

## Boron Sorption and Release by Allophane

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### ABSTRACT

To predict B behavior in soils and its influence on plants, it is crucial to understand the mechanisms of B sorption by mineral phases. Because B reacts with clay minerals and Al and Fe oxides, it should also sorb to poorly crystalline aluminosilicates such as allophane. Boron sorption, with and following allophane precipitation, was studied in batch experiments. Solutions containing  $\text{AlCl}_3$  and  $\text{Na}_2\text{SiO}_3$  (concentrations <47 mM with Al/Si molar ratio of 1:1) and  $\text{B}(\text{OH})_3$  (0, 4.4, and 32 mM) were mixed and titrated to pH 8.0 with 1 M NaOH at two rates (1 and 5  $\text{mL min}^{-1}$ ) at 23°C, then incubated at 23 and 90°C for 5 d. More B was removed from solution when B was present during allophane precipitation than when B of an equal concentration was reacted with freshly precipitated allophane. In addition, more B was removed when allophane was formed by slower mixing at a slower titration rate, with higher initial B concentration, and incubated at lower temperature. More B was released by repeated washing with deionized water from allophane precipitated in the presence of  $\text{B}(\text{OH})_3$  than from allophane reacted with  $\text{B}(\text{OH})_3$ . Boron sorption was investigated with diffuse reflectance infrared Fourier transform (DRIFT) spectroscopy. Adsorbed B was both trigonally and tetrahedrally coordinated, with the former being predominant. Boron reacted with allophane precipitate was surface sorbed. Coprecipitated B occurred only in tetrahedrally coordinated positions, presumably by substituting for Si in the tetrahedral layer. The structurally coprecipitated B is expected to be more resistant to release than the adsorbed B.

**T**HERE has been broad interest in studying the interaction between B and soil constituents because of the relatively small range between B concentrations that cause deficiency and toxicity symptoms in plants. Abundant literature exists on B sorption by soils and soil minerals, yet the mechanisms of B sorption are still not

fully understood. Insight into mechanisms controlling B partitioning between solid and solution phases is crucial for a quantitative understanding of B behavior in soils and its effects on plants.

In this study, the term sorption is defined as the attachment of species to a solid. The sorption phenomena include the processes of adsorption, coprecipitation, and inclusion. Adsorption is the process through which a net accumulation of a substance occurs at the interface of two phases, whereas coprecipitation is isomorphic substitution of one ion for another of comparable radius in a soil mineral, and inclusion is an association of a morphologically distinct solid phase containing a trace element with the host mineral (Sposito, 1984, p. 234).

Boron is known to be removed from aqueous solution by precipitation of sparingly soluble minerals. Kitano et al. (1978) found that B is easily removed by aragonite (but not calcite) formation at pH 7.5 to 8.2 in a  $\text{Ca-HCO}_3$  solution. Ichikuni and Kikuchi (1972) concluded that B contained in travertines deposited from thermal waters occurred via an adsorption mechanism. Beyrouty et al. (1984) precipitated Al hydroxide in the presence of 0.75 M  $\text{B}(\text{OH})_3$  and concluded that all sorbed B was held onto the hydroxide surface.

Allophane is the name for the group of hydrous aluminosilicate clays characterized by short-range order (x-ray amorphous) in the structure (van Olphen, 1971). The sorption of B by allophane is potentially important because allophane occurs in a wide range of soils and it is known to retain large amounts of anions such as phosphate and sulfate (Parfitt, 1990). The interaction between B and allophane is rarely investigated and infor-

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Published in Soil Sci. Soc. Am. J. 61:69-77 (1997).

**Abbreviations:** FTIR, Fourier transform infrared; DRIFT, diffuse reflectance infrared Fourier transform; ATR, attenuated total reflectance; DTGS, deuterated triglycine sulfate; DIW, deionized water; ICP-AES, inductively coupled plasma-atomic emission spectrometry; PZC, point of zero charge; XRD, x-ray diffraction.

mation is lacking on the desorption or release of B from allophane. Bingham and Page (1971) demonstrated that B adsorption by an allophanic soil is specific, being essentially independent of the presence of phosphate, sulfate, and monosilicic acid. Bingham et al. (1971) showed that B adsorption by volcanic-ash-derived soils containing allophane attained equilibrium after 20 to 120 h. It is known that B is adsorbed to clay minerals and to Al and Fe oxides as well as being present in clay mineral structures. Boron in solution may be removed by repeated washing but may be replenished through release from less available forms (Rhoades et al., 1970; Peryea et al., 1985). Previous studies have not distinguished between adsorbed and structurally substituted B. It is expected that structurally substituted B should not be readily released to solution upon leaching.

In addition, the influence of conditions during allophane precipitation, such as mixing and titration rate and temperature, on the surface area of the precipitate and in turn on B sorption have not been studied. Recently, FTIR spectroscopy has been shown to have great potential for chemical speciation on Al and Fe oxide surfaces (Tejedor and Anderson, 1986, 1990; Biber and Stumm, 1994) and on clay mineral surfaces (Hunter and Bertsch, 1994). Since allophane suspensions greater than 100 g L<sup>-1</sup> are impossible to make due to gel formation, the in situ ATR-FTIR technique was not sensitive to the B signal in dilute allophane suspensions. Therefore, air-dried allophane samples were studied. For solid samples, the diffuse reflectance spectroscopic technique provides a convenient means of obtaining mid-infrared spectra, as an alternative to the pressed halide disk method (Ngunyen et al., 1991). Advantages of the DRIFT technique are minimal and more reproducible sample preparation, and a greater number of discernible bands for analysis. No studies have been reported on the application of DRIFT spectroscopy to B sorption. The objectives of this study were to: (i) investigate the effects of solution B concentration on the adsorption of B by allophane and B retention (via adsorption, coprecipitation, or inclusion) by allophane precipitated in the presence of B; (ii) obtain information on the coordination of different forms of B sorbed to allophane using DRIFT spectroscopy; and (iii) evaluate leachability or release of sorbed B from these materials.

