Boron Adsorption and Silicon Release by the Clay Minerals Kaolinite, Montmorillonite, and Illite[1]

Sabine Goldberg and R. A. Glaubig[2]

ABSTRACT

Boron adsorption behavior on the clay minerals kaolinite, montmorillonite, and illite was investigated. Adsorption increased at low pH, exhibited a peak in the pH range 8 to 10, and decreased at high pH. It was assumed that B adsorbs by means of a ligand exchange mechanism with aluminol groups at the edges of the clay particles. The constant capacitance model was able to describe B adsorption on kaolinites over the entire pH range studied (3–12), using only one adjustable parameter: the boron surface complexation constant. The model was able to fit B adsorption on montmorillonites and illites using three adjustable parameters; however, the chemical significance of some of the surface complexation constants is uncertain. Silicon release to solution increased in the order: kaolinite ≪ illite < montmorillonite and exhibited a minimum in the pH range 8 to 9. Boron adsorption on kaolinites was reduced only slightly in the presence of added silicate despite considerable silicate adsorption. Boron adsorption on montmorillonites was unaffected by the presence of added silicate. It is suggested that B and silicate adsorb on specific sites and that little anion competition occurs.

Additional Index Words: anion adsorption, ligand exchange, silicate adsorption, surface chemistry, constant capacitance model.

BORON IS AN ESSENTIAL ELEMENT in plant nutrition being required in low concentrations for sufficiency and producing toxicity symptoms and marked yield decrement at higher concentrations. Since the concentration range between deficiency and toxicity for B is narrow, reactions which may govern its availability are of interest.

Analyses of B sorption behavior in whole soils have indicated that clay minerals play an important role. Elrashidi and O'Connor (1982) found that clay content was significantly correlated with adsorbed B of ten soils from New Mexico. Wild and Mazaheri (1979) studied two soils from the Reading Univ. farms in Britain and found that the loamy clay soil adsorbed more than four times as much B on a per gram basis as the sandy loam soil.

The adsorption behavior of B on various layer silicate clay minerals has been investigated previously (Scharrer et al., 1956; Harder, 1961; Hingston, 1964; Fleet, 1965; Sims and Bingham, 1967; Porrenga, 1967; Couch and Grim, 1968; Singh, 1971; Jasmund and Lindner, 1973; Keren et al., 1981; Keren and Mezuman, 1981). Several researchers have studied and compared the B adsorption characteristics of illite, montmorillonite, and kaolinite under conditions of short (<24 h) contact time (Scharrer et al., 1956; Hingston, 1964; Keren and Mezuman, 1981). The three minerals exhibited increasing B adsorption with increasing pH. Adsorption peaks occurred at pH 8.5 to 10 and were followed by a gradual decline. In all three studies the order of boron adsorption on a per gram basis was: kaolinite < montmorillonite < illite. In contrast, Sims and Bingham (1967) found B adsorption on kaolinite to be much greater than on montmorillonite. They attributed this order of reactivity to the fact that the montmorillonite sample had been washed free of Fe and Al impurities while the kaolinite sample had not. Hingston (1964) was able to describe his adsorption isotherms at dilute concentrations using the Langmuir equation. Singh (1971) represented his B adsorption data on kaolinite and montmorillonite by both the Langmuir and the Freundlich equations. He found, however, that the fit of the Freundlich equation was closer to the experimental data over a wider range of solution B concentration.

Experiments investigating B sorption behavior under conditions of long term contact (28–180 d) have also been conducted (Harder, 1961; Fleet, 1965; Couch and Grim, 1968; Jasmund and Lindner, 1973). In these studies the order of magnitude for boron adsorption was the same as in the short term studies: kaolinite < montmorillonite < illite. Harder (1961) found that, unlike the adsorption on kaolinite and montmorillonite, B adsorption on a clay sample containing both illite and chlorite was not readily reversible by washing with distilled water. In order to explain this behavior, he suggested that B had become incorporated into the illite and chlorite lattices by substituting for tetrahedral Si and Al ions. Fleet (1965) suggested that B is initially chemisorbed onto illite particles and subsequently incorporated into the tetrahedral sites. Couch and Grim (1968) concurred with this mechanism, suggesting that B adsorbs as $B(OH)_4^-$ on the particle edges

