

Effect of pH and Ionic Strength on Boron Adsorption by Pyrophyllite

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ABSTRACT

The negative electrical field around clay particles whose edge thickness is small relative to the Debye length of the diffuse double layer associated with the planar surfaces may spill over into the edge region. Such a spillover may affect B adsorption by the clay. This study was conducted to determine the effect of edge surface properties of 2:1 clay on B adsorption. Pyrophyllite, which shows little deviation from the ideal formula of dioctahedral structure of 2:1 clay type, was used for that purpose. Boron adsorption by pyrophyllite was studied at $25.0 \pm 0.5^\circ\text{C}$ at ionic strengths of 0.005, 0.01, and 0.1 mol L^{-1} for pH 7 and 9 and ionic strengths of 0.01 and 0.1 mol L^{-1} for pH 5. It was suggested that B is specifically adsorbed via ligand exchange to the structural Al located on the edge surfaces. Boron adsorption increased with increasing ionic strength. The effect of ionic strength on B adsorption was smaller at pH 7 than at pH 9, consistent with the decrease in B(OH)_4^- activity fraction in equilibrium solution at pH 7 and the low affinity of the clay to B(OH)_3 . The effect of ionic strength on B adsorption was small at pH 5, attributable to the weak electrical field at this pH (electrical potential, $\psi_0 = -47 \text{ mV}$) together with the low B(OH)_4^- concentration and the low affinity of the clay for B(OH)_3 . The higher capacity of pyrophyllite, in comparison to montmorillonite, to adsorb B at pH 9 where the ψ_0 at the edge surfaces of the clay is -285 mV , supports the hypothesis that the negative electrical field associated with this planar surfaces affects B adsorption.

BORON CAN BE ADSORBED by different clay and Al and Fe oxide minerals that vary in their adsorption capacities (Goldberg and Glaubig, 1985; Keren and Bingham, 1985; Goldberg and Glaubig, 1988). Illite adsorbs more B than montmorillonite (Hingston, 1964; Keren and Mezuman, 1981) although montmorillonite has greater surface area. Kaolinite has a low B adsorption capacity on a mass basis, but on a total surface area basis kaolinite is one of the most reactive clays.

The effect of pH and clay particle size on B adsorption by clay has been intensively studied (Keren and Talpaz, 1984; Keren and Bingham, 1985). It was suggested that boron is adsorbed on the particle edge surfaces of clay minerals (e.g., montmorillonite or illite) rather than on planar surfaces. The effect of exchangeable ions on B adsorption by clay minerals was dependent on the pH of the clay suspension. Exchangeable cation species (Na^+ vs. Ca^{2+}) had little effect on B adsorption by montmorillonite at pH ≈ 7 ; there was a significant exchangeable cation effect at pH >8 , with the Ca systems adsorbing more B than Na^+ (Keren and Gast, 1981). The effect of adsorbed ion on B adsorption by montmorillonite at pH >7 was explained by the diffuse double layer theory.

Secor and Radke (1985), using the Poisson-Boltzmann equation, also showed that, for low indifferent electrolyte

concentrations, the negative electrostatic field emanating from the particle face of montmorillonite spills over into the edge surface region. The negative field may prevent borate from approaching the adsorption sites at the particle edges. This concept is also supported by the observation that by increasing the NaCl concentration from 0.02 to 0.07 or 0.36 mol L^{-1} , the amount of B adsorbed by Na-montmorillonite is increased by ≈ 10 and 50%, respectively (Keren and O'Connor, 1982).

The clay mineral pyrophyllite consists of essentially neutral tetrahedral-octahedral-tetrahedral layers. The lack of an electrical field associated with the planar surfaces may allow the evaluation of the role of edge surface reactivity in B adsorption reaction. If the diffuse double layer associated with the planar surfaces influences B adsorption by clays (especially in the pH range 8–10), B adsorption by pyrophyllite should be greater than that found in montmorillonite. This hypothesis is tested more fully in our study. The objective of our study was to determine the effect of edge surface properties on B adsorption by pyrophyllite.

