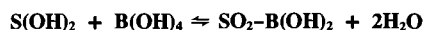


Equilibrium and Kinetics of Borate Adsorption-Desorption on Pyrophyllite in Aqueous Suspensions

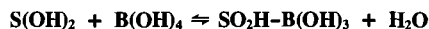
R. Keren,* P. R. Grossl, and D. L. Sparks

ABSTRACT

This study was conducted to elucidate the dynamic aspects of the adsorption-desorption of borate ions on edge surfaces of 2:1 clay minerals. A pressure-jump relaxation method was used to evaluate the elementary processes involved in the adsorption-desorption of borate ions by pyrophyllite in aqueous media at pH 9 and ionic strength of 0.01 (NaNO₃). This clay was selected because of the small deviation from the ideal structural formula of the dioctahedral 2:1 clay minerals. At pH 9, 37% of the total B in solution is in the B(OH)₄⁻ form, whereas of the total adsorbed B, the fraction of the adsorbed B(OH)₄⁻ is assumed to be ≈ 0.99 at all levels of adsorbed B studied. This high fraction is probably due to the absence of repulsive forces associated with the planar surfaces. A linear correlation ($R^2 = 0.94$) between the reciprocal value of the relaxation time, τ^{-1} , and the sum of concentrations of the free adsorption sites and borate ions in solution at equilibrium was determined. The forward rate constant, k_1 , for the adsorption was $10^{4.26}$ L mol⁻¹ and the backward rate constant, k_{-1} , for the desorption was $10^{1.11}$ s⁻¹. The desorption rate constant was three orders of magnitudes smaller than the adsorption rate constant. The intrinsic equilibrium constant obtained from the kinetic measurements ($\log_{10} K_{\text{kinetic}} = 3.15$) agreed relatively well with that calculated from the static studies ($\log_{10} K_{\text{static}} = 3.51$). The suggested reaction scheme for the B-pyrophyllite interaction is:



or



IN ASSESSING B CONCENTRATION in the soil solution, the physico-chemical characteristics of the soil must be taken into consideration because of the interaction between B and soil constituents. This is particularly important since there is a relatively small range between levels of soil solution B that cause deficiency and toxicity symptoms in plants. Existing criteria, however, make no reference to the properties of the clay minerals; therefore, the interaction of B with surfaces of clay particles dispersed in aqueous solution is a subject of continuing investigation in the agricultural and environmental sciences.

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Boron can be effectively leached from soil although the rate of removal is much slower for B than for Cl or SO₄ salts (Bingham et al., 1972). Different clay and Al and Fe oxide minerals are very different in their adsorption capacities for B (Goldberg and Glaubig, 1985, 1988; Keren and Bingham, 1985). Adsorption of B by soil constituents has been considered as a possible mechanism controlling B removal from the soil solution. Couch and Grim (1968) concluded that the surface area of the clay is one of the important factors controlling B fixation by illite and proposed a two-step mechanism for B retention. The first step was a rapid chemical adsorption of tetrahedral B(OH)₄⁻ on the clay and the second step was a much slower diffusion of B into the tetrahedral sheet of the crystal.

An area in B-clay interactions that has not received enough attention is the kinetics and mechanisms of B adsorption and desorption. Griffin and Burau (1974) studied the kinetics of B desorption from soils and observed two pseudo-first-order reactions and a very slow reaction. They speculated that the fast reactions were due to desorption from hydroxy-Fe, -Mg, and -Al materials in the clay size fraction, whereas the slowest reaction rate was due to diffusion of B from the interior of clay minerals to the solution phase.

Boron is adsorbed mainly on the edge surfaces of the 2:1 clay minerals (Keren and Bingham, 1985; Keren and Sparks, 1994; Keren and Talpaz, 1984). Since the negative electrical field (e.g., emanating from the particle face of montmorillonite) extends to the edge surface region (Secor and Radke, 1985), it influences edges, making them less accessible to approaching borate anions. To avoid the complexity associated with the negative electrical field of the planar surfaces, pyrophyllite was selected for this study. Pyrophyllite, in contrast to montmorillonite and illite, shows little deviation from the ideal formula for 2:1 clay minerals. The dioctahedral structure of pyrophyllite consists of essentially neutral tetrahedral-octahedral-tetrahedral layers. The lack of layer charge provides a means of assessing the magnitude and the reactivity of the edge charge of phyllosilicates in B adsorption and desorption reactions.

