An Introduction to Boron: History, Sources, Uses, and Chemistry

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Following a brief overview of the terrestrial distribution of boron in rocks, soil, and water, the history of the discovery, early utilization, and geologic origin of borate minerals is summmarized. Modern uses of borate–mineral concentrates, borax, boric acid, and other refined products include glass, fiberglass, washing products, alloys and metals, fertilizers, wood treatments, insecticides, and microbiocides. The chemistry of boron is reviewed from the point of view of its possible health effects. It is concluded that boron probably is complexed with hydroxylated species in biologic systems, and that inhibition and stimulation of enzyme and coenzymes are pivotal in its mode of action. — Environ Health Perspect 102(Suppl 7): 5–11 (1994)

Key words: boron, borax, colemanite, glass, boric acid, health effects, enzyme, review

Introduction

Boron is an ubiquitous element in rocks, soil, and water. Most of the earth's soils have <10 ppm boron, with high concentrations found in parts of the western United States and in other sites stretching from the Mediterranean to Kazakhstan. The average soil boron concentration is 10 to 20 ppm, with large areas of the world boron deficient. Boron concentrations in rocks range from 5 ppm in basalts to 100 ppm in shales, and averages 10 ppm in the earth's crust overall. Soils have boron concentrations of 2 to 100 ppm. Seawater contains an average of 4.6 ppm boron, but ranges from 0.5 to 9.6 ppm. Freshwaters normally range from <0.01 to 1.5 ppm, with higher concentrations in regions of high boron soil levels (*1,2*).

Highly concentrated, economically sized deposits of boron minerals, always in the form of compounds with boron bonded to oxygen, are rare and generally are found in arid areas with a history of volcanism or hydrothermal activity. Such deposits are being exploited in Turkey, the United States, and several other countries (*3*). Borate–mineral concentrates and refined products are produced and sold worldwide. They are used in a myriad of ways: in glass and related vitreous applications, in laundry bleaches, in fire retardants, as micronutrients in fertilizers and for many other purposes, as well.

The varied chemistry and importance of boron is dominated by the ability of borates to form trigonal as well as tetrahedral bonding patterns and to create complexes with organic functional groups, many of biologic importance.

The present review will give an overview of boron from its sources to its uses and chemistry to provide a background for the following papers dealing with its health effects.

History and Sources

The Babylonians have been credited with importing borax from the Far East over 4000 years ago for use as a flux for working gold. Mummifying, medicinal and metallurgic applications of boron are sometimes attributed to the ancient Egyptians. None of this very old borax history has been verified, but solid evidence exists that tinkar (i.e., $Na_2B_4O_7{\cdot}10H_2O$, tincal, the mineral borax) was first used in the eighth century around Mecca and Medina, having been brought there (and to China) by Arab traders (*4*). The use of borax flux by European goldsmiths dates to about the 12th century.

The earliest source of borax is believed to have been Tibetan lakes. The borax was transported in bags tied to sheep, which were driven over the Himalayas to India.

Volatility of boric acid with steam is believed by geologists to be the primary mechanism for the formation of borate deposits (*3*). A prime example of this are the geysers (soffioni) in Tuscany, which were an important source of boric acid in Europe from about 1820 to the 1950s. Borax also was made from Italian boric acid in England, France, and Germany.

The borate industry in Turkey commenced in 1865 with mining of the calcium borate pandermite (priceite, $4CaO{\cdot}5B_2O_3{\cdot}7H_2O$). At about the same time, several borate deposits were found in California and Nevada, including ulexite ($Na_2O{\cdot}2CaO{\cdot}5B_2O_3{\cdot}16H_2O$) and colemanite ($2CaO{\cdot}3B_2O_3{\cdot}5H_2O$) in Death Valley. These minerals could be converted to borax by reaction with trona ($Na_2CO_3{\cdot}NaHCO_3{\cdot}2H_2O$).