MATERIALS AND METHODS

Clay Preparation

Pyrophyllite [$\text{Al}_2\text{Si}_4\text{O}_{10}(\text{OH})_2$] from Robbins, NC, was used. The clay shows little deviation from the ideal formula Al_2O_3 (28.3%), SiO_2 (66.7%), and H_2O (5.0%), and the dioctahedral structure consists of essentially neutral tetrahedral-octahedral-tetrahedral layers. This mineral has prominent basal cleavages as a result of the weak bonds between adjacent layers. Because the flakes were rather thick and large, a 500-g sample of the clay was ground for 30 h in a Zirconia ball mill (Norton, Aleron, OH) to increase the fraction of clay-size particles.

The $<2\text{-}\mu\text{m}$ clay fraction was obtained by allowing larger particles to settle out of a clay-deionized water suspension and then decanting the suspension. The clay was saturated with Na by washing three times with $0.5 \text{ mol L}^{-1} \text{ NaNO}_3$. It was then washed with distilled water and separated in a high-speed centrifuge until the electrical conductance of the equilibrium solution was $<10 \mu\text{S cm}^{-1}$. A stock suspension at concentrations of 130 g L^{-1} was used for the B adsorption experiments.

The surface area of the dry clay (freeze-dried) was determined by N_2 adsorption and the BET equation (Brunauer et al., 1938). The specific surface area was $43\,700 \pm 300 \text{ m}^2 \text{ kg}^{-1}$ clay.

Boron Adsorption Studies

Boron adsorption by pyrophyllite was studied in suspension by shaking $7.4 \times 10^{-4} \text{ kg}$ of clay (on a 110°C oven-dry basis) in 0.05-L polypropylene centrifuge tubes containing 20 mL of B solution (as H_3BO_3) at ionic strengths (I) of 0.005, 0.01, and 0.1 mol L^{-1} (NaNO_3) at pH 7 and 9, at I of 0.01 and 0.1 at pH 5, and at a temperature of $25 \pm 0.5^\circ\text{C}$. A pH of 9.0 was selected for the adsorption reaction because (i) the borate anion concentration is relatively high ($\approx 37\%$ of the total B), but $\approx 99\%$ of the adsorbed B on montmorillonite is in the borate form as predicted by the adsorption model of Keren et al. (1981); and (ii) the net surface charge of the edges of the pyrophyllite is negative.

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Suspension pH was adjusted prior to B additions with HNO₃ or NaOH. The adjustments were repeated until there was no pH change during 16 h of shaking. After pH adjustment, B solution at a given concentration (9.25 mmol L⁻¹) and pH was added at various volumes to obtain a range of initial B concentration (before adsorption took place) from 0 to 3.0 mmol L⁻¹ and then a total volume of 20 mL was obtained. The samples were shaken for ≈ 16 h. Preliminary studies indicated that apparent adsorption equilibrium was established in <2 h. The suspensions were then centrifuged and the supernatant was collected by filtering through a 0.2-μm membrane filter (Gelman Sciences, Ann Arbor, MI). Aliquots of the clear supernatant were analyzed for B using the colorimetric Azomethine-H method (Gupta and Stewart, 1975).

Computations

Boron Adsorption

Adsorbed B was calculated as the difference between the amount added and that found in the equilibrium solution. An adsorption model that assumes that B(OH)₃, B(OH)₄⁻, and OH⁻ compete for the same adsorption sites (Keren et al., 1981) was used to estimate adsorbed B. The adsorption coefficients K_{HB} , K_B , and K_{OH} for the three species B(OH)₃, B(OH)₄⁻, and OH⁻, respectively, were estimated using experimentally determined values for total amount of adsorbed B, Q_{BT} (mol g⁻¹ clay), vs. equilibrium B activity (mol L⁻¹). The following form of the equation was used to estimate B adsorption:

$$Q_{BT} = \frac{T[K_{HB}(HB) + K_B(B)]}{1 + K_{HB}(HB) + K_B(B) + K_{OH}(OH)} \quad [1]$$

where T is the apparent maximum B adsorption (mol g⁻¹ of clay) and (HB), (B), and (OH) are the solution activities of the species B(OH)₃, B(OH)₄⁻, and (OH)⁻, respectively.