To obtain information about the elementary processes involved in the adsorption-desorption of borate by phyllosilicates, a pressure-jump relaxation study was con-

ducted with pyrophyllite suspensions in aqueous media. The application of relaxation methods to the investigation of rapid adsorption-desorption processes in aqueous suspensions has proven quite successful. For example, the kinetics and mechanisms of the molybdate, sulfate, selenate, and selenite adsorption-desorption on goethite was investigated by Zhang and Sparks (1989, 1990,a,b). The objectives of this study were to elucidate the dynamic aspects of the adsorption-desorption of borate on pyrophyllite surfaces and to test the suitability of the competitive adsorption model (Keren et al., 1981) to describe borate 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 in this study. The clay shows little deviation from the ideal 2:1 clay mineral 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. Since the pyrophyllite mineral flakes are still rather thick and large, however, they are resistant to grinding forces. Therefore, a ball mill was used to increase the fraction of the $<2\text{-}\mu\text{m}$ clay particles. Five hundred grams of dry clay were ground for 30 h in a hollow rotating zirconia cylinder (Norton, Aleron, OH) filled with hard balls of wear-resistant media.

The $<2\text{-}\mu\text{m}$ clay fraction was obtained by allowing larger particles to settle out of a suspension and then decanting the suspension. The clay was saturated with Na by washing three times with 0.5 M 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 $<10\text{ }\mu\text{S cm}^{-1}$. A stock suspension at a concentration of 0.13 g mL^{-1} was used for the B adsorption experiments.

The specific surface area of the freeze-dried clay was $43.7 \pm 0.3\text{ m}^2\text{ g}^{-1}$ as determined by N_2 adsorption and use of the BET equation.

Boron Adsorption Equilibrium Study

Boron adsorption by pyrophyllite was studied in suspension by shaking 0.74 g of clay (on a 383 K oven-dry basis) in 50-mL polypropylene centrifuge tubes containing 20 mL of B solution (as boric acid) at an ionic strength (I) of 0.01 (NaNO_3), a pH of 9, and a temperature of $298 \pm 0.5\text{ K}$.

A pH of 9.0 was selected for the adsorption reaction study because (i) the negative borate ion concentration in solution is relatively high ($\approx 37\%$ of the total B) at this pH and most of the adsorbed B is assumed to be in the borate form (Keren et al., 1981); and (ii) the net surface charge of the edges of the pyrophyllite is negative (the point of zero charge for this clay is 4.2, data not shown). Suspension pH was adjusted with NaOH prior to B additions and adjustments were repeated until there was no pH change during 16 h of shaking.

After pH adjustments, appropriate volumes of 9.25 mmol L^{-1} B solution (92.5 mmol L^{-1} for the highest B concentration) were added to produce initial B concentrations of 0 to 8.88 mmol L^{-1} . An appropriate volume of 0.1 M NaNO_3 solution was added to obtain a final ionic strength of 0.01, pH was adjusted to 9.0, and final solution volume brought to 20 mL. Samples were shaken for $\approx 16\text{ h}$. Preliminary studies indicated that adsorption equilibrium was established in $<2\text{ h}$ after the addition of the B to the pyrophyllite suspensions. Following equilibration, the suspensions were centrifuged and the super-

natant was filtered using a $0.2\text{-}\mu\text{m}$ 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).

Boron Adsorption-Desorption Kinetics Study

The pressure-jump instrument used (DIA-LOG Co., Dusseldorf, Germany) is similar in design to that described by Knoche (1975, 1986). The overall unit consists of (i) a system for pressure induction, which includes a pressure autoclave with a thermostat and sample and reference electrode cells, and (ii) a conductivity detection system, which includes a wheatstone bridge, digitizer, oscilloscope, and PC-compatible microcomputer containing an interactive computer program that evaluates relaxation curves.