**Table 1. Allophane precipitation in the absence of B. Each washing consisted of a 2-h shaking followed by centrifugation. All the systems were equilibrated for 5 d. The atomic Al/Si ratio of the initial solutions and the precipitates after three washes was 1.0.**

Mixing and titration rate	Incubation temp	Si concentration		Precipitates Surface area	pH†	
		Initial	Residual		Before wash	After wash
		mM			m <sup>2</sup> g <sup>-1</sup>	
Slow	23	46.3	0.07	200	7.6	9.4
Fast	23	45.1	0.11	190	8.0	9.3
Slow	90	45.9	0.37	300	7.2	9.3
Fast	90	45.8	0.10	290	7.7	9.2

† The pH at the end of titration at 23°C was 8.0.

## MATERIALS AND METHODS

### Mineral Precipitation

Allophane precipitates were made using 200 mL of freshly prepared 0.1 M AlCl<sub>3</sub> (pH 2, adjusted with HCl) added at a rate of 5 mL min<sup>-1</sup> (slow mixing) or 800 mL min<sup>-1</sup> (fast mixing) to each of 200 mL of 0.1 M Na<sub>2</sub>SiO<sub>3</sub>, or 200 mL of 0.1 M Na<sub>2</sub>SiO<sub>3</sub> + 20 mL of 0.1 M B(OH)<sub>3</sub>, or 200 mL of 0.1 M Na<sub>2</sub>SiO<sub>3</sub> + 200 mL of 0.1 M B(OH)<sub>3</sub>. The Al/Si/B atomic ratios were 1:1:0, 1:1:0.1, and 1:1:1, respectively, for the above treatments. The initial concentrations of Al, Si, and B, as well as precipitation conditions, are listed in Tables 1, 2, and 3. The precipitates were titrated to pH 8.0 by addition of 1.0 M NaOH at the rate of 1.0 mL min<sup>-1</sup> until pH 6.0 and then at 0.1 mL min<sup>-1</sup> until pH 8.0 (slow titration rate) for the slowly mixed samples. For the fast-mixed samples, the NaOH addition rate was 5.0 mL min<sup>-1</sup> until pH 6.0 was reached and then 1.0 mL min<sup>-1</sup> until pH 8.0 was achieved (fast titration rate). The suspension pH was readjusted to 8.0 the next day. For B-sorption experiments, B(OH)<sub>3</sub> solution was added 24 h after the precipitate was formed and the pH was adjusted to 8.0. Suspensions were then equilibrated in closed, 1-L high-density polyethylene bottles at 90 ± 1°C in an oven or at 23 ± 1°C for 5 d. The samples were centrifuged and supernatant solutions were analyzed for pH using a Thomas combination pH electrode<sup>1</sup> (Thomas Scientific, Swedesboro, NJ), and B concentration using a Technicon Autoanalyzer II (Technicon Industrial Systems, Tarrytown, NY) with the azomethine-H method described by Bingham (1982). Aluminum and Si were determined by ICP-AES. The precipitates

<sup>1</sup>Trade names are provided for the benefit of the reader and do not imply endorsement by the USDA.

**Table 2. Sorption of B during allophane precipitation in the presence of B(OH)<sub>3</sub>. Initial solution Al/Si atomic ratio was 1.0. Residual Al concentrations were generally <0.01 mM. Each washing consisted of a 2-h shaking in deionized water followed by centrifugation. All the systems were equilibrated for 5 d before washing.**

Mixing and titration rate	Incub. temp.	Initial conc.		Residual conc.		B sorbed			Precipitates		pH†	
		B	Si	B	Si	Before wash	After wash	B Desorption	Atomic ratio B/Si‡	Surface area	Before wash	After wash
		mM		mM		mmol kg <sup>-1</sup>		%		m <sup>2</sup> g <sup>-1</sup>		
Slow	23	4.44	44.4	3.04	0.04	212	82	61	0.014	220	7.9	9.6
Slow	23	31.7	31.7	25.0	0.06	1397	358	74	0.056	220	7.9	8.8
Fast	23	4.39	43.9	3.71	0.09	108	43	60	0.005	180	8.0	9.2
Fast	23	31.3	31.3	27.8	0.10	877	304	65	0.035	190	8.0	8.9
Slow	90	4.43	44.3	3.65	0.28	130	64	51	0.010	290	7.2	9.6
Slow	90	31.7	31.7	28.2	0.40	788	354	55	0.058	310	7.3	9.4
Fast	90	4.32	43.2	4.06	0.17	78	39	50	0.006	210	7.8	9.0
Fast	90	31.4	31.4	29.0	0.16	615	315	49	0.038	210	7.8	8.8

† The pH at the end of titration at 23°C was 8.0.

‡ The atomic Al/Si ratio of the products washed with deionized water three times was 1.0.

**Table 3. Sorption of B after allophane precipitation. For these reactions, B(OH)<sub>3</sub> solutions were added 24 h after the precipitates were formed. AU the systems were equilibrated for 5 d and then washed with deionized water three times. Each washing consisted of a 2-h shaking, followed by centrifugation.**

Mixing and titration rate	Incubation temp. °C	Initial conc.		Residual conc.		B sorbed		B Desorption %	Precipitates		pH†	
		B	Si	B	Si	Before wash	After wash		Atomic ratio B/Si‡	Surface area	Before wash	After wash
		mM				- mmol kg <sup>-1</sup> -			m <sup>2</sup> g <sup>-1</sup>			
Slow	23	4.40	44.0	3.30	0.04	164	72	56	0.011	300	7.6	9.3
Slow	23	31.4	31.4	28.2	0.06	746	312	58	0.050	300	8.0	9.2
Fast	23	4.45	44.5	3.93	0.09	77	38	51	0.006	200	8.0	9.2
Fast	23	31.9	31.9	29.1	0.14	565	264	53	0.031	200	8.0	9.1
Slow	90	4.28	42.8	3.79	0.28	90	53	41	0.008	380	7.3	9.1
Slow	90	30.2	30.2	27.9	0.40	612	339	45	0.054	350	7.8	9.0
Fast	90	4.43	44.3	4.16	0.26	65	37	43	0.006	230	7.4	8.9
Fast	90	31.9	31.9	29.8	0.16	497	282	43	0.034	200	7.8	8.8

† The pH at the end of titration at 23°C was 8.0.