and migrates by intracrystalline diffusion into tetra-hedral sites where it replaces structural Si and Al. Jas-mund and Lindner (1973) found that B adsorption on kaolinite and montmorillonite particles, as well as on illite particles increased even after 180 d of reaction time. For this reason, they suggested that B uptake by all three minerals was governed by the same adsorp-tion mechanism. Jasmund and Lindner (1973) syn-thesized B containing kaolinite, montmorillonite, and illite materials and studied the coordination of B in these mineral lattices. Using photoelectron spectros-copy (ESCA) and infrared spectroscopy, they found evidence for 4-fold coordination of B in the synthetic illite and montmorillonite. Since no such evidence was found for the B in the synthetic kaolinite, Jasmund and Lindner (1973) concluded that B substitutes for tetrahedral Al and not for tetrahedral Si.

One of the limitations of the Langmuir and Freun-dlich isotherms is their inability to describe adsorp-tion behavior over changing conditions of solution pH. A phenomenological equation was developed by Keren et al. (1981) which includes the pH variable in de-scribing adsorption. Keren and Mezuman (1981) used the phenomenological equation to fit B adsorption on kaolinite, montmorillonite, and illite at several pH values using the same set of constants: K_{HB}, K_B, K_{OH}, and the total B adsorption capacity factor, T. Keren et al. (1981) were not able to show any physical sig-nificance of the absolute values of the constants K_{HB}, K_B, and K_{OH}. Keren and Mezuman (1981) calculated B adsorption per unit of total surface area. They found that on this basis, as well as on a per gram basis, ad-sorption on illite much exceeded adsorption on mont-morillonite, despite the greater surface area of the lat-ter. From these results, Keren and Talpaz (1984) concluded that B adsorption occurred on the broken edges of clay minerals. These authors also suggested that B is adsorbed via a ligand exchange mechanism with surface hydroxyl groups on the clay edges.

Ligand exchange with hydroxyl groups has been in-voked as the mechanism of B adsorption on Al and Fe oxide minerals (Sims and Bingham, 1968; McPhail et al., 1972). Boron adsorption on oxide minerals has been observed to produce shifts in the point of zero charge (PZC) of Al and Fe oxide minerals (Fricke and Leonhardt, 1950; Alwitt, 1972; Beyrouty et al., 1984; Blesa et al., 1984). This behavior indicates specific ad-sorption of B on these materials. The constant capac-itance model (Stumm et al., 1970; Schindler and Gamsjäger, 1972; Stumm et al., 1976; Stumm et al., 1980) uses a ligand exchange mechanism to describe adsorption and includes the pH variable. It is a chem-ical model in that it defines surface species and chem-ical reactions explicitly. The constant capacitance model has been used successfully to describe B ad-sorption on four Al and three Fe oxide minerals under changing conditions of solution pH (Goldberg and Glaubig, 1985).

Silicate adsorption has been observed to produce shifts in the PZC of the Fe oxide mineral goethite (Hingston et al., 1972; Sigg and Stumm, 1981), again indicating specific adsorption. The clay minerals mus-covite (McKeague and Cline, 1963), kaolinite, and montmorillonite (Beckwith and Reeve, 1964) have

been observed to release silicate to aqueous solution. Beckwith and Reeve (1964) found that silicate release from both kaolinite and montmorillonite was lowest in the intermediate pH range. However, below pH 7.5 much greater amounts of silicate were released from montmorillonite than from kaolinite, indicating a much lower stability of the former. By studying sili-cate release as a function of time, Beckwith and Reeve (1964) observed that initial silicate release from mont-morillonite was rapid and was followed by a more gradual increase in solution concentration. They sug-gested that this initial release rate was too high to re-sult from dissolution of the mineral. Beckwith and Reeve (1964) therefore postulated that the initial sil-icate concentrations had been present in sorbed form on montmorillonite in its natural environment. Beck-with and Reeve (1963) showed that kaolinite and montmorillonite have the ability to adsorb silicate from solution at pH values >7. The authors felt, how-ever, that the adsorption range might not have been delineated due to considerable release of silicate.