A pressure-jump experiment involved filling the sample electrode cell with a clay suspension equilibrated with B. The clay suspensions were the same ones that had been prepared for the equilibrium study. A small sample from the suspension was filtered through a prewashed $0.2\text{-}\mu\text{m}$ filter (Gelman GA-8, Gelman Sciences, Ann Arbor, MI) and the supernatant collected in the reference electrode cell. Each cell has a capacity of approximately 1 mL. The cells were then covered with a thin Teflon membrane, tightly sealed, and inserted into the pressure autoclave so that the membrane cover made up part of the inner wall of the pressure chamber. The pressure chamber was sealed with a thin strip of brass foil ($\approx 0.08\text{ mm}$ thick) specifically milled to rupture when the pressure within the chamber reaches $\approx 12\text{ MPa}$. The pressure within the autoclave was increased by forcing water into the chamber with a mechanical hand pump. The hydrostatic pressure was transmitted to the sample suspension and reference solution via the thin Teflon membrane. Thus, the perturbation was achieved by raising the pressure to $\approx 12\text{ MPa}$, at which time the brass foil burst and the pressure immediately dropped ($\approx 60\text{ }\mu\text{s}$) to ambient conditions. The sample equilibrated at 12 MPa was out of equilibrium and relaxed to the new equilibrium at ambient pressure. The change in the electrical conductivity of the suspension was used to observe the reestablishment of the equilibrium after the pressure jump.

Models and Computations

Boron Adsorption Equilibrium Study

Adsorbed B was calculated as the difference between the amount added and that found in the equilibrium solution. A B adsorption model (Keren et al., 1981) was used to estimate adsorbed B assuming that $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$ and OH^- compete for the same adsorption sites. The adsorption coefficients K_{HB} , K_{B^-} , and K_{OH^-} for the three species $\text{B}(\text{OH})_3$, $\text{B}(\text{OH})_4^-$, 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:

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

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

Ionic strength corrections were made using single-ion or single-molecule activity coefficients. The equation employed to compute the activity coefficients, γ , is:

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

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 $= 1/2 \sum C_i Z_i^2$, C_i is the concentration of species i , Z_i is the valence of the species, and B° is a parameter dependent on the value of the ionic strength. In this study, $B^\circ = 0.3 AZ^2$ ($I \leq 0.5 M$). For the neutral species $B(OH)_3$ at all values of I , $B^\circ = 0.1 L mol^{-1}$ (Helgeson, 1969). Because $Z = 0$, the first term in Eq. [1] 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 is 5.9×10^{-10} at 298 K. Other hydrolysis species ($K_{h2} = 5.0 \times 10^{-13}$ and $K_{h3} = 5.0 \times 10^{-14}$) were ignored (Ingri et al., 1957). As a result, the B species in solution can be calculated using the following equations:

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

and

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

where $[BT]$ is the total B concentration in solution ($mol L^{-1}$), and

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

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 that were used were appropriate to the ionic strengths investigated (Owen and King, 1943). The negative adsorption of borate ions by the clay was neglected.

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

The amount of adsorbed $B(OH)_4^-$ (Q_{B^-}) was calculated using

$$Q_{B^-} = \frac{TK_B(B^-)}{1 + K_{HB}(HB) + K_B(B^-) + K_{OH}(OH)} \quad [7]$$

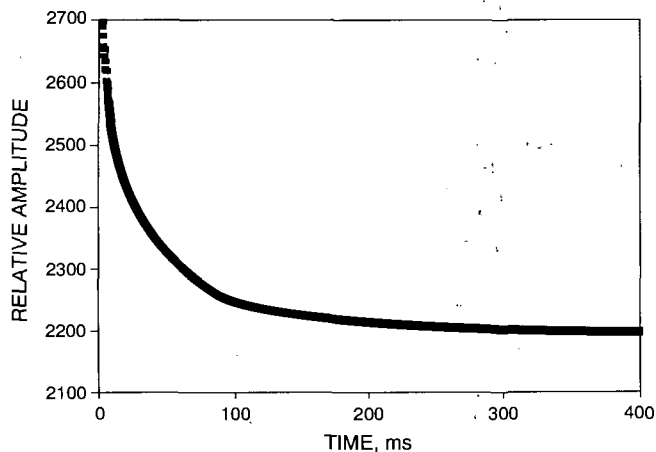


Fig. 1. Typical relaxation curve in the aqueous B-pyrophyllite suspension observed by the pressure-jump technique with electrical conductivity detection.