The Kramer deposit, at what is now Boron, California, in the Mojave Desert, was discovered in 1913, first as a colemanite ore source. In 1925, tincal ore was found and in 1926, the new mineral rasorite (kernite, $Na_2O{\cdot}2B_2O_3{\cdot}4H_2O$) was encountered (*4*). It is the largest borate deposit outside of Turkey and has supplied a sizable portion of world borate demand for over 50 years.

Turkey has supplied colemanite for many years to boric acid producers in Europe. Sodium borates were discovered at Kirka in 1960 and other deposits have since been found and developed in Anatolia. As a result, today Turkey is the largest producer of borate products in the world (*5*), exporting mineral concentrates of tincal, colemanite, and ulexite, plus refined borax decahydrate, borax pentahydrate ($Na_2O{\cdot}2B_2O_3{\cdot}5H_2O$), anhydrous borax ($Na_2O{\cdot}2B_2O_3$), and boric acid ($B[OH]_3$).

Borates in the United States are produced entirely in the Mojave Desert of southern California. United States Borax

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Figure 1. Aerial view of the US Borax mine and refinery at Boron, CA. (US Borax, Inc. photo)

Table 1. Important refined borate products and mineral concentrates.

Name	Formula	Percent B_2O_3
Borax pentahydrate	$Na_2[B_4O_5(OH)_4]\cdot 3H_2O$	47.8
Borax (tincal)	$Na_2[B_4O_5(OH)_4]\cdot 8H_2O$	36.5
Colemanite	$Ca[B_3O_4(OH)_3]\cdot H_2O$	50.8
Ulexite	$NaCa[B_5O_6(OH)_6]\cdot 5H_2O$	43.0
Boric acid	$B(OH)_3$	56.3
Anhydrous borax	$Na_2B_4O_7$ (glass)	69.2

Table 2. Estimated consumption of boron minerals and chemicals in the United States (*6*).

Use	Percent
Glass and ceramics	
Insulation fiberglass	28
Textile fiberglass	12
Glass	9
Enamels and glazes	3
Detergents and bleaches	12
Alloys and metals	6
Fire retardants	5
Agriculture	4
Adhesives	2
Other chemicals	19

& Chemical Corporation, a subsidiary of Rio Tinto Zinc (RTZ), is the largest source, producing borax pentahydrate and decahydrate, and anhydrous borax from tincal ore, and boric acid from kernite ore (Equation 1).

$$Na_2B_4O_7\cdot 4H_2O + H_2SO_4 + H_2O \rightarrow 4B(OH)_3 + Na_2SO_4 \quad [1]$$

An aerial photo of the US Borax mine and refinery is shown in Figure 1. Another US Borax plant at Los Angeles harbor produces ammonium and potassium borates, boric oxide, zinc borate, and spray dried polyborates, in addition to serving as an export terminal.

North American Chemical recovers borax and boric acid as byproducts from potash, soda ash, and salt-cake extraction operations on Searles Lake brine. Ore concentrates are produced by Newport Mineral Ventures on the edge of Death Valley.

Peru and Chile produce ulexite concentrates and boric acid, and Boroquimica in Argentina operates a tincal deposit. China and the former USSR also produce some borates.

Table 1 gives a list of the commercially important refined borate products and mineral concentrates. The formulas are written in a form reflecting their structures.

Uses

Table 2 lists the uses of boron minerals and chemicals in the United States glass and related uses consume about half of the borates as boric anhydride (B_2O_3) in the United States (*6*). Fiberglass accounts for the largest share, comprising about 77% of the total (54% for insulation fiberglass, 23% for textile grade). Heat-resistant pyrex and other low-thermal expansion glasses consume about 18%, while enamels, frits, and ceramic glazes consume 5%. Small amounts are used in sealing and optical glasses, Vycor, and vitrifying nuclear waste.

