant Nutr Soil Sci 161:173–181

Gonzales-Fontes A, Rexach J, Navarro-Gochicoa MT, Herrera-Rodríguez MB, Beato VM, Maldonado JM, Camacho-Cristóbal JJ (2008) Is boron involved solely in structural roles in vascular plants? Plant Signal Behav 3(1):24–26

Green J (2009) Precambrian lunar volcanic protolife. Int J Molec Sci 10(6):2681–2721

Grew ES, Bada JL, Hazen RM (2011) Borate minerals and origin of the RNA world. Orig Life Evol Biosph 41:307–316. doi:10.1007/s11084-010-9233-y

Hall DG (2005) Structure, Properties, and Preparation Of Boronic Acid Derivatives. Overview of Their Reactions and Applications In *Boronic Acids*. Edited by Dennis G. Hall WILEY-VCH Verlag GmbH & Co. KGaA, Weinheim ISBN 3-527-30991-8.

Hollis JM, Lovas FJ, Jewell PR (2000) Interstellar glycolaldehyde: the first sugar. Astrophys J 540(2):L107–L110

Holm NG, Dumont M, Ivarsson M, Konn C (2006) Alkaline fluid circulation in ultramafic rocks and formation of nucleotide constituents: a hypothesis. Geochem Trans 7:7. doi:10.1186/1467-4866-7-7

Holm NG, Baltscheffsky H (2011) Links between hydrothermal environments, pyrophosphate, Na$^+$, and early evolution. Orig Life Evol Biosph, accepted 18 February 2011, doi:10.1007/s11084-011-9235-4.

Hu H, Penn SG, Lebrilla CB et al (1997) Isolation and characterization of soluble boron complexes in higher plants. Plant Physiol 113:649–655

Hunt CD (2003) Dietary boron: an overview of the evidence for its role in immune function. J Trace Elem Exp Med 16:291–306

Ishii T, Matsunaga T (1996) Isolation and characterization of a boron–rhamnogalacturonan-II complex from cell walls of sugar beet pulp. Carbohydr Res 284:1–9

Ishii T, Matsunaga T (2001) Pectic polysaccharide rhamnogalacturonan II is covalently linked to homogalacturonan. Phytochemistry 57:969–974

Kakegawa T, Noda M, Nannri H (2002) Geochemical cycles of bio-essential elements on the early earth and their relationships to origin of life. Res Geol 52(2):83–89

Kanzaki T, Yoshida M, Nomura M, Kakihana H, Ozawa T (1979) Boron isotopic composition of fumarolic condensates and sassolites from Satsuma Iwo-Jima. Jap Geochim Cosmochim Acta 43(11):1859–1863

Keefe AD, Miller SL (2010a) Was ferrocyanide a prebiotic reagent? Orig Life Evol Biosph 26(2):111–129

Keefe AD, Miller SL (2010b) Are polyphosphates or phosphate esters prebiotic reagents? J Molec Evol 41 (6):693–702

Kim HJ, Benner SA (2010) Comment on "The silicate-mediated formose reaction: Bottom-up synthesis of sugar silicates". Science 329:902-a.

Kirschvink JL, Weiss BP (2001) Mars, panspermia, and the origin of life: where did it all begin? Palaeontol Electron 4(2):8

Kobayashi M, Matoh T, Azuma J (1996) Two chains of rhamnogalacturonan II are cross-linked by borate-diol ester bonds in higher plant cell walls. Plant Physiol 110:1017–1020

Kolb M, Zhu W (2004) Complexes of ribose with silicates, borates, and calcium: implications to astrobiology. Proc SPIE 5555:70–77

Kolitz M, Cohen-Arazi N, Hagag I, Katzhendler J, Domb AJ (2009) Biodegradable polyesters derived from amino acids. Macromolecules 42:4520–4530

Kristof P, Hannes R, Bernd R (2005) Prebiotic chemistry: the amino acid and peptide world. Curr Org Chem 9 (12):1107–1114

Krogh-Moe J (1963) Energy and length of the boron-oxygen bond. Acta Chem Scandinavia 17:843–864

Lambert JB, Gurusamy-Thangavelu SA, Ma K (2010a) The silicate-mediated formose reaction: bottom-up synthesis of sugar silicates. Science 237:984–986

Lambert JB, Gurusamy-Thangavelu SA, Ma K (2010b) Response to comment on "The silicate-mediated formose reaction: Bottom-up synthesis of sugar silicates". Science 329:902-b.