‡ The atomic Al/Si ratio of the products washed with deionized water three times was 1.0.

were resuspended in 250 mL of DIW and shaken for 2 h before centrifugation. This quick washing process was repeated two more times such that the supernatant electrical conductivity was  $<0.08 \text{ dS m}^{-1}$  and the washed materials were stored in 150 mL of DIW. Subsamples of suspensions were dissolved in an 0.2 M ammonium oxalate (pH 3) solution and total Al, Si, and B determined.

Subsamples of mineral suspensions were air dried and gently ground. The moisture content of air-dried minerals was determined. The precipitates were examined using x-ray diffraction on randomly oriented powder mounts. Specific surface areas of the minerals were determined using a single-point BET N<sub>2</sub> adsorption isotherm on a Quantachrome Quantasorb Jr. surface area analyzer (Quantachrome Corp., Syosset, NY). Samples were degassed at 110°C before surface area determination.

### DRIFT Spectroscopy

Infrared spectra of solids were recorded with a Bio-Rad FTS-7 FTIR spectrometer with a DTGS detector and a CsI beamsplitter (Digilab, Cambridge, MA). Although intensities in diffuse reflectance spectra of the solids are most commonly described by using the Kubelka-Munk or remission function, an alternative mode of presentation in terms of diffuse absorbance was used. An absorbance format is required for spectral deconvolution. In addition, spectral subtraction produces less noise in the difference spectra, and the qualitative changes in the spectra are much more easily observed using diffuse absorbance instead of Kubelka-Munk mode (Aochi and Farmer, 1992). Diffuse absorbance is suited to a study of attachment mechanisms. Band intensities are shown in absorbance and should be considered only in relative rather than in absolute terms. The DRIFT spectra of the solids were recorded for samples diluted with powdered KBr. Air-dried allophane precipitates and pure B(OH)<sub>3</sub> and borax (Aldrich Chemical, Milwaukee, WI) samples of 5 mg were handground for 3 min and mixed with 95 mg of ground KBr. A Digilab diffuse reflectance unit of the same type as that described by Nguyen et al. (1991) was used. Stainless steel cylindrical sample cups (2 mm deep and 7 mm in diameter) were filled with the KBr-diluted sample powder and the sample surface was leveled with a flat glass slide. Infrared spectra were recorded from 4000 to 200 cm<sup>-1</sup> at 4 cm<sup>-1</sup> resolution over 125 scans after purging the sample chamber with filtered, dry air for 10 min, eliminating interference by CO<sub>2</sub> and atmospheric water.

Deconvolution of the spectra was performed to enhance the apparent resolution of overlapping peaks where the limiting resolution is the natural width of the bands, not the resolution

with which the spectra were collected. The individual peaks are assumed to have Lorentzian line shapes. A broad peak may be described as the convolution of a very sharp peak with a Lorentzian line shape function. Band area is retained in addition to peak position. However, peak amplitude is changed due to the narrowing of the band from removal of the Lorentzian line shape. Fourier deconvolution was carried out with the software provided by Bio-Rad, based on the algorithm of Kauppinen et al. (1981). The Bessel function option was used for apodization as it minimizes the amount of noise introduced by the deconvolution process. The full width at half height of the original components was assumed to be 150 cm<sup>-1</sup> and the resolution factor was set at 1.5. These optimized parameter values provided results without severe overdeconvolution.

### Boron Release by Washing

After three quick washes with DIW, aliquots of suspensions containing 0.5 g of allophane were added to 30-mL centrifuge tubes and the total solution volumes were adjusted to 30 mL by addition of DIW. The suspensions were shaken for 24 h and then centrifuged. The pH and B concentration of the supernatants were determined as described above. The B released from each washing was corrected for the residual solution B in the paste from the previous washing. The shaking and washing processes were repeated four times for the low initial B concentration systems such that B concentrations in the supernatant solutions ranged from 0.003 to 0.03 mM. The shaking and washing processes were repeated seven times for the high initial B concentration treatments such that B concentrations ranged from 0.018 to 0.10 mM. The allophane paste was air dried and examined using DRIFT spectroscopy as described above. A preliminary experiment using in situ attenuated total reflectance technique for allophane pastes and suspensions did not yield a satisfactory signal for B, due to low sensitivity under these conditions. In this study, the amount of coprecipitated B is operationally determined as the difference between the amount of B removed per mass during coprecipitation with allophane and by reaction with freshly precipitated allophane after washing.

## RESULTS AND DISCUSSION

### Chemical Characteristics of Precipitation and Boron Sorption

Tables 1, 2, and 3 give the initial and residual concentrations of Al, Si, and B in the various systems and the composition of the precipitates after three washes with

DIW. X-ray diffractograms of all 20 precipitates showed that none of the materials contain any detectable crystalline phase. Thus, the precipitates are poorly ordered aluminosilicates, which are similar to those obtained by Farmer et al. (1991).

As shown in Table 1, the surface area of the precipitates free of B was not affected by titration rate. Increased temperature resulted in an increase in surface area. Boron sorption by allophane precipitated in the presence of B is shown in Table 2. Increased B in solution increased the amount of B sorbed. In most instances, the increase in B sorbed ( $8 \times$ ) was almost the same as the increase in B in solution ( $8 \times$ ). This suggests a relatively constant partition coefficient. Boron sorption as a result of B solution reacting with existing allophane is shown in Table 3. Sorption of B to the allophane precipitates generally increased the surface area of the precipitates formed by a slow mixing and titration rate and equilibrated at 23°C. Boron sorption may have increased the negative charge of the surface, creating repulsion within aggregates and shifting the PZC to a lower pH value (Su and Suarez, 1995).

The amount of B sorbed before washing, in the experiment in which B was added after allophane precipitation, was much lower than the corresponding data shown in Table 2 (B sorbed during precipitation). In contrast, after washing, B sorbed was more comparable in both experiments. The B/Si atomic ratio in most allophane precipitates formed in the presence of B (Table 2) was slightly higher than their corresponding precipitates reacting with B after precipitate formation (Table 3).