Ionic strength corrections were made using single-ion or single-molecule activity coefficients. The activity coefficient, γ , was estimated by:

$$\log \gamma = -AZ^2I^{1/2} (1 + aBI^{1/2})^{-1} + B^0I \quad [2]$$

where A and B are parameters associated with the absolute temperature and dielectric constant of the solvent, a is a function of the ion diameter, I is the ionic strength = $0.5\sum C_i Z_i^2$ (mol L⁻¹), C_i is the concentration of species i , Z_i is the valence of species i , and B^0 is a parameter dependent on the value of the

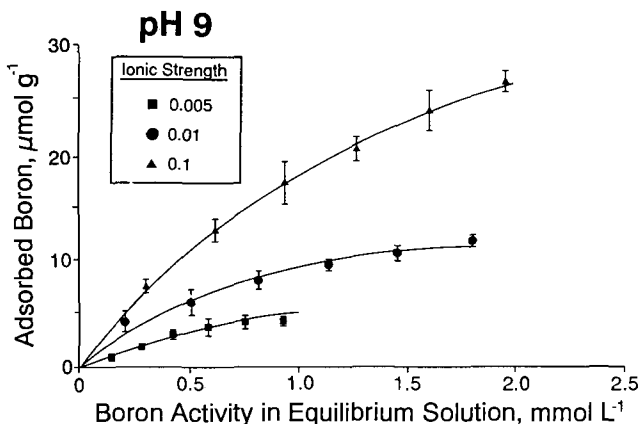
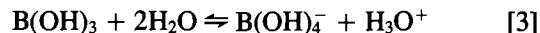


Fig. 1. Boron adsorption isotherms on pyrophyllite as a function of the total B solution activity at equilibrium and ionic strength at pH 9. The lines were calculated according to Eq. [1] by using the adsorption parameters given in Table 1.

ionic strength. In this study, $B^0 = 0.3 AZ^2$, ($I \leq 0.5 M$). For the neutral species [B(OH)₃] at all values of I , $B^0 = 0.1 L mol^{-1}$ (Helgeson, 1969). Because $Z = 0$, the first term in Eq. [2] does not contribute to the calculation of γ .

The equilibrium B(OH)₄⁻ activity can be expressed in terms of B(OH)₃ activity according to the hydrolysis reaction:



The hydrolysis constant, K_h , for this reaction at infinite dilution is 5.9×10^{-10} at 293 K. Other hydrolysis species ($K_h = 5.0 \times 10^{-13}$ and 5.0×10^{-14} , Ingri et al., 1957) were ignored because their concentrations are negligible at pH 9. As a result, the adsorbed B species included both B(OH)₃ and B(OH)₄⁻ by introducing the following equations:

$$B(OH)_3 = (BT)/(1 + E) \quad [4]$$

and

$$B(OH)_4^- = (BT)/(1 + 1/E) \quad [5]$$

where (BT) is the total B concentration in solution (mol L⁻¹) and

$$E = K_h [OH] 10^{14} \gamma_{HB} \gamma_{OH} / \gamma_B \quad [6]$$

where [OH] is the concentration of the OH⁻ ions (mol L⁻¹), and γ_{HB} , γ_B , and γ_{OH} are the activity coefficients of B(OH)₃, B(OH)₄⁻, and OH⁻, respectively. Values of K_h were corrected for I (Owen and King, 1943). Negative adsorption of borate ions by the clay was neglected.