Boric oxide can be added to the glass formulation as borax pentahydrate, boric acid, or colemanite, with price and cation compatibility determining which is used (*7*). For example, textile fiberglass requires low sodium, so boric acid or colemanite are used. Glass batch melting is aided by B_2O_3 which acts as a flux to improve the melting rate of more refractory components (e.g., SiO_2). As an added benefit, water given off by the borates also accelerates the melting.

The alkali/alkaline earth oxide content is quite important to the effect of B_2O_3 on the structure and properties of glass. Adding Na_2O, for example, progressively changes trigonal BO_3 groupings to tetrahedral BO_4^- groups, which initially causes an increase in the glass transition temperature (Tg). Further addition of Na_2O converts BO_4^- bonding groups to nonbonding BO_3^{-n} units, which decreases T_g as well as the melt viscosity. The latter helps in eliminating bubbles from the finished glass and gives good homogeneity and flattens the viscosity–temperature curve. The latter allows more latitude during manufacture (forming) of the finished glass product, and the lower viscosity allows higher production rates.

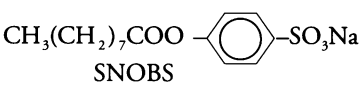
Borosilicate glass has increased thermal shock resistance because B_2O_3 lowers the expansion coefficient. In fiberglass, boric oxide gives desirable drawing qualities and increases mechanical strength and chemical durability.

Another 12% of United States B_2O_3 is consumed in detergents and bleaches; the percentage is even higher in Europe. Borax has been used as a laundry additive since about 1900. It can contribute to the softening of hard water by tying up calcium ions, as well as acting as a buffer agent. A traditional use as a sweetening agent for diaper pails is thought to involve the borate inhibition of the urease enzyme, (preventing ammonia formation). The same effect has been patented for deodorizing animal litter (*8*). Products based on borax and formulated with additives can give bleachlike activity when added to the wash.

Sodium perborates [$NaBO_3\cdot 1H_2O$ or $4H_2O$; PBS1 or PBS4] are true persalts that traditionally have been blended into powdered detergents in Europe as bleaching agents. Dilution in alkaline wash water results in hydrolysis of PBS to give hydroperoxide ion (Eq. 2).

$$\mathrm{Na_2[(HO)_2B(OO)_2B(OH)_2]} \cdot 6\mathrm{H_2O} + 2\mathrm{OH^-} \rightarrow 2\mathrm{NaB(OH)_4} + 2\mathrm{OOH^-} + 4\mathrm{H_2O} \qquad [2]$$

Sodium perborate (PBS) is effective as a broad-range bleach only at washing temperatures above about 60°C, unless an activator is present. Activators are organic acyl derivatives, which react with the hydroperoxide ion formed by hydrolysis of the perborate leading to peracid formation (Eq. 3). These peracids are effective bleaching agents at low temperature.



$$\mathrm{CH_3(CH_2)_7COO{-}C_6H_4{-}SO_3Na}$$

SNOBS

or

$$\mathrm{(CH_3CO)_2NCH_2CH_2N(COCH_3)_2}$$

TAED

$$+ 1 \text{ or } 2\cdot\mathrm{OOH^-} \rightarrow$$

$$\mathrm{CH_3(CH_2)_7COOOH} \text{ or } 2\cdot\mathrm{CH_3COOOH} \qquad [3]$$

At present, sodium 4-nonanoyloybenzenesulfonate (SNOBS) is used in several detergents with bleach products in the United States, and tetraacetylethylenediamine (TAED) is used widely in Europe as well as in many other countries. PBS-based powdered bleach also is sold in the United States. Borax or boric acid can be used to stabilize protease enzymes in liquid laundry detergents (*9,10*).

Alloy and metal production consume another 5.5% of the total B_2O_3. Welding rods and other fluxes use borates because of their excellent metal oxide solubilizing ability. Boron usage in amorphous metal alloys for electrical equipment and magnets is slowly increasing. Borates are used extensively as fire retardants, particularly borax and boric acid in shredded cellulosic insulation and zinc borate in plastics. Concerns about the toxicity of other treatments have increased the interest in borates for wood preservation.