Mixing and titration rate strongly affected B sorption. At each temperature before washing, more B was sorbed during allophane precipitation at the slower mixing and titration rate than at the faster rate (Tables 2 and 3). This may be partly due to a higher surface area of precipitates formed by a slower mixing and titration rate. Temperature also has a pronounced effect on B sorption. In general, more B was sorbed at 23 than at 90°C. This occurred despite the fact that precipitation at 90°C resulted in considerably larger surface areas than the 23°C results, indicating that temperature had a greater effect on B sorption than did the mixing and titration rate. Greater B sorption at 23 than at 90°C is consistent with the data of Goldberg et al. (1993) for goethite and gibbsite at pH 8 to 9.5 and Barrow (1992) for Al and Fe oxides.

A significant portion of sorbed B was easily desorbed by washing with DIW (Tables 2 and 3). The atomic B/Si ratios of allophane solids after three washes generally increased for allophane incubated at 90°C relative to those for allophane incubated at 23°C, except the slower mixing and titration rate and lower initial B concentration systems. As a percentage of the amount of B sorbed, more B was removed by washing the allophane incubated at 23°C than that incubated at 90°C. The results suggest that B sorbed at 90°C may be more strongly held than that sorbed at 23°C.

Almost all the added Al and Si reacted to form allophane (Tables 2 and 3). Residual Si concentration and the amount of B sorbed by allophane were independent.

The pH of allophane suspensions increased after three washes (Tables 1, 2, and 3). Washing the Na-saturated allophane resulted in hydrolysis:  $\text{Na-allophane} + \text{H}_2\text{O} \rightarrow \text{H-allophane} + \text{NaOH}$ , that produced a pH of 8 to 9 (Jackson, 1956). An increase in pH from 8 to 9.5 should have little effect on B adsorption by allophane (Su and Suarez, 1995).

Polymeric B species become a significant portion of total solution B at concentrations  $>25$  mM (Cotton and Wilkinson, 1988, p. 169). Thus, polynuclear B species should have formed when the precipitates were air dried. This change in solution speciation will affect the surface species of sorbed B and increase B concentration in the aqueous phase.

### FTIR Spectroscopy of Sorbed Boron

In order to identify the IR bands of trigonally and tetrahedrally coordinated B on air-dried allophane surfaces and in the mineral structure, we analyzed DRIFT spectra for  $\text{B}(\text{OH})_3$  and borax ( $\text{Na}_2\text{B}_4\text{O}_7 \cdot 10\text{H}_2\text{O}$ ) (Fig. 1). These spectra are used as reference materials for monomeric and polymeric B. The coordination polyhedron around a B atom is either trigonal planar or a tetrahedron. All B atoms in  $\text{B}(\text{OH})_3$  are trigonally coordinated and B atoms in borax are half trigonally and half tetrahedrally coordinated. All the B atoms are present in the two adjacent six-membered rings in the borax structure. It has been shown (Moenke, 1974) that  $\text{BO}_3$  groupings are sharply differentiated from  $\text{B}(\text{O},\text{OH})_4$  groupings by the location of their asymmetric stretching vibrations. The former absorbs strongly in the range 1450 to 1200  $\text{cm}^{-1}$  and the latter in the range 1180 to 900  $\text{cm}^{-1}$ . Bending vibrations of BOH can extend up to 1300  $\text{cm}^{-1}$ , but their weaker absorption generally distinguishes them from  $\text{BO}_3$  stretching vibrations. Accordingly, the absence of intense absorption above 1200  $\text{cm}^{-1}$  is strong evidence for the absence of  $\text{BO}_3$  groupings in borosilicates, while the presence of such absorption is evidence for  $\text{BO}_3$  groupings, provided that carbonate is absent. The published transmission IR spectra for

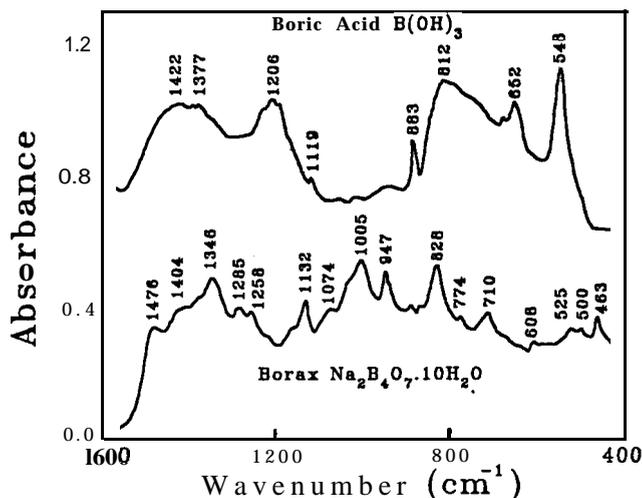


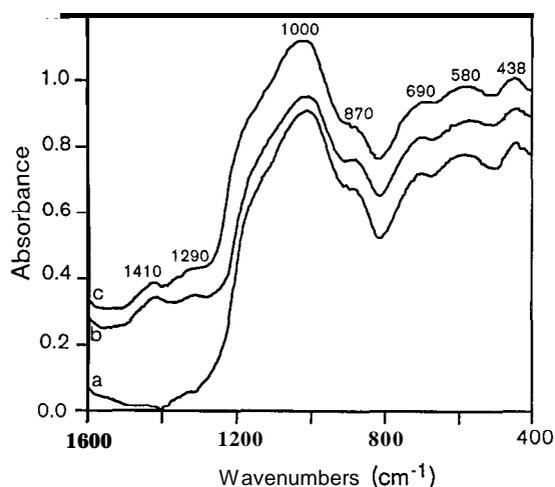
Fig. 1. DRIFT spectra of  $\text{B}(\text{OH})_3$  and borax. Samples were diluted with KBr (5mg sample in 95 mg of KBr).