McPhail et al. (1972) found that amorphous Al and Fe oxides which had previously adsorbed silicate ex-hibited a decrease in their B adsorption capacity. This decrease was progressive with the amount of silicate adsorbed by the materials. McPhail et al. (1972) sug-gested that both anions adsorb via a ligand exchange mechanism with the same set of hydroxyl groups. Prior adsorption of silicate had thus inactivated many of the B adsorbing sites. Bingham and Page (1971) stud-ied the effect of silicate pretreatment on the B adsorp-tion properties of an allophanic soil. They found that adsorption of silicate even up to four times the amount of B adsorption affected the total B adsorption only slightly. From this result, Bingham and Page (1971) concluded that B adsorption sites were essentially spe-cific and unaffected by the presence of silicate.

The purpose of the present study is to test the ability of the constant capacitance model to describe B ad-sorption on the clay minerals kaolinite, montmoril-lonite, and illite. Adsorption was studied under chang-ing conditions of solution pH. Release of silicate to solution was also measured in these systems so that the effect of this ion on the B adsorption reaction could be considered.

MATERIALS AND METHODS

Boron adsorption behavior was studied on three types of clay minerals. Samples of two kaolinites (KGa-1, well crys-tallized kaolinite; and KGa-2, poorly crystallized kaolinite), three montmorillonites (SWy-1, Na-montmorillonite, STx-1, Ca-montmorillonite, and SAz-1, Ca-montmorillonite "Cheto"), and one illite (IMt-1, illite) were obtained from the Clay Minerals Society's Source Clays Repository. One kaolinite (Georgia kaolinite) and two illites (no. 35, Fithian illite, and no. 36, Morris illite) had been obtained from Ward's Natural Science Establishment. The kaolinite and montmorillonite minerals were used without any pretreat-ment. The illite materials were ground with a mortar and pestle to pass a 50-μm sieve. Particle size distributions of all materials were determined using the hydrometer method de-scribed by Day (1965) and are listed in Table 1. Specific surface areas of all clay minerals were determined using N_2 adsorption. Multi-point BET adsorption isotherms were de-termined using a Cahn electrobalance model RG. The sam-

Table 1. Textures of the clay minerals studied.

Solid	Sand, >50 μm	Silt, 2-50 μm	Clay, <2 μm
		%	
KGa-1 kaolinite	4	51	45
KGa-2 kaolinite	4	36	60
Georgia kaolinite	17	43	40
SAz-1 montmorillonite	4	69	27
STx-1 montmorillonite	7	13	80
SWy-1 montmorillonite	1	8	91
IMt-1 illite	0†	70	30
Fithian illite	2†	68	30
Morris illite	2†	53	45

† The illites were sieved to <50 μm. Values given were obtained using the hydrometer method (Day, 1965).

Table 2. Numerical values of nonadjustable parameters used in the model.

Solid	Specific surface area, 10^4 m² kg⁻¹	Maximum adsorption density, mol m⁻³	Suspension density, kg m⁻³
KGa-1 kaolinite	0.81	0.0971	200
KGa-2 kaolinite	2.05	0.137	100
Georgia kaolinite	0.69	0.113	200
SAz-1 montmorillonite	1.86	0.140	40
STx-1 montmorillonite	5.36	0.103	40
SWy-1 montmorillonite	1.32	0.0823	30
IMt-1 illite	1.18	0.0814	50
Fithian illite	2.37	0.116	50
Morris illite	2.15	0.0879	50

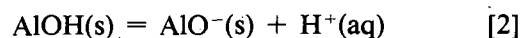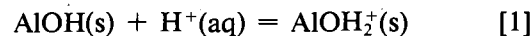ples were outgassed at 100°C. Surface area values are listed in Table 2.