Agriculturally, borates are used in fertilizer (4% of United States B_2O_3) to correct trace boron-deficiency in certain crops (*2*). Some crops susceptible to boron deficiency are apples, alfalfa, sugar beets, and oil palms. Boron is one of the more important essential elements for plant growth, and can be applied either to the soil or to the foliage. Although small amounts of boron are needed by all plants, high concentrations can be toxic to certain species. Borates and combinations of borates with organic herbicides are used to control weeds.

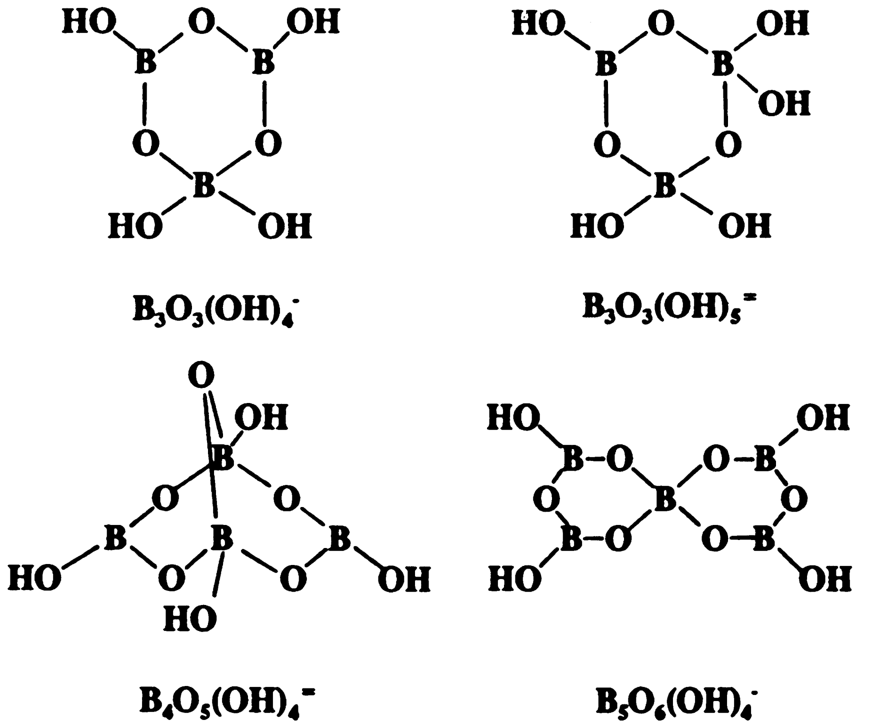


Figure 2. Polymeric borate anions (*14*).

The exact role of boron in plant metabolism is not known. Boron deficiency alters the plasmalemma of root cells, which results in reduced absorption of potassium, chloride, and rubidium, as well as cessation of root growth. Enzymes such as glucan synthetase involved in pollen tube cell wall growth apparently require boron. Boron also may control the amount of phenols in cells. Apical meristem abnormalities may be a secondary effect of vascular tissue damage caused by lack of boron. An adequate supply of boron is essential for proper seed set and normal fruit development. Breakdown of parenchyma in cell walls which results in reduced lignification is another symptom of boron starvation. Sugar buildup in leaves of boron-deficient plants is attributed to reduced sugar consumption and plasmalemma abnormalities inhibiting sugar transport out of the leaves. Adequate boron is required for incorporation of phosphorus into RNA and DNA. Lack of boron also is suspected of elevating indoleacetic acid (IAA) in plants by inhibiting IAA oxidase (*2*).

Borates are used extensively in treating wood to protect against decay by brown and white rot, and staining by fungi (*11*).