Boron adsorption parameters were estimated by nonlinear regression using the method proposed by Marquardt (1963), improved by Ralston and Jenrich (1978) and computerized by Goodnight and Sall (1982). The computer code used the PROC NLIN of the SAS package. This method used the first partial derivative of Eq. [1], namely, $\partial Q_{BT} / \partial T$, $\partial Q_{BT} / \partial K_{HB}$, $\partial Q_{BT} / \partial K_B$, and $\partial Q_{BT} / \partial K_{OH}$.

Electrical Potential

Because H⁺ and OH⁻ ions, which establish the surface charge, are also potential-determining ions, the clay edge's surface electric potential, ψ_0 , also varies with pH of the equilibrium solution according to the Nernst relationship:

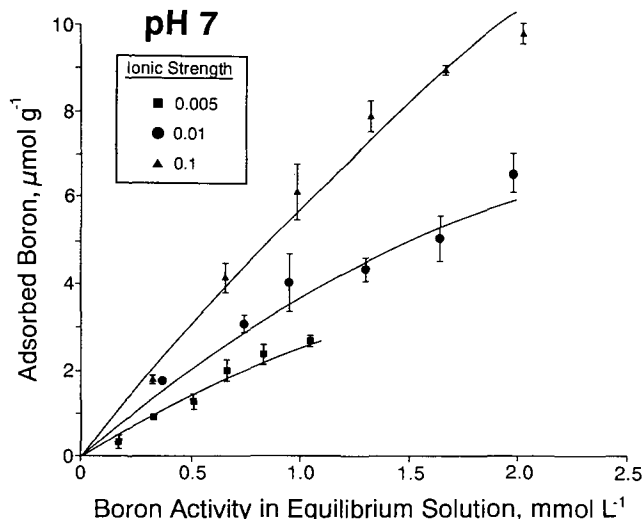


Fig. 2. Boron adsorption isotherms on pyrophyllite as a function of total B solution activity at equilibrium and ionic strength at pH 7. The lines were calculated according to Eq. [1] by using the adsorption parameters given in Table 1.

$$\psi_0 = -\frac{RT}{F} \ln \frac{(H^+)}{(H^+)_{pzc}} \quad [7]$$

where R is the gas constant ($8.316 \text{ J mol}^{-1} \text{ deg}^{-1}$), T is the absolute temperature, F is the Faraday constant ($6.02 \times 10^{23} \text{ e C/eq}$), e is the electronic charge, (H^+) is the activity of the proton in the equilibrium solution, and $(H^+)_{pzc}$ is the activity of the proton in the equilibrium solution at the point of zero charge (PZC), when the sum of all positive and negative charges on the clay surface is zero. If the PZC is known, the Nernst equation can be used to calculate ψ_0 at a given pH:

$$\psi_0 = \frac{2.302RT}{F} (\text{pH}_{PZC} - \text{pH}_i) \quad [8]$$

Use of this relationship assumes that the chemical potential of the potential-determining ions H^+ and OH^- on the clay surface is constant across the surface potential range of interest (Levine and Smith, 1971; Wright and Hunter, 1973). The PZC, as determined by the potentiometric titration method at several I is 4.2 for pyrophyllite (data not shown), similar to that for kaolinite, 4.7. (Ferris and Jepson, 1975).

The change in the electric potential at distance x from the surface, $\psi_{(x)}$ (changes with distance), associated with the pH-dependent charge surface was calculated using Eq. [8] (Babcock, 1963):

$$Y_{(x)} = 2 \ln \frac{e^{kx} + \tanh(Y_0/4)}{e^{kx} - \tanh(Y_0/4)} \quad [9]$$

where the parameters

$$Y_{(x)} = \frac{|Z_i| e \psi_{(x)}}{kT} \quad [10]$$

$$Y_0 = \frac{|Z_i| e \psi_0}{kT} \quad [11]$$

$$\kappa = \left(\frac{8\pi Z_i^2 e^2 n_0}{DkT} \right)^{1/2} \quad [12]$$

where e is the electronic charge, Z_i is the ion valance, k is the Boltzmann constant, T is the absolute temperature, D is the dielectricity, and n_0 is the electrolyte concentration in solution (ions cm^{-3}).