Boron adsorption experiments were carried out in batch systems using the identical procedure as was used by Goldberg and Glaubig (1985). Sample sizes of clay material used in our study are given in Table 2. The decantates were analyzed for pH, filtered, and analyzed for B and silicate concentration. Both anions were determined using a Technicon Auto Analyzer II. Boron was determined with the Azomethine-H method described by Bingham (1982). Silicate was determined with the heteropoly blue method (American Public Health Association, 1976) using ascorbic acid as the reducing agent (Technicon Auto Analyzer II Industrial Method No. 105-71W/B). To investigate the effect of the silicate anion, B adsorption on the kaolinites and the montmorillonites was studied in the presence of 15 g m⁻³ added silica under identical conditions as above. As illites are known to contain high concentrations of native B (Harder, 1961; Fleet, 1965; Couch and Grim, 1968; Jasmund and Lindner, 1973), B and silicate release from these materials into 0.1 M NaCl solution was studied. Conditions for this experiment were identical to the B adsorption studies with the exception that no B was added to the equilibrating solution. The Morris illite, no. 36, was found to release the largest amount of B to solution. Leaching of this material with 0.1 M NaCl solution was therefore continued for eight successive extractions in an effort to determine the location of the native B. A Na₂CO₃ fusion analysis was carried out in triplicate on the unleached starting material and the leached residue using the method described by Lim and Jackson (1982). Insoluble silica was analyzed by volatilization with hydrofluoric acid as described by Chapman and Pratt (1961). Boron adsorption was studied on the leached residue under identical conditions as had been used for the untreated material.

The constant capacitance model (Stumm et al., 1980) was used to describe the B adsorption behavior of the clay minerals. The computer program FITEQL (Westall, 1982) was used to fit intrinsic surface equilibrium constants to the experimental data using the model assumptions and procedure given in Goldberg and Sposito (1984). To apply the constant capacitance model to B adsorption on clay minerals, it is necessary to assume that the reactive functional groups undergo protonation-dissociation and ligand exchange reactions. Of the two types of edge surface hydroxyl groups found on clay mineral surfaces—the silanol group, SiOH, and the aluminol group, AlOH—only the latter undergoes both the protonation and the dissociation reaction (Sposito, 1984). Therefore, it will be assumed that B and silicate adsorb via a ligand exchange mechanism with the reactive surface aluminol groups located at the edges of the clay mineral particles.

Similar to the application of the model to B adsorption on Al and Fe oxide minerals (Goldberg and Glaubig, 1985), the following surface reactions are defined

$$AlOH(s) + H^+(aq) = AlOH_2^+(s) \qquad [1]$$

$$AlOH(s) = AlO^-(s) + H^+(aq) \qquad [2]$$

$$AlOH(s) + H_3BO_3(aq) = AlH_2BO_3(s) + H_2O \quad [3]$$

where AlOH(s) represents 1 mol of reactive aluminols bound to an Al^{3+} ion at the clay mineral edge. We also considered the species $AlH_3BO_3^+(s)$ and $AlHBO_3^-(s)$ in our optimization but found these species to play a minor role and therefore chose to neglect them. The following intrinsic conditional equilibrium constants describe the surface reactions

$$K_+(int) = \frac{[AlOH_2^+]}{[AlOH][H^+]} \exp (F\Psi/RT) \qquad [4]$$

$$K_-(int) = \frac{[AlO^-][H^+]}{[AlOH]} \exp (-F\Psi/RT) \qquad [5]$$

$$K_B(int) = \frac{[AlH_2BO_3]}{[AlOH][H_3BO_3]} \qquad [6]$$

where F is the Faraday constant (C mol⁻¹), Ψ is the surface potential (V), R is the molar gas constant, T is the absolute temperature and square brackets represent concentrations (mol m⁻³). Mass balance for the surface aluminol group, AlOH, and charge balance require the following equations, respectively

$$[AlOH]_T = [AlOH] + [AlOH_2^+] + [AlO^-]$$
$$+ [AlH_2BO_3] \qquad [7]$$

$$\sigma = [AlOH_2^+] - [AlO^-] \qquad [8]$$

where the net surface charge, σ, also has units of mol m⁻³. The chemical equilibrium problem formulated above is solved by FITEQL (Westall, 1982) using a system of simultaneous equations and a nonlinear least squares optimization routine.

