

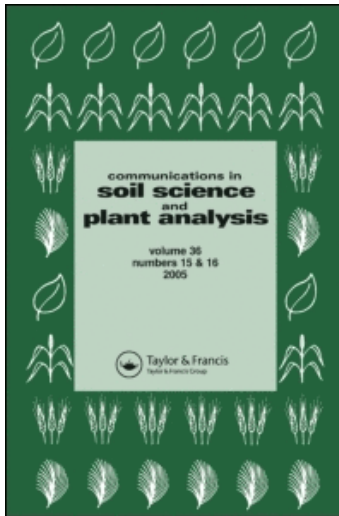
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ON THE CHEMISTRY AND MINERALOGY OF BORON
IN PURE AND IN MIXED SYSTEMS: A REVIEW¹

KEY WORDS: B adsorption, B desorption, B kinetics

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ABSTRACT

Boron (B) is the third member of the third periodic group. It is a nonmetal with an atomic number of five and a constant valence of 3^+ . Boric acid $[B(OH)_3]$ and $H_2BO_3^-$ are the most common geologic forms of B, with boric acid the predominant form of B in agricultural soils. Boron occurs mainly in silicate minerals. The 10 $\mu\text{g/g}$ B concentration of the earth's crust is distributed among common rock types.

Less than five percent of total soil B is available for crop uptake. This helps to explain the occurrence of B deficiency in 41 of the 50 states. The availability of soil B depends on soil texture, pH, and soil moisture content.

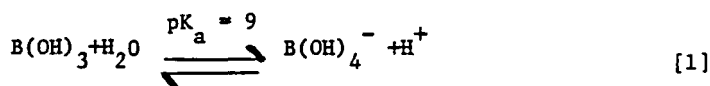
A number of soil components have shown an affinity for B. These include Al- and Fe- hydroxy compounds, ferromagnesian minerals found in sand and silt separates, Al- and Fe- oxides, and organic matter.

Studies have shown B adsorption to increase with increasing pH. Boric acid predominates at pH values less than 7.0 and borate ions predominate in solutions of higher pH. Boron adsorption data are usually described by: the Langmuir equation at low concentrations, a quadratic curve described by a BET relationship; and phenomenological equations which describe B

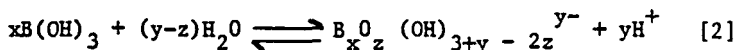
adsorption as a function of both the equilibrium B concentration and the pH of the suspension solution.

General Boron Solution Chemistry

Boron (B) is the first member of the third periodic group. It has an atomic number of five, and is a nonmetal with a constant valence of 3+ (3). Boron occurs in aqueous solution as boric acid, $B(OH)_3$ (4) which is a weak monobasic acid that acts as an electron acceptor or as a Lewis acid (5). Boric acid $B(OH)_3$ hydrolyzes reversibly to the borate ion above pH 7.0 according to the reaction below (4):



When B occurs in solution at concentrations above 0.1 m, polyborate species are formed by the addition of one OH^- ion per $B(OH)_3$ molecule present. The reaction proceeds as follows:



where x = number of B atoms

y = apparent number of OH^- ions in a hydrolysis product

z = charge on an ion. The most common products of Eq. [2] are $B(OH)_4^-$, $B_2O(OH)_5^-$, $B_3O_3(OH)_4^-$ and $B_4O_5(OH)_4^{2-}$, with the trimeric anion being the polyborate formed under most conditions (4). X-ray diffraction, the extended Hückel method, and B nuclear magnetic resonance spectra have been applied to study the bonding patterns of the borane structures (6). Utilization of Raman and infrared spectroscopy has shown $B(OH)_3$ molecules to be trigonal and $B(OH)_4^-$ to be tetrahedral in aqueous solution (4).

Boron (III) occurs chiefly as an oxyanion due to its small size (ionic radius = 0.23Å) and its tendency to form covalent bonds (3). When F^- ions are present in solution, a series of hydroxyfluoroborates forms at low pH. The BF_4^- species is a

stable species but it forms slowly. Thus, the hydroxyfluoroborates are usually present in small, metastable quantities (7).