Larralde R, Robertson MP, Miller SL (1995) Rates of decomposition of ribose and other sugars: implications for chemical evolution. Proc Natl Acad Sci USA 92:8158–8160

Li Q, Ricardo A, Benner SA, Winefordner JD, Powell DH (2005) Desorption/ionization on porous silicon mass spectrometry studies on pentose-borate complexes. Anal Chem 77:4503

Lodders K (2010) Solar system abundances of the elements. In: Goswami A, Reddy BE (eds) Principles and perspectives in cosmochemistry. Astrophysics and space science proceedings. Springer, New York, pp 379–417

Loomis WD, Durst RM (1992) Chemistry and biology of boron. Biofactors 3:229–239

Martin AR, Mohanan K, Luvino D, Floquet N, Baraguey C, Smietana M, Vasseur JJ (2009) Expanding the borononucleotide family: synthesis of borono-analogues of dCMP, dGMP and dAMP. Org Biomol Chem 7:4369–4377

Martin AR, Barvik I, Luvino D, Smietana M, Vasseur JJ (2011) Dynamic and Programmable DNA-Templated Boronic Ester Formation. Angew Chem Int Ed, article first published online: 28 MAR 2011 doi:10.1002/anie.201007170.

McClendon JH (1976) Elemental abundance as a factor in the origins of mineral nutrient requirements. J Mol Evol 8:175–195

McDonald GD, Storrie-Lombard MC (2010) Biochemical constraints in a protobiotic earth devoid of basic amino acids: the "BAA(-) World". Astrobiology 10(10):989–1000

McKay CP, Porco CC, Altheide T, Davis WL, Kral TA (2008) The possible origin and persistence of life on enceladus and detection of biomarkers in the plume. Astrobiology 8(5):909–19

Mellersh AR, Smith PM (2010) The alkaline world and the origin of life. J Cosmol 10:3230–3242

Miwa K, Fujiwara T (2010) Boron transport in plants: co-ordinated regulation of transporters. Ann Bot 105:1103–1108

Morchio R, Traverso S (2005) Prebiotic phosphate: a problem insoluble in water? Riv Biol 98(1):18–23

Mulkidjanian AY, Galperin MY (2009) On the origin of life in the Zinc world. Validation of the hypothesis on the photosynthesizing zinc sulphide edifices as cradles of life on Earth. Biol Direct 4:27

Nielsen FH (1996) Evidence for the nutrition essentiality of boron. J Trace Elem Exp Med 9:215–229

Nielsen PE (2007) Peptide nucleic acids and the origin of life. Chem Biodivers 4(9):1996–2002

Otsuka H, Uchimura E, Koshino H, Okano T, Kataoka K (2003) Anomalous binding profile of phenylboronic acid with N-acetylneuraminic acid (Neu5Ac) in aqueous solution with varying pH. J Am Chem Soc 125:3493–3502

Palme H and Jones A (2005) Solar system abundances of the elements. In: Treatise od Geochemistry, Chap.1.03, vol.1:41-61, Holland HD and Turekian KK, eds

Park M, Li Q, Shcheynikov N, Muallen S, Zeng W (2004) NaBC1 is a ubiquitous electrogenic Na^+-coupled borate transporter essential for cellular boron homeostasis and cell growth and proliferation. Mol Cell 16(3):331–341

Park M, Li Q, Shcheynikov N, Muallen S, Zeng W (2005) Borate transport and cell growth and proliferation: not only in plants. Cell Cycle 4(1):24–26