Values of the intrinsic protonation-dissociation constants $K_+(int)$ and $K_-(int)$ can be calculated from batch titration data as described in Goldberg and Sposito (1984). In this study the numerical values used for these constants, log $K_+(int) = 7.38$ and log $K_-(int) = -9.09$, were the averages of a literature compilation of experimental values for Al oxide minerals (see Table 1, Goldberg and Sposito, 1984). These two constants were also fit simultaneously with the B surface complexation constant $K_B(int)$ using FITEQL in identical fashion as in the oxide mineral study (Goldberg and Glaubig, 1985). The value of the capacitance parameter was fixed at C = 1.06 F m⁻². The model is very insensitive to this empirical parameter. Table 2 lists values of experimental model parameters.

RESULTS AND DISCUSSION

Boron adsorption as a function of pH is shown in Fig. 1 for three kaolinite minerals. The shapes of the
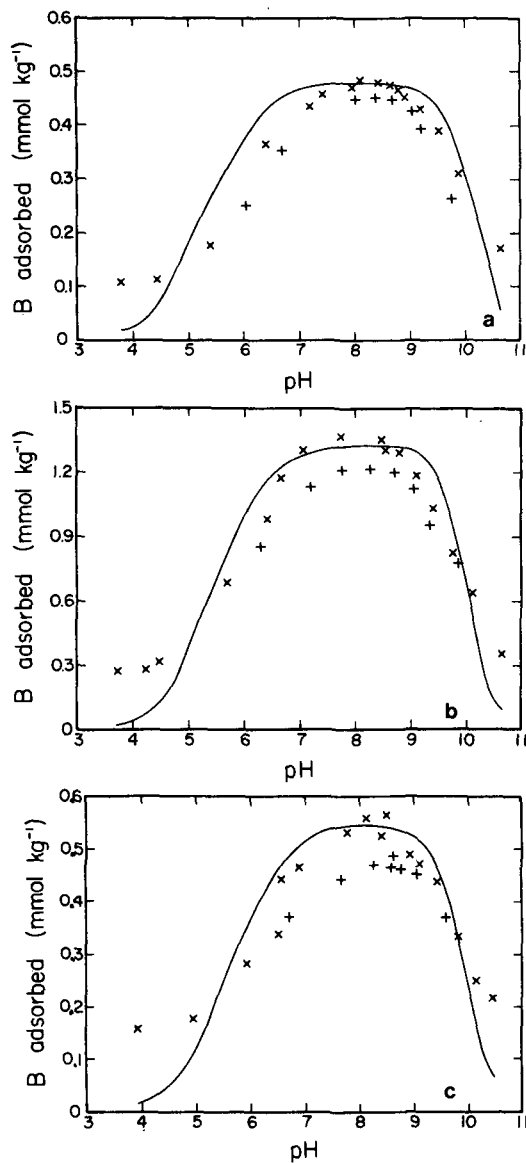
Fig. 1. Boron adsorption on kaolinites: (a) KGa-1, well crystallized kaolinite, (b) KGa-2, poorly crystallized kaolinite, and (c) Georgia kaolinite. Crosses represent experimental adsorption data without added silica. Model results for these data are represented by a solid line. Plusses represent experimental adsorption data in the presence of added Si.
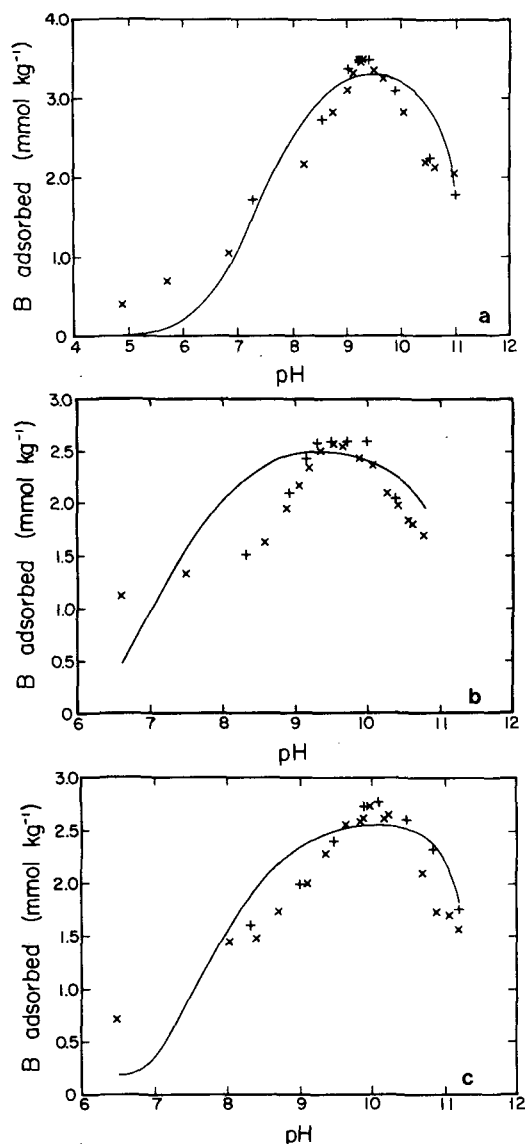