Geochemistry of Boron

Boric acid and H_2BO_3^- are the most common geologic forms of B. Boric acid is the major form of B found in soils with H_2BO_3^- predominant only above pH 9.2 (8).

Boron occurs mainly in silicate minerals at a concentration of approximately 10 $\mu\text{g/g}$ in the earth's crust. The distribution of B among the common rock types is shown below (3).

The abundance of B in shales suggests that dissolved borates have been predominant in sea water throughout the earth's history (3). Some of the more common B containing minerals can be found in Table 2 (3).

The anhydrous borates and complex borosilicates are high temperature minerals, whereas hydrous borates are low temperature minerals. Micas show the highest B content of igneous rock minerals. The primary mineral tourmaline which is highly resistant to weathering is the most common of the high temperature minerals (3).

Borate minerals are easily brought into solution with water (9). These borate minerals are formed from original precipitation or can be altered by changes in temperature after deposition. Weathering of the B-containing rocks gives borate in solution,

TABLE 1

Distribution of B in Common Rock Types

<u>Rock Class</u>	<u>Rock Type</u>	<u>Concentration</u> — $\mu\text{g/g}$ —
Igneous	Granite	15
	Basalt	5
Sedimentary	Limestone	20
	Sandstone	35
	Shale	100
	Soils	7-80

TABLE 2
Boron Containing Minerals

<u>Class</u>	<u>Subclasses</u>	<u>Chemical Formula</u>
Hydrous borates	borax	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$
	kernite	$\text{Na}_2\text{B}_4\text{O}_7 \cdot 4\text{H}_2\text{O}$
	colemanite	$\text{Ca}_2\text{B}_6\text{O}_{11} \cdot 5\text{H}_2\text{O}$
	ulexite	$\text{NaCaB}_5\text{O}_9 \cdot 8\text{H}_2\text{O}$
Anhydrous borates	ludwigite	$\text{Mg}_2 \text{FeBO}_5$
	kotoite	$\text{Mg}_3(\text{BO}_3)_2$
Complex borosilicates	tourmaline	$\text{Na}(\text{Mg}, \text{Fe}, \text{Mn}, \text{Li}, \text{Al})_3$ $\text{Al}_6\text{Si}_6\text{O}_{18} (\text{BO}_3)_3$ $(\text{OH}, \text{F})_4$
	axinite	$(\text{Ca}, \text{Mn}, \text{Fe})_3\text{Al}_2\text{BO}_3\text{Si}_4$ $\text{O}_{12}(\text{OH})$

predominantly H_3BO_3 . Boron is found in large accumulations in evaporite deposits due to this high solubility.

Boron Content and Forms in Soils

All of the plant micronutrients are found in the soil in chemical "pools" (10) which are listed below:

- 1) H_2O -soluble ions
- 2) exchangeable ions
- 3) adsorbed, chelated, or complexed ions
- 4) secondary clay minerals and metal oxides
- 5) primary minerals

Soil analyses have shown H_2O -soluble B concentrations ranging from 2 to 100 $\mu\text{g/g}$ but the general range is 7-80 $\mu\text{g/g}$ (3). Water-soluble B contents can be categorized by climatic zone. Temperate and boreal regions contain a range of B concentrations, the lowest (1-2 $\mu\text{g/g}$) found on sands and podzols. Tropical humid regions also contain low concentrations of B, in the range of 1-2 $\mu\text{g/g}$. However, arid and semiarid region soils show average to high boron concentrations (10-40 $\mu\text{g/g}$ or more) (11,12).

Soil B falls into three categories: total, acid soluble, and water-soluble. Less than five percent of the total soil B

is usually available for crop use (13). This partly explains the phenomenon that B deficiency is the most widespread micronutrient deficiency in America, being found in 41 of the 50 states (14). Water-soluble B values in soils have been categorized to give a general guide for B supplying power (15) to plants:

Category I: less than 1 $\mu\text{g/ml}$ - insufficient water soluble B for normal plant growth.