Insecticidal use of borates is attractive because of their low mammalian toxicity and lack of insect resistance compared with the organic insecticides. The literature contains over 150 references in this field. Species showing promise for control by borate-based insecticides are the powder post beetle (*Lyctus brunneus*) in hardwoods (*12*) and larvae of several other beetles which attack soft wood. Some species of subterranean termites like Coptotermes and Reticulitermes which contain gut protozoa are susceptible, because boron is toxic to these cellulose-digesting organisms and leads to starvation of the host as well as systemic effects. Less research has been done on drywood termites, but some success has been obtained with Cryptotermes. Sodium octaborate, a highly soluble polyborate, is of interest both for pre and posttreatment of wood.

Control of cockroaches with boric acid has had great success, particularly against the German roach *Blattella germanica* in

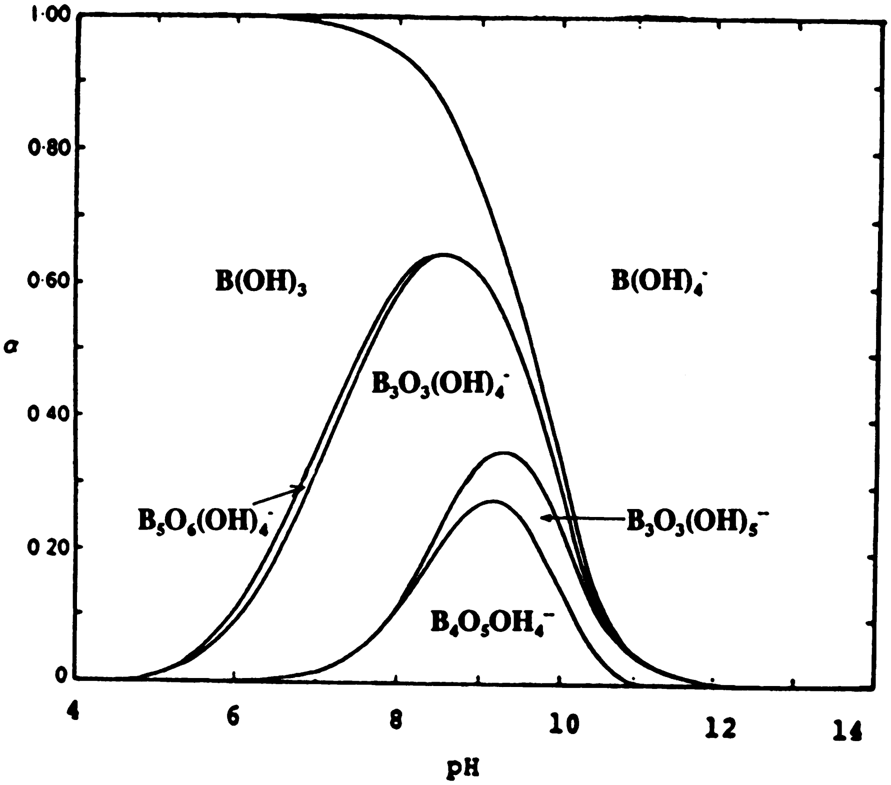


Figure 3. Distribution of polyborate species as a function of pH, 0.40M boric acid (*15*).