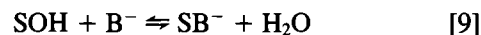
Boron Adsorption-Desorption Kinetics Study

Pressure-jump relaxation kinetics is based on the fact that chemical equilibria are dependent on pressure. This dependence is given by

$$\left(\frac{\partial \ln K}{\partial P}\right)T = \frac{-\Delta V^\circ}{RT} \quad [8]$$

where K is the chemical equilibrium constant, P is the pressure, ΔV° is the standard molar volume change of the reaction, R is the gas constant, and T is the absolute temperature.

One can describe the adsorption-desorption of $B(OH)_4^-$ on surface hydroxyl groups, SOH, using the general mass action equation



where SOH is a surface hydroxyl group, SB^- is adsorbed borate, and B^- was defined previously.

The relationship between the reciprocal relaxation time for the reaction in Eq. [9] and the concentration of reacting species is based on the rate law expression written for any point in time during the chemical relaxation:

$$\frac{d[SB^-]}{dt} = k_1[SOH][B^-] - k_{-1}[SB^-] \quad [10]$$

where $[SB^-]$ and $[SOH]$ are the concentration of adsorption sites occupied and unoccupied by borate ions, respectively, and $[B^-]$ is the borate concentration in the equilibrium solution.

The concentration of the species can be expressed in terms of the equilibrium concentrations, $[SOH]_{eq}$, $[B^-]_{eq}$, and $[SB^-]_{eq}$, and their displacement x from equilibrium. Conservation of mass dictates that the concentrations of SOH and B^- are shifted from equilibrium by the same amount, and SB^- is also displaced by the same amount but with opposite sign. Thus, Eq. [10] can be rewritten in terms of the displacement x as:

$$dx/dt = -k_1([SOH]_{eq} + x)([B^-]_{eq} + x) + k_{-1}([SB^-]_{eq} - x) \quad [11]$$

Rearranging Eq. [11] yields:

$$dx/dt = -[k_1([SOH]_{eq} + [B^-]_{eq}) + k_{-1}]x - k_1x^2, \quad [12]$$

since (Bernasconi, 1976):

$$-d[SB^-]_{eq}/dt = k_1[SOH]_{eq}[B^-]_{eq} - k_{-1}[SB^-]_{eq} = 0 \quad [13]$$

Equation [12] can be further simplified assuming that the perturbation from equilibrium is small ($x \ll [SB^-]_{eq}$). In this case, the term k_1x^2 is negligibly small compared with the other terms and Eq. [12] becomes

$$dx/dt = -[k_1([SOH]_{eq} + [B^-]_{eq}) + k_{-1}]x \quad [14]$$

Eq. [14] can be written as

$$dx/dt = -\tau^{-1}x \quad [15]$$

where

$$\tau^{-1} = k_1([SOH]_{eq} + [B^-]_{eq}) + k_{-1} \quad [16]$$

An interactive software program provided by the manufacturer enables the computer to display the relaxation curve (Fig. 1, for example) and allows direct evaluation and, hence, calculation of the relaxation time, τ . The relaxation time is the time it takes the relaxation to reach 1/e of the initial relative amplitude. To ensure that the chemical relaxations were indeed

due to borate adsorption-desorption on pyrophyllite, an experiment was conducted on samples prepared under the same conditions with the exception that B was omitted. No relaxations were observed. Likewise, no relaxation was observed when only the clay was excluded.

As is evident from Eq. [16], k_1 and k_{-1} can be evaluated from the concentration dependence of τ , τ^{-1} being linearly related to $[\text{SOH}]_{\text{eq}} + [\text{B}^-]_{\text{eq}}$.

The $[\text{SOH}]_{\text{eq}}$ was calculated using Eq. [7] and

$$[\text{SOH}]_{\text{eq}} = (T_{\text{B-}} - Q_{\text{B-}})/V \quad [17]$$

where $T_{\text{B-}}$ is the adsorption capacity of pyrophyllite for $\text{B}(\text{OH})_4^-$ ions (mol g^{-1}), $Q_{\text{B-}}$ is the amount of adsorbed $\text{B}(\text{OH})_4^-$ (mol g^{-1}) and V is the volume of solution per unit mass of clay (L g^{-1}).