Category II: 1-5 $\mu\text{g/ml}$ - sufficient water-soluble B for normal plant growth.

Category III: greater than 5 $\mu\text{g/ml}$ - quantities which could cause toxic effects to plants.

Soil Factors Affecting B Availability

The availability of soil B depends on soil texture, pH, and soil moisture content. Boron concentrations are usually higher in clay and loam soils than in sandy soils (16). Olson and Berger (17) suggested that the B fixing ability of humid region soils was caused by a mineral or a group of minerals whose activity predominates in the clay fraction. Kubota et al. (18) found that the B was most mobile in surface horizons of sandy soils, but that mobility decreased in subsoil horizons due to increased clay content and reduced water movement. Wilson et al. (19) showed that B movement was rapid in sandy soils, that accumulations of applied B were greatest in the 39-90 cm zone for sandy loam soils, and that B was restricted to the upper 15 cm in clay soils.

Excessive liming of acid soils immobilizes B due to the lower solubility of B at high pH. Therefore, B leaching occurs to a lesser extent in high pH soils (11). However, the remaining available B in these soils is easily leached and deficiencies can occur in highly leached alkaline soils. In silt loam soils, B fixation increased rapidly as the pH was raised above 7.0, and the amount of Ca salts added to the soil did not affect B fixation unless by their addition the pH was increased above 7.0(17). The fixation of B due to overliming was thus created by the alkalinity produced rather than by the Ca added. The influence

of pH on available B is greater than that of organic matter in many alkaline soils. Berger and Truog (13) showed that increased pH (above 7.0) was important in reducing the quantity of available B. From pH 4.7 to 6.7 the available B in cultivated soils increased.

Deficiencies are prevalent in humid regions due to leaching, but they can also be induced by drought. Much of the total B in soils is held by organic matter and is released by microbial action. However, under droughty conditions microbial activity is decreased and thus the B remains complexed and unavailable to the plant (14). Semi-arid and arid soils are rich in B (11). Boron toxicity for many plants occurs in the range of 0.5-5.0 mg/l. This level of B is found in many irrigation waters in arid regions. The B from irrigation thus acts as a buffer which inhibits the removal of toxic levels of soluble soil B with leaching (20).

Boron Sorption in Pure and in Mixed Systems

A number of studies have been conducted to determine the mechanism of B sorption in clays and in soils (21,22,23,24,25,26, 27,28,29,30,31,32,33,34,35). However, most studies on soil systems are confined to the older soil chemistry literature (1945-1968). Since the soil is a complex, heterogeneous system, many researchers have turned to studies on pure clays, Al- and Fe- oxides, and organic compounds to help explain soil B phenomena. These studies have suggested a number of mechanisms between B and soil including: 1) sorption of borate ions; 2) sorption of molecular boric acid; 3) formation of organic complexes; 4) precipitation of insoluble borates with Al and Si; and, 5) entry of B into the clay structure.

A number of conclusions about B adsorption have been made. Probably the most definitive one has been the increase in B adsorption with pH. Illite is the most reactive clay on a weight basis (21,22), with adsorption increasing from pH 5.0-8.5. This increase is due to adsorption of borate ions (21,22) or changes in the clay surface which favor adsorption site formation

(21). Sorption of B on montmorillonite increases extensively from pH 7.0-9.5 (21).