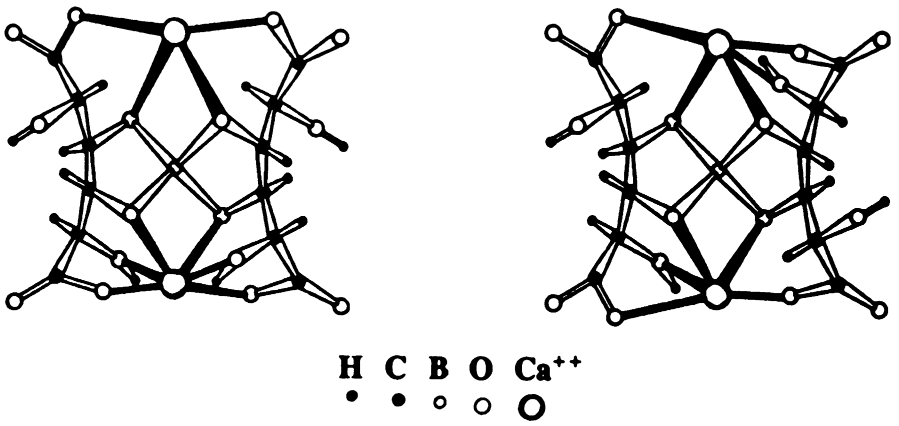


Figure 4. Diastereomeric borate–saccharate complexes showing calcium coordination (*18*).

the US Boric acid does not act as a repellant, (a problem with many organic blatticides), and it is inexpensive, safe, and effective (*13*). When powdered boric acid is combined with an anticaking agent, the roach contacts the chemical and eventually dies through cuticular absorption and ingestion by grooming.

Promising work also has been done with boron insecticides on ants, carpet beetles, and fleas.

Miscellaneous applications in starch adhesives, raw material for sodium borohydride, borides, boron trifluoride, semiconductor dopants, and a multitude of other small uses comprise 21% of the utilization of B_2O_3 in the United States.

Chemistry

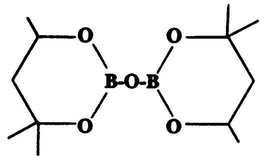
The aqueous chemistry of the borates is dependent on concentration and pH. Dilute aqueous boric acid solutions are comprised solely of $B(OH)_3$ and $B(OH)_4^-$ species. Rapid exchange on the nuclear magnetic resonance (NMR) time scale results in a single peak in the boron-11 NMR spectrum which moves steadily up as the pH is increased. Concentrated solutions have been shown by NMR and Raman spectra, as well as by titrimetric evidence, to contain polyborate ions of the types shown in Figure 2 (*14*). The distribution of these species as a function of pH is given in Figure 3 (*15*).

At the pH of human blood (7.4), the expected low concentrations of borate will be present as 98.4% $B(OH)_3$ and only 1.6% as the $B(OH)_4^-$ ion because of the weak acidity (pK_a 9.2) of boric acid.

Simple alcohols react with boric acid to give esters (Eq. 4). In aqueous solution, this equilibrium usually lies far to the left.

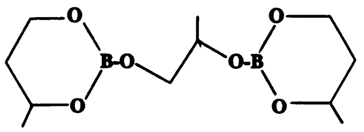
$$B(OH)_3 + 3ROH \rightarrow B(OR)_3 + 3H_2O \qquad [4]$$

The partially esterified species $(RO)_2BOH$ and $ROB(OH)_2$ probably also are involved (*16*). Polyhydric alcohols form cyclic esters with boric acid. For example, hexylene glycol boric anhydride (Structure 1)



Structure 1

and 1,3-butylene glycol biborate (Structure 2)



Structure 2

are mixed to give the jet fuel microbiocide Biobor JF. This additive prevents the growth of *Cladosporium resinae* and *Pseudomonas aeruginosa* in fuel tanks by distributing itself between the water and fuel phases. This hydrocarbon-metabolizing fungus and bacterium grow at the fuel–water interface and can cause corrosion as well as foul the fuel filter (*17*).

Sugars with the proper disposition of hydroxyl groups also form ester complexes with boric acid. A striking example is the sugar diacid disodium saccharate (glucarate) which forms a 2:1 sugar acid:borate complex in aqueous solution that has the ability to complex calcium ions. The two