RESULTS AND DISCUSSION

The B adsorption isotherm for pyrophyllite at pH 9 and an ionic strength of 0.01 is presented in Fig. 2. The symbols represent experimental results, whereas the solid line was calculated according to Eq. [1], using the adsorption coefficient values $1.65 \times 10^{-5} \text{ mol g}^{-1}$, 124 L mol^{-1} , 30461 L mol^{-1} and $838006 \text{ L mol}^{-1}$ for T , K_{HB} , $K_{\text{B-}}$ and K_{OH} , respectively (Keren and Sparks, 1994). The agreement between the calculated line and the experimental results indicates that this equation does describe B adsorption on pyrophyllite in suspension for a wide concentration range. This agreement was shown previously for montmorillonite, illite, kaolinite, and soils (Keren and Bingham, 1985) and for hydroxy-Al (Keren and Gast, 1983).

The amount of adsorbed B on pyrophyllite at pH 9 is significantly higher than that found for montmorillonite (Keren and O'Connor, 1982). For example, the amount of adsorbed B on pyrophyllite in equilibrium with solution B at an activity of 1 mmol L^{-1} is about $9 \mu\text{mol g}^{-1}$ for an ionic strength of 0.01 (Fig. 2), whereas the amount adsorbed by montmorillonite at the same pH is $2 \mu\text{mol g}^{-1}$ for an ionic strength of 0.02. These results indicate that the affinity of pyrophyllite for B is much greater than that of montmorillonite under similar conditions. The results in Fig. 2 also show that total adsorbed B is much higher than that found for Ca-montmorillonite

(Keren and Mezuman, 1981) at pH 9 for any given B concentration in the equilibrium solution.

The greater capacity of pyrophyllite to adsorb B occurs even though the specific surface area of pyrophyllite ($43.7 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$) is much lower than for montmorillonite ($800 \text{ m}^2 \text{ g}^{-1}$). Assuming that the cross-sectional area of the boric acid 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 of $T = 1.65 \times 10^{-5} \text{ mol L}^{-1}$ is $1.99 \text{ m}^2 \text{ g}^{-1}$. The coverage is smaller than the total surface area of the clay ($43.7 \pm 0.3 \text{ m}^2 \text{ g}^{-1}$). The edge surface area of plate particles with a size of $2 \times 10^{-6} \text{ m}$ is $8.7 \text{ m}^2 \text{ g}^{-1}$, assuming that the particles have a square planar surface shape with a thickness of $0.25 \times 10^{-6} \text{ m}$ (Fig. 3). Thus, the coverage of B becomes more significant only if the edge surface is considered.

The most reactive surface functional group on the edge surfaces 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) located in the octahedral sheets and Si(IV) located in the tetrahedral sheets. The schematic atomic arrangement on the edge surface of a unit cell of a 2:1 clay mineral (e.g., pyrophyllite) is given in Fig. 4. At the edge of the octahedral sheet, the Al(III)·H₂O 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 Si⁴⁺ cations. Contrary to the situation for montmorillonite, the dioctahedral structure of pyrophyllite consists of essentially neutral tetrahedral-octahedral-tetrahedral layers held together by van der Waals forces. Therefore, no potential barrier originating from the planar surfaces exists for borate ions approaching the adsorption sites on the edge surfaces. Thus, the B adsorption reaction on the edge surfaces of the clay and their intrinsic adsorption-desorption coefficients can be evaluated.

As predicted from the adsorption model (Eq. [7]), the affinity of clays for $\text{B}(\text{OH})_4^-$ is much higher than that for $\text{B}(\text{OH})_3$. Under these assumptions, the $\text{B}(\text{OH})_4^-$ frac-

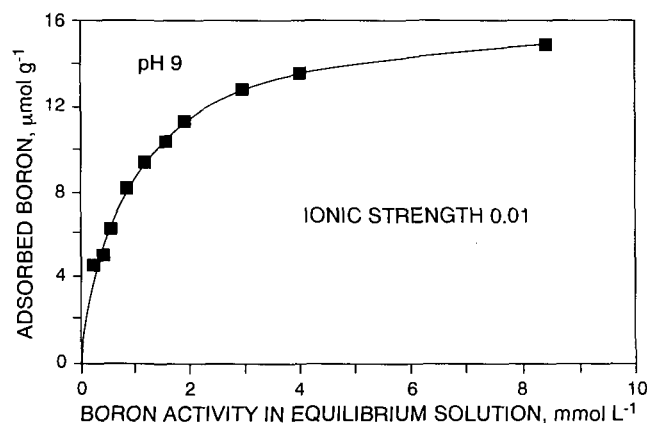


Fig. 2. Boron adsorption isotherm for pyrophyllite as a function of the total B activity in solution at equilibrium.