Boric acid molecules predominate at pH values less than 7.0, borate ions predominate in solutions of higher pH. Since solution B speciation is pH dependent, two mechanisms for B fixation have been postulated: (1) adsorption of borate ions in which B adsorption would increase from pH 5 to 10 and competition from OH^- ions at pH values greater than 10 would decrease B adsorption, and (2) sorption of $\text{B}(\text{OH})_3$ in which it is proposed that increasing the pH favors site formation which increases the adsorption of $\text{B}(\text{OH})_3$. The concentration of $\text{B}(\text{OH})_3$ molecules drops at high pH which results in decreased adsorption. Hingston (21) favored this second argument as his studies with three soil clays, a Willalooka illite, a Kent sand kaolinite, and a Marchagee montmorillonite showed no change in the amount of B adsorption with increases in CaCl_2 concentration. These data thus suggested adsorption of uncharged B species. Couch and Grim (23) stated that B fixation in illitic clays increased at a given $\text{B}(\text{OH})_3$ concentration as the concentration of electrolyte in solution increased. This may be a result of a greater $\text{B}(\text{OH})_3$ dissociation to $\text{B}(\text{OH})_4^-$ induced by the halide salts. In addition to B sorption increasing with pH, sorption also increased with increased B solution concentration (23).

At low concentrations, (less than 30 mg/l) adsorption of B on clays has been shown to conform to the linear Langmuir equation which is given below (21,24):

$$\frac{C}{x/m} = \frac{1}{kb} + \frac{C}{b} \quad [3]$$

where C = concentration of B in equilibrium solution ($\mu\text{gB/ml}$)
 b = 1/slope or the maximum adsorption parameter
 k = slope/intercept and is a constant related to bonding energy

and x/m = B adsorbed per mass of adsorbent.

For kaolinite, illite, and montmorillonite, the b value increased

with pH and the k value decreased for kaolinite and montmorillonite, but increased for illite up to pH 8.5 (21).

The linear form of the Langmuir equation was also found to describe B adsorption in soils after different degrees of wetting and drying. However, deviations were found as the number of wetting and drying cycles increased. Soils were found to vary in their capacity to fix B and in the energy of retention. The k values increased with clay content (24). Adsorption of B on tropical amorphous soils, formed from volcanic ash, was described by the Langmuir equation, with higher B values found compared to non-tropical soils (25). Adsorption maxima occurred at pH 8-9 in the amorphous soils and amorphous Al_2O_3 appeared to provide the sites for B adsorption (25). The Langmuir equation described B sorption on tropical soils within a B concentration range of 0-50 $\mu\text{g/ml}$ (26). Singh (27) proposed a quadratic curve described by a BET relationship to explain B sorption in soils over a wide range of B concentrations:

$$\frac{C}{E} = (C_0 - C) \left(\frac{1}{E_{mc}} + \frac{c-1}{E_{mc}} \cdot \frac{C}{C_0} \right) \quad [4]$$

where C = concentration of B in dilute solution

C_0 = the solubility of B

E = B adsorbed on the surface

E_m = B adsorbed on surface at completely monomolecular coverage

c = a constant

However, the solubility of B(C_0) is difficult to obtain and thus the Langmuir equation is perhaps more useful.

The merits of the Langmuir equation for use in B adsorption studies have been widely discussed in the soil chemistry literature. Though it predicts a linear relationship at low concentrations, it cannot accurately predict B adsorption as a function of pH (22). Other disadvantages in using this semiempirical equation are (28): (1) the Langmuir equation does not allow for two B species with varying affinities for the clay as is the case in B adsorption. Also, as the concentration of the species in

solution varies with pH; (2) different values of b and k must be assigned at given pH values to predict sorption.

Attempts have been made to formulate equations which mitigate the above difficulties. One such phenomenological equation has been given by Keren et al. (28):

$$Q_{BT} = T \left\{ 1 + \frac{PR}{F(Q_T - Q_{BT})} [1 + K_{OH}(\text{OH})] \right\}^{-1} \quad [5]$$

where Q_{BT} = total adsorbed B
 Q_T = total B in suspension
 $P = K_h(\text{OH}) 10^{14} + 1$
 and K_h = hydrolysis constant for the reaction

$$\text{B}(\text{OH})_3 + 2\text{H}_2\text{O} \rightleftharpoons \text{B}(\text{OH})_4^- + \text{H}_3\text{O}^+$$

 R = solution to clay ratio (liter/g clay)
 $F = K_{HB} + K_B(P-1)$

where K_{HB} , K_B , K_{OH} are the constants related to binding for

$\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, and OH^- , respectively.