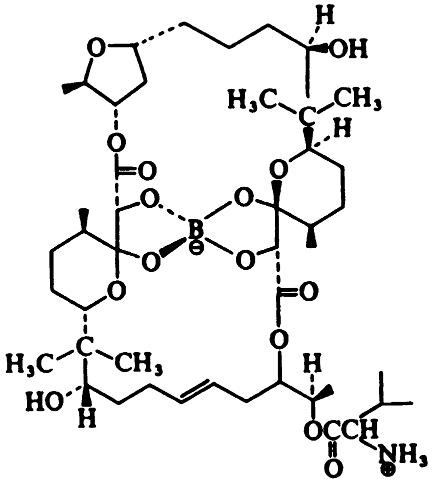
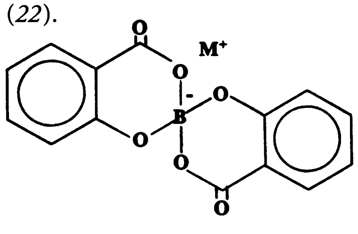


Figure 5. Boromycin (*20*).

diastereomeric forms of this complex are shown in Figure 4. Proton and carbon-13 NMR spectra showed that the 3,4-diol portion of the tetrol fragment was involved in coordinating with the boron atom (*18*). These complexes are of interest as biodegradable builders to replace phosphate in detergents (*19*).

A small group of boron-containing antibiotics contain a single tetrahedral boron atom in the center of the structure, complexed with two vicinal diol groups. The first to be isolated and identified was boromycin (*20*) (Figure 5) from *Streptomyces antibioticus*. The related aplasmomycin was obtained from *S. griseus* (*21*); both show antibiotic activity against gram-positive bacteria and represent the only isolated natural products containing boron.

Bis(salicylato)borate salts (Structure 3) are readily formed in aqueous solution from salicylic acid solution and boric acid (*22*).



Structure 3

2-Aminoalkanols form borate esters readily because of the added stabilization of the N–B dative bond. A striking example is the formation of triethanolamine borate (Structure 4) from a 1:1 aqueous solution of boric acid and triethanolamine (*16*).

Boron in plant roots is believed to be reversibly bound as polysaccharide–borate complexes (*2*).

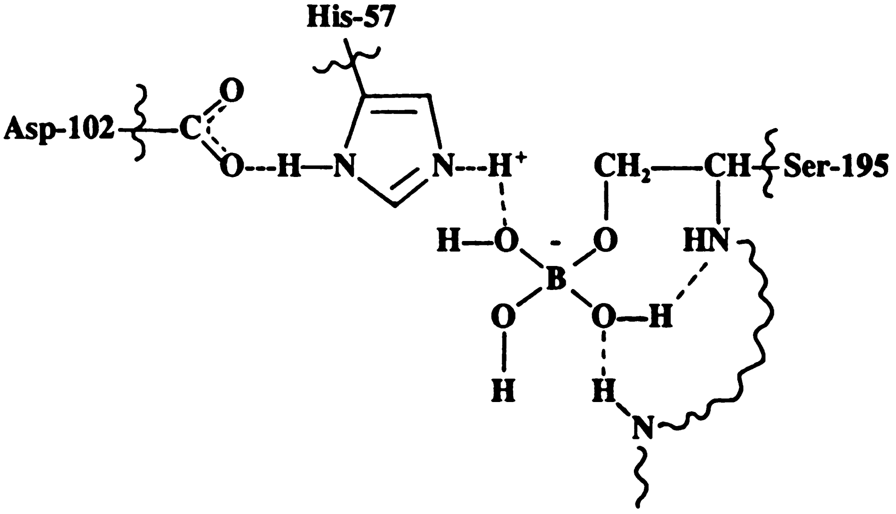


Figure 6. Borate intermediate in serine hydrolase inhibition.(*32*)