Fig. 2. Boron adsorption on montmorillonites: (a) SAz-1, Ca-montmorillonite, (b) STx-1, Ca-montmorillonite, and (c) SWy-1, Na-montmorillonite. Crosses represent experimental data. Model results are represented by a solid line. Plusses represent experimental adsorption data in the presence of added Si.

adsorption curves for the three kaolinites are very similar, showing adsorption peaks in the pH range 8 to 9. Boron adsorption is highest for the poorly crystallized KGa-2 kaolinite. This behavior agrees with the observations of Porrenga (1967) that B adsorption was higher on layer silicates of reduced crystallinity. Figure 2 shows B adsorption as a function of pH for two Ca- and one Na-montmorillonite. The shapes of these adsorption curves are somewhat different from those for the kaolinite minerals. Adsorption peaks occur in the pH range 9 to 10 and exhibit a more pointed shape and a more rapid rise and decline. Boron adsorption on three illite minerals as a function of pH is shown in Fig. 3. The shapes of these adsorption curves are less pointed than those for the montmorillonite minerals. Adsorption peaks occur near pH 9.

Contrary to the observations of previous researchers (Hingston, 1964; Keren and Mezuman, 1981), the order of reactivity found in the present study was: kaolinite < illite < montmorillonite. This discrepancy may have occurred because the present studies were carried out on whole clay samples and not on the clay fraction as in the studies cited. Overall the illite samples contained a greater proportion of coarser size particles (see Table 1), which would contribute to their lower reactivity toward B. This dependence on particle size has been previously observed by Keren and Talpaz (1984) for B adsorption on montmorillonite.