This equation was found to agree with experimental results on a Na-montmorillonite (28) and on whole soil systems (29). Equation [5] describes B adsorption as a function of both equilibrium B concentration and the pH of the suspension solution.

Further work has employed Eq. [5] to predict adsorption of B on other forms of montmorillonite and illite. Due to the very small fraction of total surface area occupied by B on montmorillonites ($0.72 \text{ m}^2/\text{g}$ clay), particle edge adsorption prevails over planar surface adsorption (21). It has also been shown that specific surface sites of illites are the most important single property involving irreversible B uptake (23). Since on montmorillonites and illite there is an equal surface area due to broken edges, B adsorption should be the same regardless of exchangeable ions. The Ca- forms of montmorillonite, illite, and kaolinite gave experimental results which agreed with predictions of the theoretical equation proposed (22). This agreement again emphasizes the superiority of this equation over the Langmuir in simultaneous prediction of B adsorption as a function of pH and B concentration in solution.

Studies have presented data showing the adsorption maximum of B on Ca-montmorillonite at pH 9.7, on Ca-kaolinite at pH 9.0, and on Ca-illite at pH 9.3. Where other anions such as $\text{SO}_4^{=}$, F^- , and $\text{PO}_4^{=}$ showed maximum adsorption at their pK_a values, maximum B adsorption depended on the ratio of the affinity coefficients (K_{HB} , K_{B} , K_{OH}) of the three species ($\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, and OH^-) which are competing for the same sites on the clay (22). This same dependence on affinity coefficients applied to B adsorption on a loamy sand, a loam, and a clay soil (29). This competition for adsorption sites and variation in affinity presented an explanation for the pH dependence of B adsorption. Boric acid is the species which predominates below pH 7.0. It has a low affinity for clay and thus low adsorption values occur in this pH range. Above pH 7.0 and increasing to pH 9.0, the $\text{B}(\text{OH})_4^-$ concentration in solution increases and an increase in adsorption occurs. The $\text{B}(\text{OH})_4^-$ has a greater affinity for clay than does $\text{B}(\text{OH})_3$. Above pH 9.0, the OH^- concentration becomes significant and competition for sites occurs. This explains the decrease in B adsorption in the very alkaline pH ranges (22,28).

Variations of the clay surface saturation have been investigated as to their effect on B adsorption. Montmorillonite and kaolinite were studied at different solution to clay ratios at two pH's (pH 7.4 and 8.3 for Ca-montmorillonite and pH 7.0 and 8.0 for Ca-kaolinite) and it was found that water content did not affect B-surface interaction (as expressed by adsorption parameters) for either clay (22). The pH maximum depended on the affinities of the $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$ and OH^- for the clay surface. Boron can be adsorbed specifically on these surfaces by a ligand exchange process. This type of exchange entailed displacement of OH^- (or H_2O) from the surface by the adsorbed B species. The adsorbed species formed partly covalent bonds with structural cations (30).

An earlier study using chemical solutions of compounds thought to simulate soil components revealed an increase in the amount of B precipitated in the presence of Ca. This fixation

was attributed to B entrance into the Ca and Al complex. Evidence has also shown the possibility of B entrance into complexes of Ca with Si or into Ca- aluminosilicates as a substitution product for Al^{3+} ions. This could be expected due to the similarities in the chemistry of B and Al (31).

Differences in the adsorbed cations on the clay surface introduced variation in B adsorption on a montmorillonitic clay. At pH 7.0, adsorption of B by Ca- and Na- montmorillonite was found to be the same. At higher pH's, Ca- montmorillonite adsorbed more B than Na systems. Calcium montmorillonite exists as several clay platelets together or as tactoids. These tactoids are surrounded by a thick water film on the internal surfaces. The film makes the negative electric field on the edges of the platelets smaller in Ca- montmorillonite than in the Na- form which exists as single platelets. This could cause an inability of negative borate ions to move close enough to interact at the Na- clay surface (30).