Pelmore H, Symons MCR (1986) NMR studies of complexes formed by D-fructose and borate ions in aqueous solution. Carbohydr Res 155:206–211

Petasis NA (2007) Expanding roles for organoboron compounds versatile and valuable molecules for synthetic biological and medicinal chemistry. Aust J Chem 60:795–798

Power PP, Woods WG (1997) The chemistry of boron and its speciation in plants. Plant Soil 193:1–1

Prieur BE (2001) Étude de l'activité prébiotique potentielle de l'acide borique. C R Acad Sci Ser IIC Chem 4:667–670

Raymond F, Gesteland TR, Cech JF, Atkins C (2005) The RNA World, In Cold Spring Harbor Monograph Series 43, third edition, Spring Harbor Laboratory Press, pp. 768.

Raven JA (1980) Short and long distance transport of boric acid in plants. New Phytol 84:231–249

Redondo-Nieto M, Reguera M, Bonilla I, Bolaños L (2008) Boron dependent membrane glycoproteins in symbiosome development and nodule organogenesis. A model for a common role of boron in organogenesis. Plant Signal Behav 3(5):298–30

Rezanka T, Sigler K (2008) Biologically active compounds of semi-metals. Phytochemistry 69:585–606

Ricardo A, Carrigan MA, Olcott AN, Benner SA (2004) Borate minerals stabilize ribose. Science 303:196

Riggs JA, Litchfield RK, Smith BD (1996) Molecular recognition and membrane transport with mixed-ligand borates. J Org Chem 6:1148–1150

Rossa DS (2008) Quantitative evaluation of the iron-sulfur world and its relevance to life's origins. Astrobiology 8(2):267–273

Rowe RI, Eckert CD (1999) Boron is required for zebra¢sh embryogenesis. J Exp Biol 202:1649–1654

Saladino R, Barontini M, Cossetti C, Di Mauro E, Crestini C (2011) The effects of borate minerals on the synthesis of nucleic acid bases, amino acids and biogenic carboxylic acids from formamide. Orig Life Evol Biosph 41:317–330. doi:10.1007/s11084-011-9236-3

Schaeffer R (1964) In Progress in Boron Chemistry, edited by H. Steinberg, A. L. McCloskey, MacMillan, New York, pp. 453-459.

Schulze-Makuch D, Irwin LN (2008) Life in the universe. In Expectations and constraints, 2 ed. Springer, Verlag, pp 251

Schwartz AW (2006) Phosphorus in prebiotic chemistry Phil. Trans R Soc B 361:1743–1749. doi:10.1098/rstb.2006.1901

Scorei R, Cimpoiasu VM (2006) Boron enhances thermostability of carbohydrates. Orig Life Evol Biosph 36(1):1–11

Segre D, Eli DB, Deamer DW, Lancet D (2001) The lipid world. Orig Life Evol Biosph 31:119–145

Shakir A, Humaira F, Ram P, Mohammad N, Rzutraya I, Yadavc S, Ahmadd F (2010) Boron stabilizes peroxide mediated changes in the structure of heme proteins. Int J Biol Macromol 47:109–115

Shaw DM (1995) Lunar behaviour of boron contrasted with the terrestrial boron cycle. Meteoritics 30(2):199–208

Silva JJR, Frausto DA, Paton R, Williams J (2001) The biological chemistry of the elements: the inorganic chemistry of life. In Oxford University Press, 2-edition, New York, pp. 575.

Sleep NH (2010) The Hadean-Archaean Environment Cold Spring Harb Perspect Biol. 2(6):a002527.

Smith BD, Gardiner SJ, Munro TA, Paugam MF, Riggs JA (1998) Facilitated transport of carbohydrates, catecholamines, and amino acids through liquid and plasticized organic membranes. J Inclus Phenom Mol 32:121–131

Spivak-Birndorf LJ, Wadhwa M, Williams LB (2008a) The Boron Isotopic Composition of Nakhla Iddingsite. In 39th Lunar and Planetary Science Conference, Lunar and Planetary Science XXXIX, League City, Texas, LPI Contribution No. 1391, pp. 1904.