RESULTS AND DISCUSSION

Boron adsorption isotherms for pyrophyllite at pH 9, 7, and 5 at various I values are presented in Fig. 1,

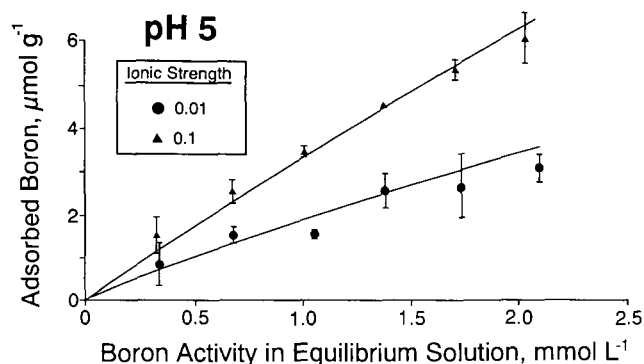


Fig. 3. Boron adsorption isotherms on pyrophyllite as a function of total B solution activity at equilibrium and ionic strength at pH 5. The lines were calculated according to Eq. [1] by using the adsorption parameters given in Table 1.

2, and 3, respectively. The symbols in these figures represent, data points, whereas the solid lines were calculated according to Eq. [1], using the adsorption coefficients T , K_{HB} , K_B , and K_{OH} , as summarized in Table 1. The R^2 values for the predicted adsorption isotherms at the various I values were 0.9826, 0.9864, and 0.9984 for the systems at pH 9, 7, and 5, respectively. The agreement between the calculated lines and the experimental results indicates that this equation reasonably describes B adsorption on pyrophyllite in suspension at various I . This agreement has been shown previously for montmorillonite, illite, kaolinite (Keren and Bingham, 1985), hydroxy-Al (Keren and Gast, 1983), and organic matter (Yermiyaho et al., 1988).

The apparent adsorption capacity of pyrophyllite is 11.1, 16.5, and 49.8 mmol kg^{-1} for solution I of 0.005, 0.01, and 0.1, respectively (Table 1). The adsorption capacities at the two lower I are similar to the values for Na- and Ca-illite (Keren and Mezuman, 1981; Keren and O'Connor, 1982). However, the apparent B adsorption capacity for pyrophyllite at an I of 0.1 is about three times higher than the value obtained for illite at I of 0.36.

Like montmorillonite and illite (Keren and O'Connor, 1982), B adsorption on pyrophyllite depends on equilibrium B activity in solution, suspension pH, and ionic strength. Boron adsorption increases with pH and I , within the pH range 5 to 9. The amount of adsorbed B, on a mass basis, by pyrophyllite at pH 9 is greater than that for montmorillonite on a mass basis (Keren and O'Connor, 1982). For example, the amount of adsorbed B by pyrophyllite in equilibrium with solution B at an activity of 1 mmol L^{-1} is $\approx 9 \text{ mmol kg}^{-1}$ for an I of 0.01 (Fig. 1), whereas the amount adsorbed by montmorillonite is 2 mmol kg^{-1} for an $I = 0.02$ (Keren and O'Connor, 1982). Because the specific edge surface area of these two clays is similar, these results indicate that the affinity of pyrophyllite for B is much greater than montmorillonite under similar conditions.