Calcium and Na^+ ions have a non-specific effect on B adsorption by montmorillonite as shown by the reversibility of B adsorption reactions (22,30). This reversibility was reduced by drying and wetting cycles. The lack of complete reversibility suggested a different B species was adsorbed or a different mechanism was involved (30). Drying and wetting cycles are believed to be part of the weathering process which breaks down primary and secondary clay minerals (32).

A "wet" treatment which consisted of shaking clays for 48 hours in B solution and extracting the B showed no adsorption by H- saturated kaolinite or bentonite. However, base saturated clays with the exception of NH_4^- saturated clay, adsorbed a large amount of B. A "dry" treatment which involved drying the clays at $50^{\circ}C$ after 48 hours of shaking in B solution and then rehydration and subsequent extraction showed more fixation with H- saturated kaolinite than with NH_4^- , Ca-, Mg-, and K- saturated kaolinite and bentonite (32).

More recent work has shown an increase in adsorbed B in montmorillonite suspensions dried after B additions (30). This

again suggests a change in the B species adsorbed and/or a change in the association of the B with the surface upon drying. Drying may also cause a breakdown of the montmorillonitic crystal structure following positioning of B near the crystal's edges which would then ease entry of the species into the clay structure. The behavior of B in dried-rewetted suspensions also suggested two types of adsorbed B - one type which is reversibly adsorbed and one which is more strongly adsorbed (30).

Effect of Al- and Fe- Hydroxy Compounds on B Adsorption

Hatcher et al. (33) have shown that when acid soils are limed, the primary reaction is the replacement of exchangeable Al and hydroxy-Al cations and their precipitation as aluminum hydroxide ($\text{Al}(\text{OH})_3$). Studies on 28 soils showed that freshly precipitated $\text{Al}(\text{OH})_3$ adsorbed large quantities of B and that it and related hydroxy-Al materials are the major solid constituents responsible for B adsorption (33).

Continuing research by Sims and Bingham (34) on various clay minerals resulted in more possible mechanisms for B adsorption. Boron adsorption on interlayer material of South African vermiculites was shown to be pH-dependent. The Na-form adsorbed a maximum amount of B, 90 $\mu\text{g B/g}$, at approximately pH 10.5. The collapsed K^+ form retained a maximum of only 10 $\mu\text{g/g}$ at pH 9.5 to 10. These data inferred the importance of accessible interlayer sites of 2:1 layer silicates in B adsorption. With kaolinite, there was no difference in the adsorption maximum for both Na^+ - and K^+ - forms at pH 9-10. Low B retention by Na^+ - and K^+ - forms of montmorillonite which had been previously treated with a solution 2N in NaCl and 0.1N in HCl to remove the hydroxy-Al forms suggested the importance of this interlayer material in B adsorption (34).

Studies of this type have introduced three possible mechanisms for interlayer adsorption:

- 1) Hydrogen bonding of $\text{B}(\text{OH})_3$ onto the oxygen-rich interlayers of platelets. This is unlikely as the pH range of maximum adsorption is 9-10.5 and $\text{B}(\text{OH})_4^-$ is the predominant species in this range.

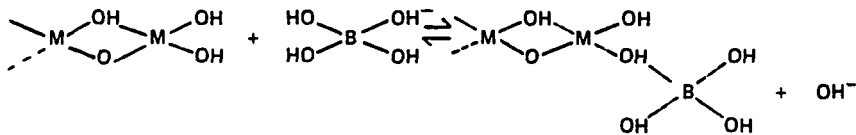
- 2) Borate ions could be ionically bound to materials adsorbed on interlayer surfaces such as hydroxy-Al forms.
- 3) Interlayer materials could "bleed" to external sites or to solution followed by reactions with borate ions.

All three of these mechanisms point out the importance of the Fe and Al species present as interlayer materials, coatings or impurities, and of access to interlayer positions as necessities for maximum B retention (34).