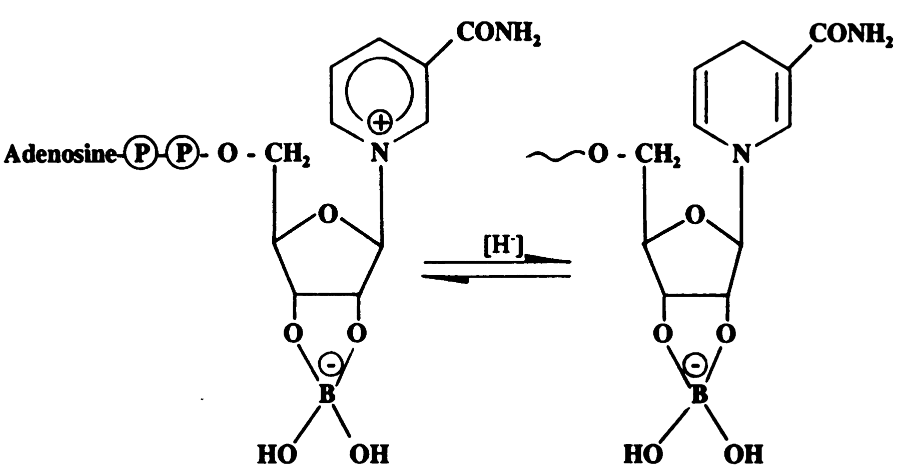
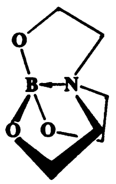


Figure 7. Borate inhibition of hydrogenase coenzyme by fibityl group complexing (*31*).

A recent mechanistic study of boric acid complexation with 4-isopropyltropolone and with chromotropic acid, a 1,8-dihydroxynaphthalene derivative, has shown that the rate-determining step is the change in boron coordination from trigonal to tetrahedral (*23*).



Structure 4

Tetrahedral borate or boronate complexes have been shown to be involved in enzyme inhibition. Serine proteases were proposed in early Russian work to be inhibited by boric acid (*24*), and simple borates have been patented as protease stabilizers in liquid detergent formulations (*9,10*).

Reactions such as acylation and deacylation are catalyzed by enzymes through lowering of the energy of activation. Binding and stabilization of the near tetrahedral oxyanion transition state by the active site of the enzyme is how this is accomplished. Thus, a transition state analog inhibitor is a species which binds the active site in a way similar to that of the substrate. 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.

X-ray structures have been worked out for the benzeneboronic and 2-phenylethaneboronic acid (PEBA) complexes of subtilisin BPN'(Novo) (*25*) and for the PEBA complex of α-chymotrypsin (α-CHT) dimer (*26*). Further stabilization of the hydroxyls on boron is gained by hydrogen bonding to other amido groups lining the oxyanion hole (Figure 6).

Subtilisin Carlsberg (*27*) and cholesterol esterase (*28,29*) also are inhibited by a range of aliphatic and aromatic boronic acids. Work on inhibiting α-CHT and cell replication with a variety of boronic acids concluded that the α-CHT activity was associated with chromatin in normal and tumorous tissue of mice (*30*). It has been demonstrated that certain boronic acids inhibit protease activity in rat liver chromatin (*31*). It was concluded that good boronate inhibitors of CHT, like PEBA, inhibit cell replication and that this effect is expected to be higher in rapidly proliferating cancer cells than in normal tissue (*30*).

Complexing of the ribose group of nicotinamide adenine dinucleotide (NAD) is preferred electrostatically over that of reduced nicotinamide adenine dinucleotide (NADH), leading to inhibition of this coenzyme system (Figure 7) (*32*). The effects of boron compounds on enzyme catalyzed reactions have been thoroughly reviewed through 1979 by Kliegel (*33*).

Conclusions

Boron is present in every part of the environment and it is likely that life evolved in the presence of the element. Boron is essential to plant life, but can be herbicidal at high levels. Borates have effects on a variety of bacteria, fungi, and insects. Boron in biological systems can be expected to be associated with one or more OH groups.

Borates are used widely in industrial and domestic applications. Boron has been shown to influence a variety of enzymes, involving both stimulation and inhibition. Enzyme interactions probably represent the most important feature of boron chemistry from the point of view of the health effects considered in the following papers.

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