**Table 4. Region of absorption for minerals containing trigonal and tetrahedral B (from Ross, 1974).**

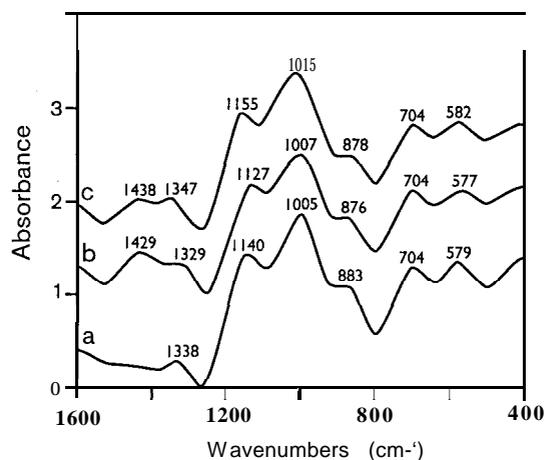
Region	Cause of absorption
cm <sup>-1</sup>	
1500-1300	Asymmetric stretching, trigonal B
1300-1000	OH in-plane bending
1100-850	Asymmetric stretching, tetrahedral B
950-850	Symmetric stretching, trigonal B
850-700	Symmetric stretching, tetrahedral B, OH out-of-plane bending
700-400	Bending modes of trigonal and tetrahedral B

borates (Ross, 1974) and borosilicates (Moenke, 1974) support the above generalizations. Table 4 lists regions of absorption for minerals containing trigonal and tetrahedral B (Ross, 1974). This table serves as a useful but not absolute guide in assigning peaks to trigonally and tetrahedrally coordinated B in allophane precipitates, since the IR absorbance characteristics of sorbed B may be different from those of pure crystalline borates. Determination of coordination of sorbed B is not straightforward since the tetrahedrally coordinated B is especially difficult to identify, due to band overlapping with Si-O groups in allophane.

The air-dried allophanes had an average moisture content of  $129 \pm 23$  g kg<sup>-1</sup>; thus, they have water films on their surfaces. Original DRIFT spectra of allophane formed by the slower mixing and titration rate and incubated at 23 °C are presented in Fig. 2, and their deconvoluted spectra in Fig. 3. Similar spectra were obtained for samples incubated at 90 °C. Bands at 1410 and 1290 cm<sup>-1</sup> were assigned to asymmetric stretching of trigonally coordinated B (Fig. 2b and 2c). All spectra in Fig. 2 are typical of hydrous feldspathoid (Farmer et al., 1979) with: (i) characteristic maxima at 1000, 690, and 438 cm<sup>-1</sup> arising from a tetrahedral aluminosilicate network, (ii) a band at 580 cm<sup>-1</sup> arising from octahedral Al, and (iii) a shoulder at 870 cm<sup>-1</sup> arising from Si-OH groups. The two bands assigned to trigonally coordi-



**Fig. 2. DRIFT spectra of allophane precipitated by a slower mixing and titration rate and incubated at 23 °C for 5 d: (a) in the absence of B; (b) reacted with 31.4 mM B after allophane precipitation; and (c) reacted with 31.7 mM B during allophane precipitation. The spectra were offset for display purposes. The precipitates were washed three times with deionized water. Air-dried samples were diluted with KBr (5-mg sample in 95 mg of KBr).**



**Fig. 3. Deconvoluted spectra of Fig. 2 by a Lorentzian function with a half-width of 150 cm<sup>-1</sup> and a peak width narrowing factor of 1.5.**

nated B shifted from 1410 and 1290 cm<sup>-1</sup> to 1429 and 1329, and 1438 and 1347 cm<sup>-1</sup> in the deconvoluted spectra (Fig. 3b and 3c). The band at 1338 cm<sup>-1</sup> in Fig. 3a is most likely a side lobe due to overdeconvolution. Deconvolution is useful in determining peak position in complex contours, but it can generate side lobes (Kaupinen et al., 1981). The distinct shoulder in the range 1120 to 1160 cm<sup>-1</sup> in the deconvoluted spectra (Fig. 3) indicates the presence of a silica-rich component, but the absence of adsorption at 800 cm<sup>-1</sup> argues against the presence of appreciable amounts of discrete silica. This shoulder shifted from 1140 cm<sup>-1</sup> for allophane precipitated in the absence of B to 1155 cm<sup>-1</sup> for allophane precipitated in the presence of B (Fig. 3a and 3c). In contrast, freshly precipitated allophane reacting with B exhibited a downward shift from 1140 to 1127 cm<sup>-1</sup> (Fig. 3a). The peak shift in the Si-O band from 1005 to 1015 cm<sup>-1</sup> suggests that the symmetry of SiO<sub>4</sub> tetrahedra were reduced after B sorption during allophane precipitation. There was more distortion in SiO<sub>4</sub> tetrahedra caused by B sorption during allophane precipitation than by B sorption after allophane precipitation. Boron sorption did not change the octahedral Al band near 580 cm<sup>-1</sup>, suggesting that B associated with allophane does not have six coordination and must be three or four coordinated.

There was little difference between the raw spectra of allophane precipitated by the slower mixing and titration rate (Fig. 2) and allophane precipitated by the faster mixing and titration rate (Fig. 4). However, significant differences were found between their deconvoluted spectra (Fig. 3 and 5). At a faster mixing and titration rate, trigonally coordinated B bands in the range 1420 to 1320 cm<sup>-1</sup> were at lower wavenumbers than the slower rate. Boron sorption by freshly precipitated allophane had no noticeable effect on the Si-O stretching vibrations (Fig. 5a and 5b). In contrast, B sorption during allophane precipitation shifted the Si-O bands from 1115 to 1126, and from 1003 to 1007 cm<sup>-1</sup> (Fig. 5c), indicating noticeable, reduced Si-O symmetry. We interpret this reduced symmetry to substitution of B, which is likely in four coordination with O.