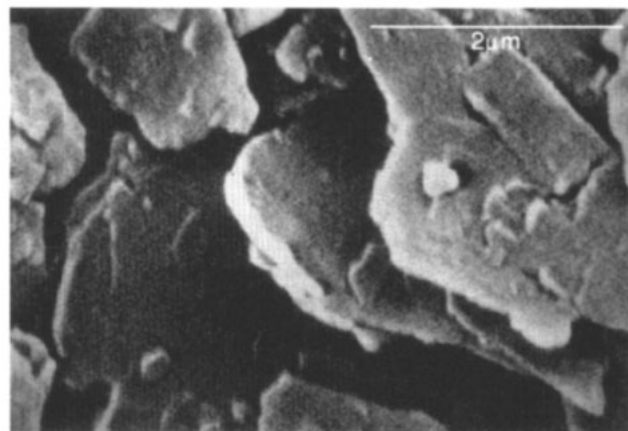


Fig. 3. Scanning electron micrograph of pyrophyllite showing particles size $< 2 \times 10^{-6} \text{ m}$.

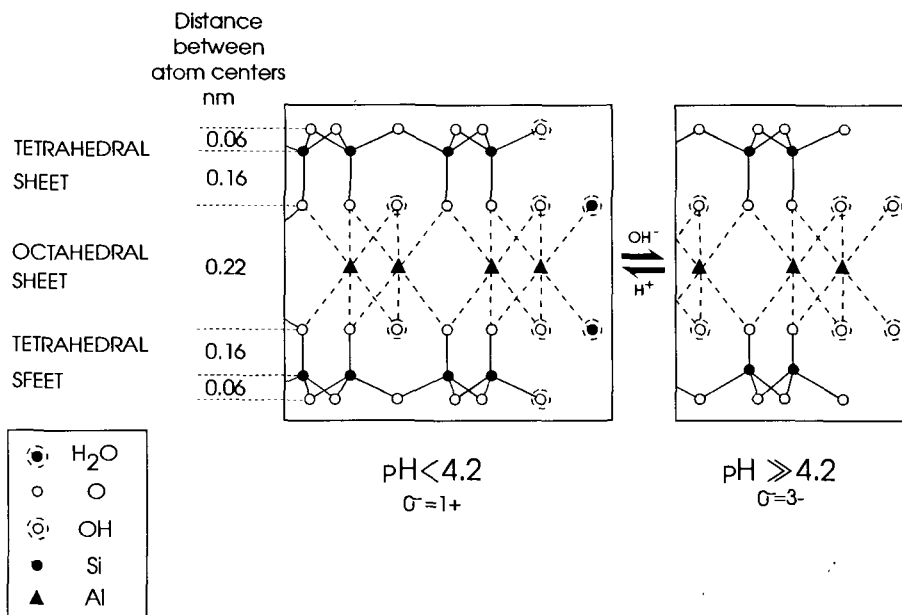


Fig. 4. Atomic arrangement in the unit cell of pyrophyllite (schematic).

tion of the total adsorbed B on pyrophyllite is about 0.99, at pH 9 and ionic strength of 0.01 for all levels of adsorbed B despite the fact that only 37% of the B in solution is in the $B(OH)_4^-$ form. This high fraction is probably due to the absence of repulsive forces associated with the negative electrical field since the permanent electrical charge of the clay is negligible. The fraction of adsorption sites occupied by B^- as a function of B activity in the equilibrium solution for pyrophyllite at an ionic strength of 0.01 was calculated using Eq. [7], and the values are presented in Fig. 5. The calculated fraction of occupied adsorption sites by B^- increases sharply at the low range of B activities in the equilibrium solution, reaching a value of 80% at a B activity in the equilibrium solution of about 3 mmol L^{-1} . These results may indicate that borate ions are the major B species

