



Review

Biologically active compounds of semi-metals

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Abstract

Semi-metals (boron, silicon, arsenic and selenium) form organo-metal compounds, some of which are found in nature and affect the physiology of living organisms. They include, e.g., the boron-containing antibiotics aplasmomycin, borophycin, boromycin, and tartrolon or the silicon compounds present in “silicate” bacteria, relatives of the genus *Bacillus*, which release silicon from aluminosilicates through the secretion of organic acids. Arsenic is incorporated into arsenosugars and arsenobetaines by marine algae and invertebrates, and fungi and bacteria can produce volatile methylated arsenic compounds. Some prokaryotes can use arsenate as a terminal electron acceptor while others can utilize arsenite as an electron donor to generate energy. Selenium is incorporated into selenocysteine that is found in some proteins. Biomethylation of selenide produces methylselenide and dimethylselenide. Selenium analogues of amino acids, antitumor, antibacterial, antifungal, antiviral, anti-infective drugs are often used as analogues of important pharmacological sulfur compounds. Other metalloids, i.e. the rare and toxic tellurium and the radioactive short-lived astatine, have no biological significance.

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Keywords: Semi-metals; Boron; Silicon; Arsenic; Selenium; Organometallic compounds; Bacteria; Fungi; Higher plants**Contents**

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1. Introduction

In the periodic table of elements, semi-metals (metalloids) are found along the line that distinguishes metals from nonmetals. Together with metals and nonmetals, metalloids form one of the three categories of chemical elements as classified by ionization and bonding properties (Rochow, 1966; Venugopal and Luckey, 1978). They have some of the qualities of both metals and nonmetals. Unlike the true metals, metalloids are usually semiconductors rather than conductors and have therefore received intensive attention from the computer and electronics industries. Their relative abundance in the environment is summarized in Table 1.

When involved in chemical bonding, the metalloids again exhibit intermediate qualities. They are capable of taking electrons from most metals and will readily lose electrons to most nonmetals. Their electronegativity values are also mid-range. They usually establish covalent bonding, ionic bonding being rather rare.

The reactivity of the metalloids depends on the counter-element. Boron acts as a nonmetal when reacting with sodium yet as a metal when reacting with fluorine. In organic compounds, they can substitute other elements such as sulfur. Boron and arsenic form compounds with lipids, sugars, phenols, organic acids and some polymers. Organic arsenic compounds are components of the food chains of many organisms including humans and may play important biological roles in them. Selenium is found in living organisms in its soluble inorganic forms and as protein-bound and free seleno-amino acids and volatile organoselenium compounds. Most small organic selenium

compounds in living cells are isologues of sulfur amino acids or their derivatives. The interactions of silicon with living matter are vitally important for some bacteria, which release silicon from aluminosilicates through the secretion of organic acids, or for unicellular algae – diatoms for which it serves as the basic building block of their bodies. Tellurium is highly toxic and is not thought to be required by biological systems; the highly radioactive astatine is so rare in nature that the existence of biological astatine compounds is highly improbable.

2. Boron

Boron is a ubiquitous element in rocks, soil, and water, its average concentration ranging from ~1 mg/kg in fresh water to ~100 mg/kg in rocks (Steinberg, 1964).

Tetrahedral borate or boronate complexes have been shown to be involved in enzyme inhibition. Serine proteases were proposed to be inhibited by boric acid (Antonov et al., 1968), and simple borates have been patented as protease stabilizers in liquid detergent formulations (Hora and Kivits, 1981; Severson, 1985).

Serine hydrolase enzymes react with various borates, boronates, and borinates by forming a tetrahedral complex between the serine hydroxyl group and the boron atom. Hydrogen bonding to the imidazole ring of an adjacent histidine adds further stabilization (Fig. 1). Boric acid forms complexes with sugars, phenols, organic acids, and some polymers (Boeseckem, 1949; Raven, 1980).

2.1. Boron in bacteria

In bacteria boron is an essential part of signal molecules required for quorum sensing (Goldbach and Wimmer, 2007). For instance, an AI-2 furanosyl borate diester complex (**1**) that was identified in the bioluminescent marine bacterium *Vibrio harveyi* as one of two autoinducers that regulate light production in response to cell density (Bassler et al., 1993, 1994; Cornell et al., 1996; Della Ragione et al., 1985) has been proposed to serve as a “universal” bacterial quorum-sensing boron-containing signal for

Table 1
Relative abundance of metalloids in the environment

Element	In Earth's crust (mg/kg)	In sea water (mg/L)
As	1.8–5.0	0.003
B	3–10	4.6
Se	0.05–0.09	0.00009
Si	257,000–282,000	3
Te	0.001–0.005	0
At	0	0

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