Boron adsorption at pH 9 increases with I (Fig. 1), an effect explained by the influence of electrolyte concentration on the diffuse double layer associated with the edge surfaces (Keren and O'Connor, 1982). They suggested that the negative electrical field associated with planar surfaces in Na-montmorillonite influences the extent of $B(OH)_4^-$ adsorption. The negative electrical field influences edges, making them less accessible to approaching $B(OH)_4^-$. Increasing I suppressed the diffuse double layer and, therefore, more negative borate ions are able to move close enough to interact with the adsorption sites located on the edge surfaces. The higher affinity

Table 1. Boron adsorption coefficients for Eq. [1] for pyrophyllite at various ionic strengths.

| Ionic strength | Apparent B maximum adsorption, T mmol kg^{-1} | Affinity coefficients | | |
|----------------|---|-----------------------|--------|----------|
| | | K_{HB} | K_B | K_{OH} |
| | | L mol^{-1} | | |
| 0.005 | 11.1 | 242 | 8 848 | 306 528 |
| 0.01 | 16.5 | 124 | 30 461 | 838 006 |
| 0.1 | 49.8 | 69 | 11 861 | 700 561 |

of pyrophyllite for adsorbed B at this pH in absence of permanent electrostatic charge supports this concept. At pH 9, the ψ_0 at the surface edge of the clay is -285 mV, regardless of I (NaNO_3 is an indifferent electrolyte in respect to the ψ_0 on pyrophyllite). Even though ψ_0 at this pH does not vary with electrolyte concentration, increasing I depresses the negative electrical field associated with the clay particle edges (Fig. 4). It is important to note that ψ_0 is affected by the specific adsorption of borate species on the edge surfaces. The ψ_0 , however, was calculated for the pH-dependent charge surfaces of pyrophyllite in the absence of adsorbed B. In the presence of adsorbed borate, the ψ_0 is even higher (in absolute value). As a result, the repulsion forces between the negative surface charge and $\text{B}(\text{OH})_4^-$ species decrease with increasing I , resulting in higher adsorption capacity (Fig. 1). The strong effect of I on B adsorption at pH 9 was due to the higher affinity of the clay for $\text{B}(\text{OH})_4^-$ than for $\text{B}(\text{OH})_3$. At this pH, 37% of the B in solution is in the $\text{B}(\text{OH})_4^-$ form; however, the proportion of adsorbed $\text{B}(\text{OH})_4^-$ to total adsorbed B is much higher than 37% because the affinity of clays for $\text{B}(\text{OH})_4^-$ is much higher than for $\text{B}(\text{OH})_3$, as predicted from the adsorption model (Keren et al., 1981; Keren and Mezuman, 1981).

The most reactive surface functional group on the edge surface is the hydroxyl exposed on the outer periphery of the clay mineral. This functional group is associated with two types of sites that are available for adsorption: Al(III) and Si(IV), which are located on the octahedral and tetrahedral sheets, respectively. At the edge of the octahedral sheet, the $\text{Al}(\text{III})\cdot\text{H}_2\text{O}$ is a Lewis acid site. The hydroxyl group associated with this site can form an inner sphere surface complex with a proton at low pH values or with a hydroxyl at high pH values. At the edge of the tetrahedral sheet, hydroxyl groups are singly coordinated to Si^{4+} cations.

Therefore, the available sites for B adsorption at pH 9 are most likely associated with the structural Al. In this reaction B can be specifically adsorbed on the clay surface through a ligand-exchange mechanism, whereby the adsorbed species displaces OH^- from the surface and forms partly covalent bonds with the structural Al. The distance