Reproducibility of the kaolinite and montmorillonite adsorption maxima was evaluated. Adsorption maxima were defined as the data point of highest B adsorption. Average maximum adsorption with its corresponding standard deviation (SD) in mmol kg⁻¹
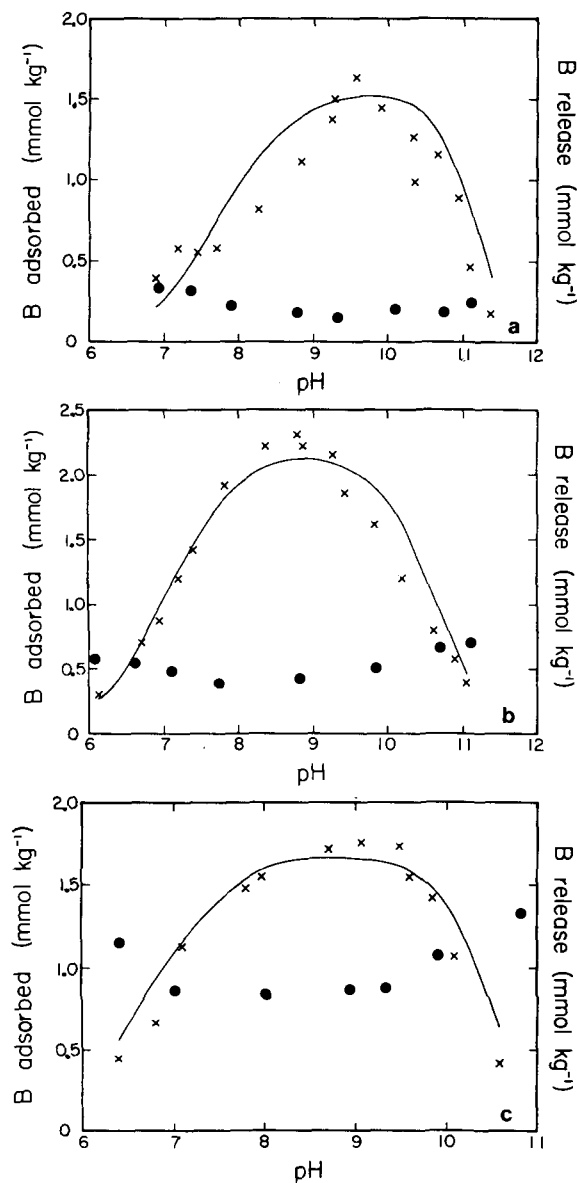
Fig. 3. Boron adsorption on illites: (a) IMt-1 illite, (b) Fithian illite, and (c) Morris illite. Crosses represent experimental adsorption data. Model results for these data are represented by a solid line. Circles represent boron release to solution in systems without added B.

Table 3. Surface complexation constants obtained from FITEQL.

Solid	Log K_+ (int)	Log K_- (int)	LogK_B (int)	Log K_B (int)†
Kaolinites				
KGa-1	7.30	−10.38	5.05	5.38
KGa-2	6.84	−10.29	4.69	5.20
Georgia	7.15	−10.74	4.62	5.03
Averages	7.10 ± 0.23	−10.47 ± 0.24	4.79 ± 0.23	5.20 ± 0.18
Montmorillonites				
SAz-1	9.87	−10.73	5.68	5.68
STx-1	9.54	−11.57	5.61	7.07
SWy-1	12.45	−9.08	7.82	7.63
Averages	10.62 ± 1.59	−10.46 ± 1.27	6.37 ± 1.26	6.79 ± 1.00
Illites				
IMt-1	10.77	−10.08	6.25	7.10
Fithian	8.65	−11.05	4.87	4.52
Morris	8.49	−10.16	5.04	6.64
Averages	9.30 ± 1.27	−10.43 ± 0.54	5.39 ± 0.75	6.09 ± 1.38

† Log K_B (int) was optimized while holding log K_+ (int) and log K_- (int) constant. All intrinsic surface complexation constants were obtained using concentrations in mol L^{-1}. All confidence limits were at the 95% level of significance.

(see the literature compilation in Table 1 of Goldberg and Sposito, 1984). We emphasize that in this case log K_B(int) is the only parameter optimized by the FI-TEQL program. The numerical values of all other nonexperimental parameters remained fixed at the identical values used in previous modeling studies of B adsorption on Al and Fe oxide minerals (Goldberg and Glaubig, 1985).

The constant capacitance model is well able to describe B adsorption on kaolinites, fitting a smooth curve through the experimental data (Fig. 1). In all three cases, the closer fit was obtained by optimizing only the B surface complexation constant and was graphed in Fig. 1. This behavior is identical to that found for Al and Fe oxide minerals (Goldberg and Glaubig, 1985). Average values for log K_+(int), log K_-(int), and log K_B(int) obtained by FITEQL for kaolinite minerals are not statistically different at the 95% level of confidence from those obtained using FI-TEQL for Al oxide minerals by Goldberg and Glaubig (1985). Average values for log K_B(int) obtained by the two methods are not statistically different at the 95% level of confidence (see columns 4 and 5 of Table 3).