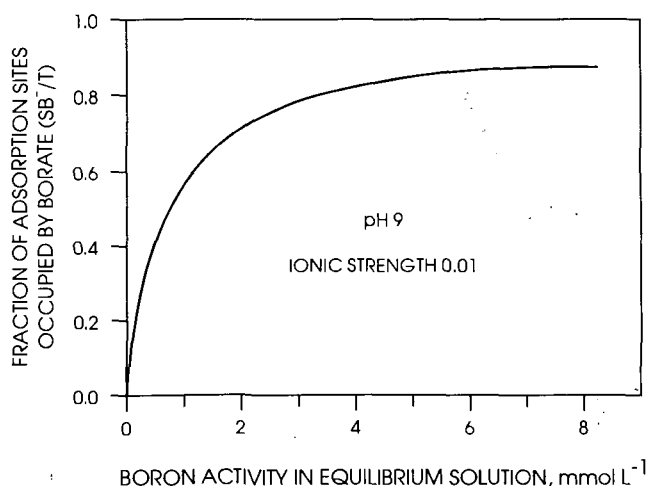
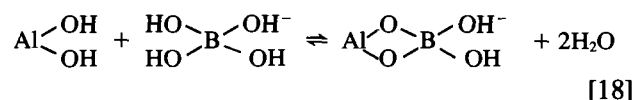


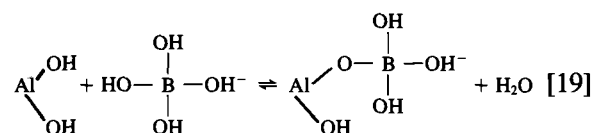
Fig. 5. Fraction of adsorption sites occupied by borate ions as a function of B activity in equilibrium solution at pH 9 and ionic strength of 0.01.

interacting with pyrophyllite adsorption sites at pH 9 and ionic strength of 0.01.

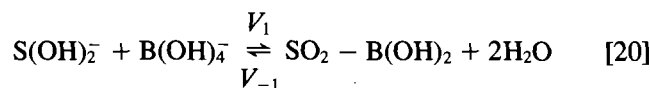
Since the adsorption of boric acid by pyrophyllite under these conditions is negligible, only the borate anions were considered. Based on previous results (Keren and Bingham, 1985) the adsorption of B on the edge surfaces, associated with Al for example, can be described by the following mechanisms:



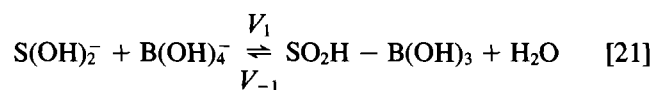
or



If these mechanisms are valid, the total reaction scheme can be written as



or



where $S(OH)_2^-$ is the concentration of the free adsorption sites on the clay in suspension (mol L^{-1}), $B(OH)_4^-$ is the activity of borate ions in solution, the first term on the right-hand side of the equations is the concentration of the adsorption sites occupied by borate ions (mol L^{-1}), and V_1 and V_{-1} are the reaction rates for borate adsorption and desorption, respectively. Such specific

Table 1. Intrinsic equilibrium constants for $B(OH)_4^-$ adsorption on pyrophyllite as determined from equilibrium measurements at various B concentrations in clay suspension.

Equilibrium B concentration in solution	Equilibrium constant (K_{static})†
mmol L ⁻¹	L mol ⁻¹
0.363	3266
0.807	3267
1.800	3253
2.855	3286
3.935	3212
6.122	3192
8.323	3238

† Average value $K_{static} = 3245 \pm 31$ L mol⁻¹.

adsorption reactions occur, irrespective of the sign of the net surface charge (Keren and Bingham, 1985).

At equilibrium, when $V_1 = V_{-1}$ the equilibrium constant, K_{static} of the reactions in Eq. [20] or [21] can be expressed as

$$K_{static} = \frac{(SB^-)}{(SOH)(B^-)} \quad [22]$$

The activity coefficient ratio of $\gamma_{SB^-}/\gamma_{SOH}$ was assumed to be one (Davis et al., 1978).

The activities of (SB^-) and (SOH) were calculated using Eq. [7], based on the B adsorption constants and suspension volume, for all B concentrations given in Fig. 2. The equilibrium constant for the borate adsorption-desorption reaction expressed in Eq. [22] was $\log_{10} K_{static} = 3.51$ (Table 1). This value indicates that the strength of the borate-adsorption site complex on the clay edge surfaces may be considered as a moderately strong complex (Pankow, 1991).