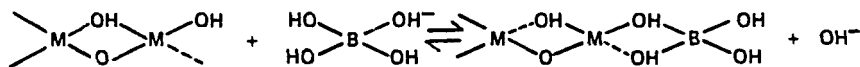
Sims and Bingham (35) continued studies on interlayer materials with pure Al and Fe compounds and found that both showed affinity for B and pH-dependent adsorption. Maximum retention occurred at pH 8.5. Aluminum hydrous oxide also showed maximum adsorption of $B(OH)_3$ in this pH range (36). Explanations for these findings could fall under either of Hingston's (21) arguments for adsorption onto clays as cited earlier (35,36).

On Al- and $Fe(OH)_x$ compounds, $B(OH)_4^-$ adsorption seems most likely. The decrease in adsorption above pH 8 to 9.0 is due to increasing OH^- competition for sites, to negative charge taken on by hydrous oxides causing repulsion of $B(OH)_4^-$, and to dissolution of the adsorbent, resulting in formation of Al^{3+} ions. Two mechanisms have been proposed by Sims and Bingham (35):

- 1) Anion exchange mechanism:



- 2) Borate becoming the end member of Al- and $Fe(OH)_x$ polymers:



Aluminum hydrous oxides adsorbed more B per unit mass than Fe hydrous oxides, while adsorption by the latter conformed to the Langmuir equation up to 16mM B. Aluminum hydrous oxide adsorption followed the Langmuir equation up to 6mM B (36). The B adsorption capacity of both hydroxy - Al and - Fe compounds decreased with increased aging (37). This reduction seemed to be a result of changes in the surface properties of the solid matrix. As the fresh precipitates aged or dried, their crystallinity increased and therefore surface area decreased. With less surface exposed, aged material had less capacity for B adsorption (36). Aged hydroxy - Fe material was more ordered with increases in crystalline Fe_2O_3 and decreases in hydroxyl bearing intergrade material relative to fresh hydroxy Fe. Increased order would provide fewer sites for hydroxyl exchange with borate. The higher retention in Al material was possibly due to $\text{Al}(\text{OH})_3$'s abundance of OH^- groups relative to the Fe_2O_3 dominated hydroxy Fe material (35). Furthermore, Al-coated compounds were found to have a greater affinity for B than Fe-coated compounds.

Effect of $\text{Mg}(\text{OH})_x$ Material on B Adsorption

Minerals commonly found in the sand and silt fractions of the soil have been studied to draw a comparison to adsorption by silicate clays. Many ortho- and chain-silicate minerals such as olivine, augite, tremolite, and diopside have a greater capacity for B sorption than the micaceous layer silicates such as chlorite, talc, phlogopite; muscovite, vermiculite and biotite. Their affinity was greater per unit weight than micaceous layer silicates. The minerals of the sand and silt fraction with high B retention were generally ferromagnesian minerals. They were comparatively easily weathered, with large amounts of Fe and Mg, and some Al. Their high B sorption capacity could be due to hydroxy-Al and -Fe compounds existing as surface coatings (20).

The large quantity of B sorption on diopside, tremolite, and enstatite which are minerals devoid of Fe and Al, suggested magnesium-hydroxy coatings as active sites for sorption. Experi-

mentation on MgO and $Mg(OH)_2$ suspensions showed that $Mg(OH)_2$ had a significant ability to remove B from solution. The capacity of $Mg(OH)_2$ for sorption of B was not altered by aging as was that of $Al(OH)_3$ and $Fe(OH)_3$ except at very short reaction times. X-ray diffractograms showed that B was possibly incorporated into the $Mg(OH)_2$ crystal structure. Rhoades et al. (20) concluded that magnesium-hydroxy coatings or clusters on weathered mineral surfaces were the site of sorption by ferromagnesian minerals. These $Mg(OH)_x$ coatings or clusters imparted appreciable B-sorption to the sand and silt fractions as well as to the clay fractions in arid-zone soils (17).