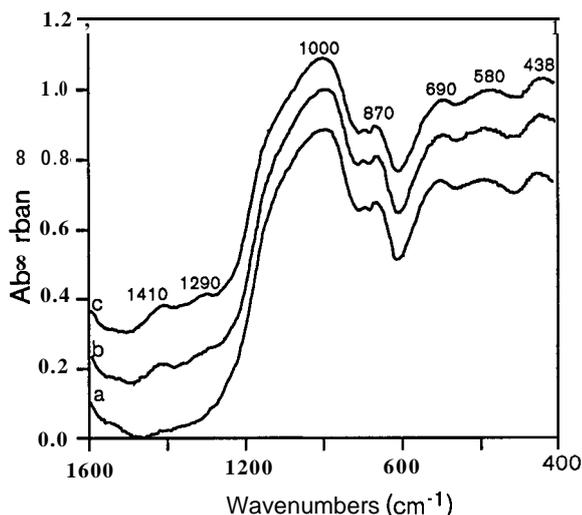


Fig. 4. DRIFT spectra of allophane precipitated by a faster mixing and titration rate and incubated at 23°C for 5 d: (a) in the absence of B; (b) reacted with 31.9 mM B after allophane precipitation; and (c) reacted with 31.3 mM B during allophane precipitation.

An upward shift in bands in the range 1460 to 1340  $\text{cm}^{-1}$  for the trigonally coordinated B was observed in both the raw (Fig. 6) and deconvoluted spectra (Fig. 7) of allophane reacted with the lower initial B concentration, compared with the higher initial B concentration. The significance of this shift is not clear. Again, coprecipitated B shifted the shoulder Si-O stretching band upward from 1129 to 1142  $\text{cm}^{-1}$ .

An estimation of the distribution of trigonally vs. tetrahedrally coordinated B on allophane for the adsorbed B is difficult due to band overlapping of  $\text{Si}(\text{Al})\text{O}_4$  with  $\text{B}(\text{O},\text{OH})_4$  tetrahedra. Nevertheless, we expect that there should be more trigonally than tetrahedrally coordinated B on the allophane surface due to consideration of expected B speciation. At pH 8, about 90 % of the total solution B exists as neutral  $\text{B}(\text{OH})_3$  molecules and 10% as the  $\text{B}(\text{OH})_4^-$  anion. In addition, DRIFT spectral subtraction of allophane precipitated then reacted with B

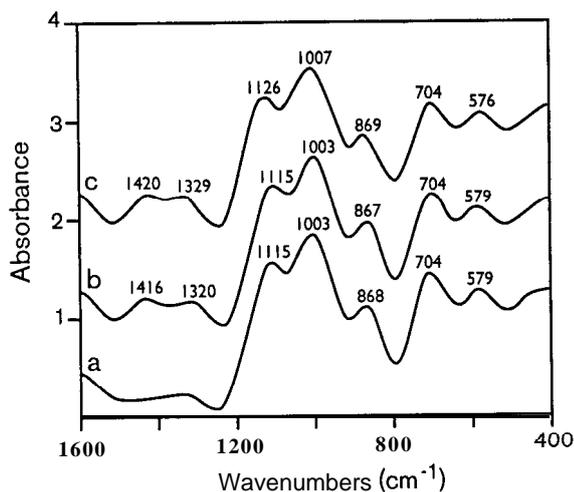


Fig. 5. Deconvoluted spectra of Fig. 4 by a Lorentzian function with a half-width of 150  $\text{cm}^{-1}$  and a peak width narrowing factor of 1.5.

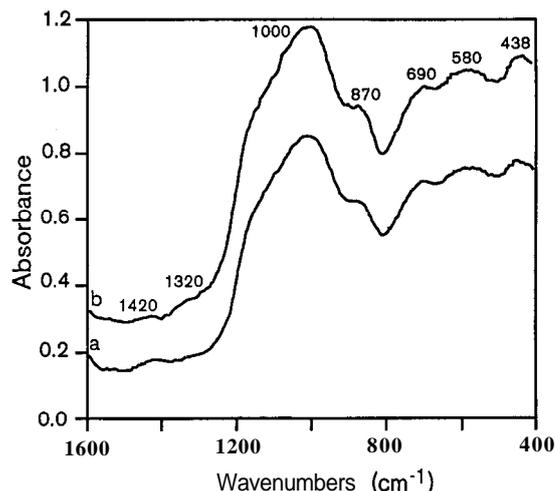


Fig. 6. DRIFT spectra of allophane precipitated by a slower mixing and titration rate and incubated at 23°C for 5 d: (a) reacted with 4.4 mM B after allophane precipitation; and (b) reacted with 4.4 mM B during allophane precipitation.

and allophane precipitated in the absence of B (not shown) suggests that  $\text{B}(\text{OH})_3$  is the species preferred by the surface at pH 8. The relatively weak expression of tetrahedrally coordinated B, compared with the trigonally coordinated B, in the difference spectra may be explained by the occurrence of relatively few adsorption sites with  $\text{B}(\text{OH})_4^-$  anion preference over the neutral  $\text{B}(\text{OH})_3$  molecule. Alternatively, the presence of both coordinations of adsorbed B may be explained by polymerization of adsorbed B on allophane surfaces. Although even at an initial B concentration of 100 mM B, the sum of polynuclear species of  $\text{B}_3\text{O}_3(\text{OH})_4^-$ ,  $\text{B}_4\text{O}_5(\text{OH})_4^{2-}$ , and  $\text{B}_5\text{O}_6(\text{OH})_4^-$  is less than 15% of the total B at pH 8 (Bloesch et al., 1987), the polymerization of adsorbed B on the allophane surface cannot be completely excluded. For example, if we assume both  $\text{B}(\text{OH})_3$  and  $\text{B}(\text{OH})_4^-$  have an area of 0.2  $\text{nm}^2$ , allophane incubated at 90°C and reacted with 31.9 mM B (Table 3) should have an adsorbed B surface coverage of 30% before any washing and 17% after three washes. This high B coverage sug-

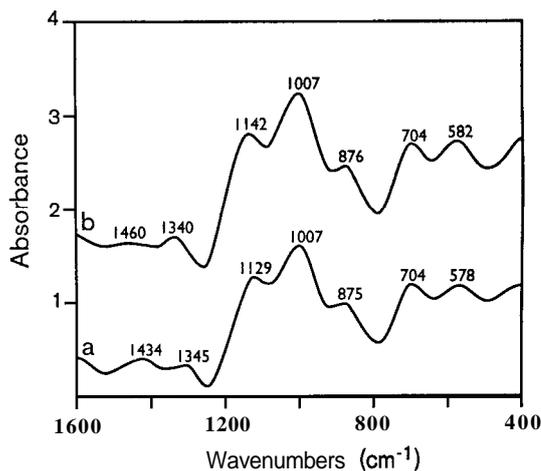


Fig. 7. Deconvoluted spectra of Fig. 6 by a Lorentzian function with a half-width of 150  $\text{cm}^{-1}$  and a peak width narrowing factor of 1.5.

gests that B polymerization is possible on the allophane surface. Polymerized B species containing both trigonally and tetrahedrally coordinated B exist in many hydrated borates (Christ and Clark, 1977). In this study, trigonally coordinated B should still be predominant over the tetrahedrally coordinated B in the polymerized species.