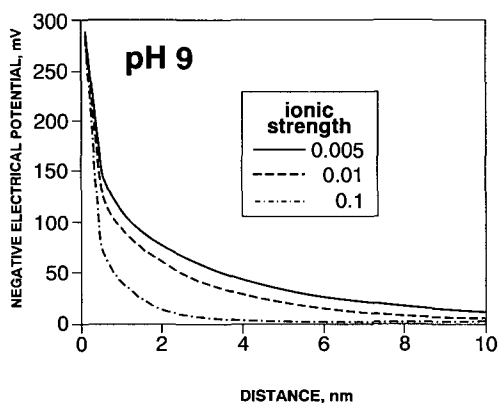


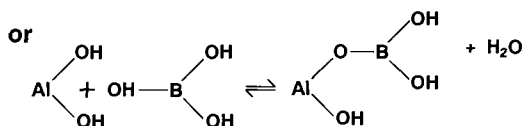
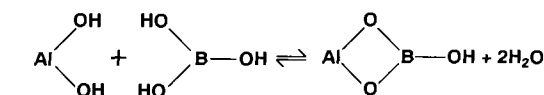
Fig. 4. Electrical potential changes for pyrophyllite edge surfaces as a function of distance from the surface and ionic strength at pH 9.

between two adjacent hydroxyls in the octahedral sheet of the edge surface is 0.22 nm. This distance fits well with the distance between two adjacent hydroxyls in the H_3BO_3 molecule (0.23 nm) and in the borate ion (0.19 nm) (Muettterties, 1967). Boron may, therefore, interact with the clay surface by forming either two bonds or a single bond with the structural Al (Fig. 5).

The results in Fig. 1 show that the total adsorbed B is much higher than that found for montmorillonite (Keren and Mezuman, 1981) at pH 9 for any given B concentration in the equilibrium solution. The greater capacity for pyrophyllite to adsorb B occurs even though the specific area of pyrophyllite is much lower than for montmorillonite ($8 \times 10^5 \text{ m}^2 \text{ kg}^{-1}$). Assuming that the cross-sectional area of the H_3BO_3 molecule (or borate ion) is $2 \times 10^{-19} \text{ m}^2$ (Hingston, 1964), the total surface area covered by B at an apparent adsorption capacity (T values in Table 1) are 1.34×10^3 , 1.99×10^3 , and $5.99 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$ for I of 0.005, 0.01, and 0.1, respectively. The coverage is smaller than the total surface area of the clay ($4.37 \times 10^4 \text{ m}^2 \text{ kg}^{-1}$). The edge surface area of particles with a size of $2 \times 10^{-6} \text{ m}$ is $8.7 \times 10^3 \text{ m}^2 \text{ kg}^{-1}$, assuming that the particles have a square planar surface shape with a thickness of $2.5 \times 10^{-7} \text{ m}$. The edge surface area increase as the particle size decreases. The apparent coverage of B becomes more significant, however, if B adsorption is restricted to edge surface.

Boron adsorption by pyrophyllite at an I of 0.005 and 0.01 is only slightly greater than that found for illite (Keren and Mezuman, 1981; Keren and O'Connor, 1982). The small difference in B adsorption for pyrophyllite and illite can be explained by considering the structure of these two clays. In illite, K ions usually satisfy the net negative charge on the planar surfaces and no interlayer swelling with water occurs. Only the ions on the external

For boric acid



For borate ion

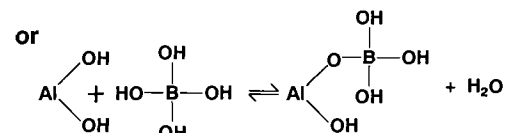
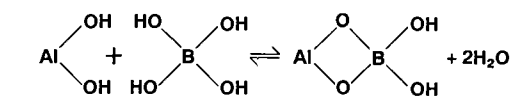


Fig. 5. Possible B-structural Al complex configurations on edge surfaces of pyrophyllite.