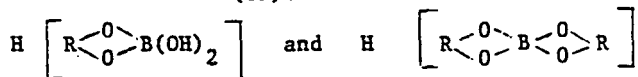
Boron Adsorption on Organic Matter

Increased borate adsorption was found to occur on Al-saturated podzol soils and Maine peat moss with increasing lime rates. This fixation was chemical rather than biological and its maximum occurred at a slightly alkaline pH. The organic matter content of these soils seemed responsible for this lime induced B fixation (38).

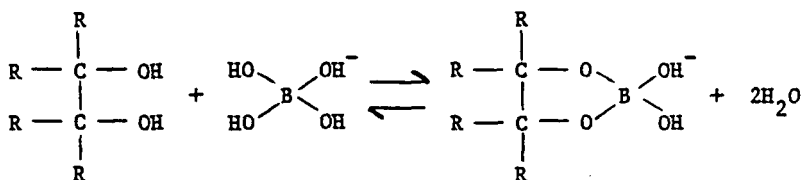
Other studies on cultivated soils have shown a relationship between organic matter, pH, and B availability. Organic matter was found to have the greatest influence on B availability in soils of pH less than 7.0, where increased organic matter content caused an increase in available B (13). Berger (14) also found a large part of the total B content of soils held in organic matter and postulated its becoming available through microbial release. Gupta (16) showed that the relationship between hot-water soluble B and organic matter is better than that with total B which suggests that clays hold only a small part of replaceable B.

Humus has been shown to have a chemical affinity for B. Boron is usually high in high organic matter soils and is not readily leached. Boron may combine with compounds such as xylose, mannose, glucose and galactose that are formed as organic matter decomposes (32). The existence of boron-diol complexes has been proven. If a favorable diol complex (2-oxy acids) was present in

aqueous boric acid solution, $R \begin{array}{c} \diagup O \\ \diagdown O \end{array} BOH$ was found to be the ring compound primarily formed. This compound converted to the mono-basic acid form due to the tendency of boric acid to exist in the pentavalent condition (39):



One borate-diol complex formed by the reaction:



occurred at low pH. The reaction equilibrium shifted to the right as the pH increased (37).

The boron-diol complexes may be affected by moisture supply. Adequate moisture enhanced a continuous cycle of decomposing complex polysaccharides. The polysaccharides have B fixing capacities, and thus B would be released upon decomposition. If moisture was inadequate, breakdown of these diol complexes would not occur - and B would remain unavailable (32).

Boron Kinetics Studies

Studies of B dynamics are few and those existing rely on Langmuir theory. Though there are deviations from the Langmuir equation, conformity was sufficient to allow further interpretation of the dynamics utilizing the Thomas-Heister-Vermeulen equations which describe adsorption and desorption in soil columns. These equations showed that the volume of water con-

taining B needed to obtain equilibration with the soil decreases as the B concentration of water increases. Elution required more water than saturation (40).

Kinetic studies have shown that in the desorption reaction:



the rate limiting reaction is the release of B from the interface as boric acid. Results produced two distinct linear sections of a plot of $\log (B_0 - C)$ vs. time, where B_0 was total desorbable B adsorbed on the soil at $t = 0$, and $C =$ concentration of desorbed B in solution at any time t . These distinct sections indicated that two separate pseudo first-order reactions were involved in desorption. Results also indicated a third slow reaction (41). This two site adsorption mechanism had been alluded to previously by Okazaki and Chao (26) and by Bingham et al. (25). Griffin and Bureau (41), postulated hydroxy compounds were sites of easily desorbable B due to the large magnitude of initial release and the work of Sims and Bingham (37), stating dominance of hydroxy compounds over clay in adsorption of B. Their slow reaction was equated to diffusion out of the crystal lattice. This two site theory was corroborated by results obtained using an analog of the one site Langmuir equation in equilibrium desorption studies. Early in the leaching of high B soils, the high affinity, low capacity site 2 is filled and desorption occurs from low affinity, high capacity site 1. Site 2 takes over when site 1 is devoid and dominates the efficiency of leaching removal (41).

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