The pressure-jump detection system that was employed is only able to monitor reactions that involve a conductivity change. Thus, the generated relaxation curves were solely due to the $B(OH)_4^-$ ions reacting with the pyrophyllite surfaces. As predicted by the adsorption model (Eq. [7]), the fraction of total adsorbed B as adsorbed $B(OH)_4^-$ is about 0.99 for pyrophyllite at pH 9. Under such conditions, it is valid to consider only the $B(OH)_4^-$ ions in the adsorption-desorption reactions. For each sample, 9 to 18 relaxation curves were generated. The relaxation time for the B^- -pyrophyllite reaction ranged from 15 to 70 ms for a total B concentration range of 0.55 to 8.8 mmol L⁻¹. A second relaxation was observed at approximately 900 ms for all experiments. This relaxation could not be associated with borate adsorption on pyrophyllite since it did not vary with increasing borate concentration. It is most likely that this relaxation was due to the hydration of CO₂, which has been found to have a relaxation time of about 1 s (Knoche, 1986).

The plot of τ^{-1} as a function of the concentration term $[SOH]_{eq} + [B^-]_{eq}$ (Eq. [16]) was linear with $R^2 = 0.94$ (Fig. 6). This suggests that the mechanism represented by Eq. [20] or [21] is plausible. The forward rate constant, k_1 (or the adsorption rate constant), was $10^{4.26}$ L mol⁻¹ s⁻¹ while the backward rate constant, k_{-1} (or the desorption rate constant), was $10^{1.11}$ s⁻¹.

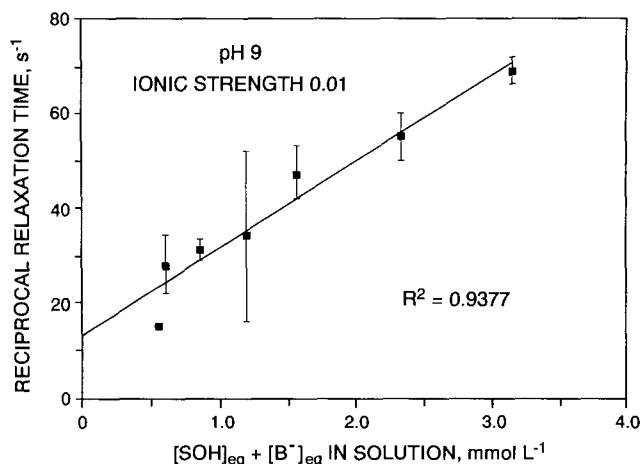


Fig. 6. Reciprocal relaxation time as a function of the equilibrium concentration sum of unoccupied adsorption sites (for B) and borate ions in solution at pH 9 and ionic strength of 0.01.

The desorption rate constant was three orders of magnitude smaller than the adsorption rate constant. This slower rate of desorption is consistent with the well-known observation that B removal from sodic soils is much lower compared with Cl⁻ (Bingham et al., 1972). The much smaller desorption rate constant may indicate that a high-energy bond is associated with B adsorption by the clay and may suggest that the ligand exchange mechanism described in Eq. [18] or [19] is plausible. The distance between two adjacent hydroxyls in the octahedral sheet of the edge surface, for example, is 0.22 nm (Fig. 4). This distance fits well with the distance between two adjacent hydroxyls in the boric acid molecule (0.23 nm) and in the borate ion (0.19 nm) (Muetterties, 1967).

Using the rate constants for the forward and backward reactions, it is possible to calculate the equilibrium reaction constant based on kinetic measurements for Eq. [20] or [21] employing the relationship

$$K_{kinetic} = k_1/k_{-1} \quad [23]$$

The equilibrium constant for the borate adsorption-desorption reaction expressed in Eq. [20] or [21] calculated from the kinetic study is $\log_{10} K_{kinetic} = 3.15$.

The intrinsic equilibrium constant ($K_{kinetic}$) obtained from the kinetic measurements agreed relatively well with those calculated from the static studies (Table 1). This agreement further indicates that the proposed mechanism presented in Eq. [20] or [21] was correct.

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