surfaces can be exchanged for other cations. Thus, the diffuse double layer of the internal surfaces is suppressed regardless of the exchangeable ion species, and similarly, the diffuse double layer associated with external surfaces is reduced because of charge compensation within the illite structure. The net effect is that the negative electrical field around the clay packets of illite is small, and B adsorption is only slightly influenced by the type of exchangeable cation or ionic strength (Keren and O'Connor, 1982). The negative electric field associated with planar surfaces influences the edges, making the latter less accessible to approaching $B(OH)_4^-$ species. This may have a major effect on B adsorption because the affinity of the adsorption sites for $B(OH)_4^-$ is much higher than that for $B(OH)_3$ as indicated from adsorption isotherms of pH 5 and 9 (Keren et al., 1981; Keren and Mezuman, 1981; Goldberg and Glaubig, 1988). The small difference between pyrophyllite and illite, and the substantial difference between these two clays and montmorillonite suggest that most of the adsorption sites in the phyllosilicate clays are located on the edge surfaces. At the higher I (0.1), the apparent B adsorption capacity was about three times higher than the value obtained for illite at I of 0.36 (Keren and O'Connor, 1982). This difference between the two clay systems can be explained as follows: The surface charge density of the edge surfaces, at a given pH, increases with I in suspension. Because the electrostatic charge density on the edge surfaces is negative at this high pH, the accessibility of $B(OH)_4^-$ species to the illite surfaces on the edges at this high I is less than that observed for pyrophyllite at a lower I . The I of 0.1, however, was high enough to compress the diffuse double layer associated with the edge surfaces (Fig. 4). As a result, the apparent B adsorption capacity of the pyrophyllite under these conditions was higher than that observed for illite.

Boron adsorption by pyrophyllite at pH 7 (Fig. 2) was lower than the amount adsorbed at pH 9 (Fig. 1). The lower amount of adsorbed B at any total B activity in solution and I value is due to the decrease in the fraction of $B(OH)_4^-$ in solution and the lower affinity of adsorption sites for H_3BO_3 than for borate ions (Keren et al., 1981). Although the $B(OH)_4^-$ activity fraction of the total B in equilibrium solution is only 6×10^{-3} at pH 7, the amount of adsorbed B is relatively high. This can be explained as follows. During the adsorption process (before reaching an equilibrium), the fraction of $B(OH)_4^-$ ions decreases below the equilibrium value due to the preferential adsorption of $B(OH)_4^-$ over $B(OH)_3$ since the affinity of the surface for borates is higher. As a result, the $B(OH)_4^-$ activity decreases below the equilibrium activity and more $B(OH)_3$ species dissociate to form $B(OH)_4^-$ ions. This process continues to take place until the system as a whole reaches an equilibrium.

Similar to pyrophyllite at pH 9, the effect of I on B adsorption at pH 7 is pronounced. The ψ_0 is -166 mV and the electrical field is extended. It is expected, therefore, that the negative electrical field associated with the edge surfaces decreases more sharply with increasing I , making the edges more accessible to approaching $B(OH)_4^-$. Thus, more negative borate ions are able to

move close enough to interact with the adsorption sites on the surfaces of pyrophyllite. As observed at pH 9, B adsorption by pyrophyllite at pH 7 was higher than that found for montmorillonite but similar to Ca-illite (Keren and Mezuman, 1981). As discussed above, these results also support the hypothesis that B adsorption is taking place on sites located on the edge surfaces despite the existence of net negative charge.

At pH 5, the amount of adsorbed B on pyrophyllite is low for both $I = 0.01$ and 0.1 (Fig. 3). At this pH, $B(OH)_3$ is the main B species in solution (99.994% of the total B activity in solution). These results indicate that the affinity of pyrophyllite to $B(OH)_3$ species is low, as was also observed from the K_{HB} values (Table 1). A lower affinity of hydroxy-Al to $B(OH)_3$ was also observed when pH decreased from 7 to 5 (Keren and Gast, 1983; Goldberg and Glaubig, 1985).

These results indicate that the effect of I on the absolute amount of adsorbed B at pH 5 is relatively small (compared with the systems at higher pH). This small effect can be attributed to the low electrical field at pH 5. The ψ_0 is only -47 mV and is sharply reduced with distance from the edge surfaces. This low negative electrical field, together with the low concentration of $B(OH)_4^-$ present in solution at this pH and the low affinity coefficient for $B(OH)_3$ (Table 1), can explain the low amount of adsorbed B and the small effect of I that was observed.

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