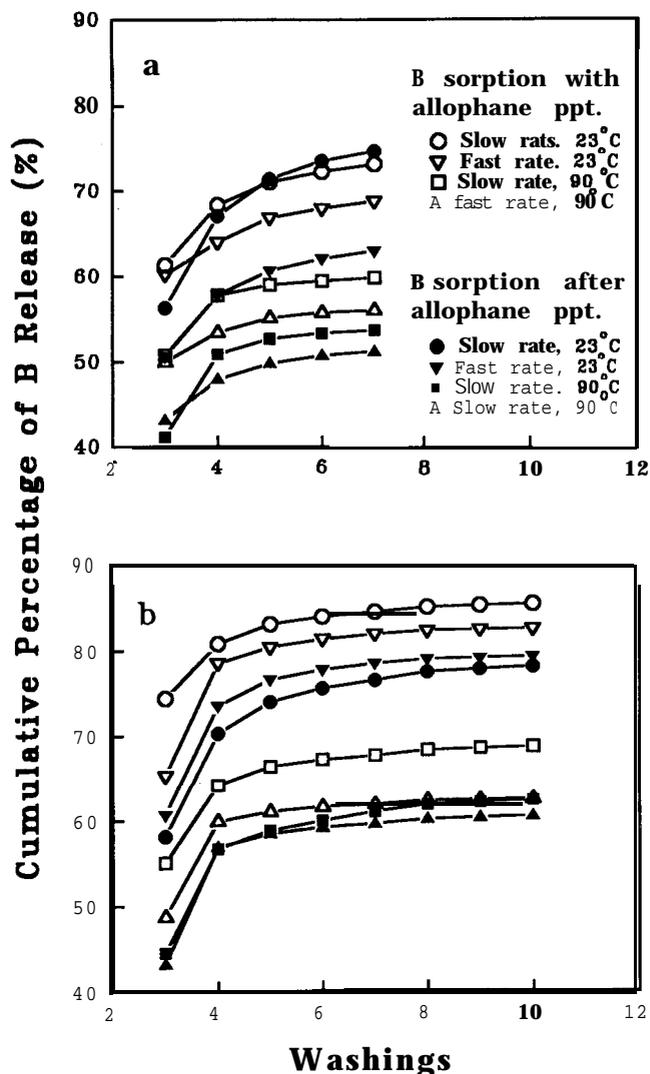
No bands were resolved for the frequency range 1600 to 1250  $\text{cm}^{-1}$  in the difference spectra (spectra of allophane precipitated in the presence of B minus spectra of freshly precipitated allophane reacted with B, data not shown). This provides evidence for B substitution into the allophane structure. Boron sorbed during allophane precipitation was greater than B sorbed by freshly precipitated allophane. If this increased sorption resulted only in increased adsorption, then spectral subtraction of allophane precipitated before  $\text{B}(\text{OH})_3$  addition from allophane precipitated in the presence of B should have resulted in positive peaks corresponding to both trigonal and tetrahedral coordination. As evidenced by the difference spectra, all of the increased sorption is due to tetrahedral coordination, consistent with structural substitution of B for Si.

The DRIFT spectra of allophane after a total of both seven and 10 washes were similar to those after three washes, except that the absorbance of bands attributable to trigonally coordinated B were lower than samples after only three washes.

### Boron Release by Washing

Release of B from allophane after more than three washes is presented in Fig. 8. The pH of the supernatant solutions after the last washing ranged from 9.4 to 9.6 for all samples due to allophane hydrolysis. Boron release rate decreased with successive washing. Generally, for both low and high initial B concentration systems, a greater percentage of sorbed B was released cumulatively from allophane precipitated in the presence of B than from allophane precipitated before  $\text{B}(\text{OH})_3$  was added, when other conditions were equal. Additionally, for most samples, the cumulative percentage of B release from allophanes precipitated in the presence of added  $\text{B}(\text{OH})_3$  was increased by an almost comparable value as the B release percentage from allophanes precipitated before  $\text{B}(\text{OH})_3$  addition. This data is consistent with both the initially, slightly higher B concentration in the solid with coprecipitated B, and with the FTIR data discussed above. We expect that coprecipitated B is leached slower than adsorbed B. Data presented in Table 5 are the amounts of B remaining in the allophane solids after a total of seven washes for the low initial B concentration treatments, and 10 washes for the high-concentration treatments. We also present the percentages of coprecipitated B based on the amounts of initially sorbed B. The low percentage of coprecipitated B in allophane (<9%) suggests that coprecipitation of B is a minor contributor, compared with surface adsorption, to the overall removal of B from solution by allophane.

Ligand exchange with reactive surface hydroxyl groups has been proposed as the mechanism of B adsorption on Al and Fe oxides and clay minerals (Goldberg,



**Fig. 8.** Cumulative percentage of B release from allophanes reacted with  $\text{B}(\text{OH})_3$  of (a) lower initial concentrations of approximately 4.4 mM and (b) high initial concentrations of approximately 32 mM as a function of number of washings. Each of the first three washes consisted of a 2-h shaking followed by centrifugation. After that, each washing consisted of a 24-h shaking followed by centrifugation. The solid to solution ratio was 1:100 (w/v) for the first three washes, and 1:60 (w/v) afterwards. Boron release percentage was calculated on the basis of the initially sorbed B before washing.