Spivak-Birndorf LJ, Wadhwa M, Williams LB (2008b) Boron isotopes in the nakhlites: Implications for crustal fluids on Mars, Goldschmidt Conference Abstracts, A889.

Sponer JE, Sumpter BG, Leszczynski J, Sponer J, Fuentes-Cabrera M (2008) Theoretical study on the factors controlling the stability of the borate complexes of ribose, arabinose, lyxose, and xylose. Chemistry 14:9990–9998

Springsteen G, Wang B (2002) A detailed examination of boronic acid-diol complexation. Tetrahedron 58:5291–5300

Springsteen G, Joyce GF (2004) Selective derivatization and sequestration of ribose from a prebiotic mix. J Am Chem Soc 126(31):9578–9583

Strasdeit H (2010) Chemical evolution and early earth's and mars' environmental conditions. Palaeodivers 3:107–116

Takano J, Miwa K, Yuan L, von Wiren N, Fujiwara T (2005) Endocytosis and degradation of BOR1, a boron transporter of *Arabidopsis thaliana*, regulated by boron availability. Proc Natl Acad Sci USA 102:12276–12281

Tanaka M, Fujiwara T (2007) Physiological roles and transport mechanisms of boron: perspectives from plants. Pflugers Archives-Eur J Physiol 456:671–677

Verstraeten SV, Lanoue L, Keen CL, Oteiza PI (2005) Relevance of lipid polar headgroups on boron-mediated changes in membrane physical properties. Arch Biochem Biophys 438(1):103–10

Voges D, Zwickl P, Baumeister W (1999) The 26s proteasome: a molecular machine designed for controlled proteolysis. Annu Rev Biochem 68:1015–1068

Wächtershäuser G (2000) Origin of life: life as we don't know it. Science 289(5483):1307–1308

Weber AL (2007) The sugar model: autocatalytic activity of the triose-ammonia. Orig Life Evol Biosph 37:105–111

Weber AL (2008) Sugar-driven prebiotic synthesis of 3,5(6)-dimethylpyrazin-2-one: A possible nucleobase of a primitive replication process. Orig Life Evol Biosph 38:279–292

Weser U (1967) Chemistry and structure of some borate polyol compounds of biochemical interest. In: Jorgensen C, Neilands J, Nyholm R, Reinen D, Williams R (eds) Structure and bonding, vol 2. Springer, New York, pp 160–180

Weser and Kaup (2002) Borate, an Effective Mummification Agent in Pharaonic Egypt, Z. Naturforsch. 57b:819-822.

Westmark PR, Gardiner SJ, Smith BD (1996) Selective monosaccharide transport through lipid bilayers using boronic acid carriers. J Am Chem Soc 118:11093–11100

Westmark PR, Smith BD (1996) Boronic acids facilitate the transport of ribonucleosides through lipid bilayers. J Pharm Sci 85(3)

Wolkenstein K, Gross JH, Falk H (2010) Boron-containing organic pigments from a Jurassic red alga. PNAS 107(45):19374–19378. doi:10.1073/pnas.1007973107

Yamagata Y, Watanabe H, Saitoh M, Namba T (1991) Volcanic production of polyphosphates and its relevance to prebiotic evolution. Nature 352:516–519

York WS, Darvill AG, McNeil M, Albersheim P (1985) Structure of plant-cell walls: 16. 3-Deoxy-D-manno-2-octulosonic acid (KDO) is a component of rhamnogalacturonan-II, a pectic polysaccharide in the primary-cell walls of plants. Carbohyd Res 138:109–126

Zittle C (1951) Reaction of borate with substances of biological interest. In: Advances in Enzymology, edited by F. Ford, New York, Interscience Publishers, 12:493–527.

Zubay G (1988) Biochemistry, 2nd edn. Macmillan, New York

Zubay G, Mui T (2001) Prebiotic synthesis of nucleotides. Orig Life Evol Biosph 31:87–102