1993). Ligand exchange with hydroxyl groups is a mechanism whereby anions become specifically adsorbed on mineral surfaces. Specific adsorption of anions causes a shift in the PZC of adsorbent to a more acidic value. A shift in PZC was observed following B adsorption on Al oxides (Beyrouty et al., 1984; Su and Suarez, 1995) and allophane (Su and Suarez, 1995), indicating specific adsorption. In ligand exchange, B acts as a Lewis base in direct contrast to its Lewis acid solution chemistry behavior (Goldberg, 1993). Therefore, it can be concluded that most B sorbed to allophane is associated with surface functional groups, presumably via ligand exchange, rather than with the allophane interior structure via isomorphic substitution. Nevertheless, the coprecipitated B is noteworthy in that long-term (e.g., years to decades) release of B from allophane may be tied to

**Table 5. Desorption of B from allophane by repeated washing with deionized water. Each of the first three quick washes consisted of a 2-h shaking followed by centrifugation. Afterwards, each of the continuing washes consisted of a 24-h shaking followed by centrifugation.**

Total washes	Remaining B		Coprecipitated B	Percentage of coprecipitated B†
	During allophane formation	After allophane formation		
	mmol kg <sup>-1</sup>			%
7	46	36	10	4.7
10	149	109	40	2.9
7	31	26	5	4.6
10	85	49	36	4.1
7	47	36	11	8.5
10	186	170	16	2.0
7	32	30	2	2.6
10	138	105	33	5.4

† Estimated as the percentage of coprecipitated B based on the amounts of initially sorbed B before washing.

this portion of sorbed B since the surface adsorbed B is expected to be released at a faster rate.

For most samples, there was no significant difference in the amount of coprecipitated B (as estimated by the difference between B sorption with and after allophane precipitation) for samples after three washes compared with samples after seven or 10 washes. This suggests that the estimate of the percentage of B coprecipitated may be a reasonable one because the B coprecipitated in the allophane structure should be less readily leached than the surface-adsorbed B.

### Quantity and Coordination of Coprecipitated Boron

The quantities of coprecipitated B are between 2.0 and 8.5% of the amount of initially sorbed B (Table 5). Coprecipitation is influenced by mixing and titration rate, temperature, and initial B concentration in the system. Generally, the highest amount of coprecipitated B was found under the conditions of slow mixing and titration rate, incubation at 23°C, and high initial B concentration. The fast mixing and titration rate generally decreased the amount of coprecipitated B when other conditions were equal. A small amount of B coprecipitated with allophane prepared by the faster mixing and titration rate, incubation at 90°C, and with the lower initial B concentration. The subtraction spectra of those allophanes exhibited no detectable IR bands in the frequency range 1600 to 400 cm<sup>-1</sup>, consistent with the near equal amounts of sorbed B, and near equal amounts of both trigonally and tetrahedrally coordinated B (data not shown).

Stubican and Roy (1962) reported that BO<sub>4</sub> groups can be substituted in the silica layer of synthetic phlogopite and saponite at 350 to 710°C. Our results show that the substitution may occur at far lower temperatures in allophane. The cationic radii for B(IV), Si(IV), and Al(IV) are 11, 26, and 39 pm (Shannon, 1976), respectively. Substitution of B for Al in the octahedral positions is thus less likely than is B-Si substitution.

The structure of allophane is still in dispute (van

Reeuwijk and De Villiers, 1968; Wada and Kubo, 1975; Farmer, 1982; Parfitt, 1990). Van Reeuwijk and De Villiers (1968) proposed that allophane consists of octahedral Al surrounding a negatively charged tetrahedral core with Si partially substituted by Al in fourfold coordination. This structural model is supported by Wilson et al. (1986), who used FTIR and <sup>29</sup>Si and <sup>27</sup>Al solid-state nuclear magnetic resonance spectroscopy to characterize allophane. Since Al can substitute for Si in the tetrahedral layer of allophane with atomic Al/Si ratio close to unity (Wilson et al., 1986), it is logical that B could also substitute for Si owing to the related chemistry of B and Si. Christ (1965) pointed out that it is unlikely that B proxies directly for Al. He suggested a definite mechanism by which B can proxy for Si, namely the replacement of an SiO<sub>4</sub>, in which the O does not make a second tetrahedral bond, by a BO<sub>3</sub>OH. The average Si-O bond length in silicates is about 0.161 nm (Smith and Bailey, 1963), and the average tetrahedral B-OH bond length in hydrated borates is 0.147 nm (Clark et al., 1964). Hence, the replacement of an SiO<sub>4</sub> by a BO<sub>3</sub>OH would cause a nominal linear reduction of only 8.7%, which does not seem infeasible. The presence of a proton in the BO<sub>3</sub>OH group not only leads to the correct charge for the substitution, but is also in agreement with the crystal-chemical principle that an O bonded to only one B usually has a great tendency to attach a proton (Christ, 1960).

Since XRD revealed no crystalline phases formed in Al/Si/B systems of 1:1:0.1 and 1:1:1, crystalline, sparingly soluble, hydrated Al borates are unlikely to have formed. To our knowledge, there is no report of the formation or presence of amorphous Al borates; this leaves adsorption and coprecipitation as the likely mechanisms for B sorption.

### CONCLUSIONS

This study showed that B sorption by allophane depends on the mixing and titration rate, temperature, and initial B concentration. A large portion of initially sorbed B was released by repeated washing with water. A larger portion of initially sorbed B was released from precipitates incubated at 23 than at 90°C.

Both B(OH)<sub>3</sub><sup>0</sup> and B(OH)<sub>4</sub><sup>-</sup> species are adsorbed to allophane at pH 8, presumably via a ligand exchange mechanism. Polymerization of adsorbed B to give both trigonally and tetrahedrally coordinated B on mineral surfaces is also likely to have occurred. Coprecipitation of B depends on temperature, mixing and titration rate, and initial B concentration. Coprecipitated B is likely to occur in the tetrahedral coordination, as suggested by FTIR spectroscopy. Based on differences after seven washes for the low initial B concentration treatments, and 10 washes for the high-concentration treatments, between B sorbed during allophane precipitation and B sorbed after allophane precipitation, we estimate that less than 9% of the initially sorbed B is coprecipitated. The amount of coprecipitated B did not change significantly by repeated washing, thus it may not be readily released at pH 8 to 9.6.

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