The ability of the constant capacitance model to describe B adsorption on illites is not quite as good as for kaolinites and it is even worse for montmorillonite minerals (Fig. 2 and 3). For both types of minerals, the model fits shown in the figures were obtained by optimizing all three surface constants simultaneously. Optimization of solely log K_B(int) gave an extremely poor fit. Values of log K_+(int) are larger than the corresponding absolute values of log K_-(int) for one montmorillonite and one illite mineral. These values imply that the surface functional group undergoes the dissociation reaction at a lower pH value than the protonation reaction. This behavior is of course chemically impossible. For the one illite sample, chemical significance can be restored by considering the variability in log K_+(int) and log K_-(int). Thus when the SD of log K_+(int) and log K_-(int) are included, the question of whether the constants for IMt-1 illite are chemically reasonable or not cannot be answered with

was: 0.483 ± 0.0033 for KGa-1 kaolinite, 1.35 ± 0.026 for KGa-2 kaolinite, 0.59 ± 0.036 for Georgia kaolinite, 3.61 ± 0.16 for SAz-1 montmorillonite, 2.61 ± 0.065 for STx-1 montmorillonite, and 2.82 ± 0.11 for SWy-1 montmorillonite. Adsorption on the illites increased on a per gram basis with decreasing solid suspension density, indicating that B saturation had not been attained. For this reason, reproducibility on the illite replicates was not tested.

Table 3 lists common logarithms for the surface complexation constants obtained from the application of FITEQL to the experimental data. The first three columns of constants—log K_+(int), log K_-(int), and log K_B(int)—were obtained by optimizing all three constants simultaneously. The last column of constants in Table 3 lists values of log K_B(int) obtained by using the values log K_+(int) = 7.38 and log K_-(int) = −9.09

certainty. For the Na-montmorillonite mineral, the magnitude of the discrepancies between the constants is so large that even after including the SD of log K_+(int) and log K_-(int) chemical significance remains lacking. Average values for log K_-(int) and log K_B(int) for both illites and montmorillonites are not statistically different at the 95% level of confidence from those obtained using FITEQL for Al oxide minerals by Goldberg and Glaubig (1985). The same holds true for log K_+(int) for illites. For montmorillonites however, log K_+(int) is statistically different at the 95% level of confidence from that for Al oxide minerals. Average log K_B(int) values obtained by the two methods are not statistically different at the 95% level of confidence (see columns 4 and 5 of Table 3) for either mineral. Investigations of additional illite and montmorillonite minerals are needed to establish the chemical significance of the surface complexation constants obtained by the model. For the present, all optimizations producing a value of log K_+(int) larger than the absolute value of log K_-(int) must be considered curve fitting procedures.

In an effort to describe the differences in model fit and parameter significance, we measured the amount of Si released to solution in the B adsorption experiments. Figure 4 shows Si release as a function of pH for all three clay minerals. The release curves all exhibit roughly parabolic behavior and a minimum in the pH range 8 to 9. Silicon release from the kaolinites (Fig. 4a) is very low, while release from the 2:1 clay minerals is substantial (Figs. 4b and 4c). Release is highest from the montmorillonite samples where it exhibits the sharpest minimum. In the montmorillonite system, solution concentrations of Si are high at pH values below 9. A certain similarity between the B adsorption maxima and the Si release minima can be noted, especially in the pointed character of both for the montmorillonite materials. We therefore considered that the presence of large amounts of Si in solution might be depressing B adsorption.

Boron adsorption on the kaolinites and the montmorillonites was studied using equilibrating solutions containing B and Si in an approximately molar ratio of 2:1. With the exception of the addition of silicon, the experimental conditions remained the same as before. The effect of the presence of Si on B adsorption on the kaolinites was slight (see Fig. 1). However, over the entire pH range studied and for all three kaolinites, the amount of B adsorption in the presence of Si was consistently lower than in its absence. Apparently, silicate effectively competes for or blocks a small number of B adsorbing sites. Boron adsorption on the montmorillonites was completely unaffected by the presence of added silicate (see Fig. 2). The amount of Si remaining in solution was measured at the end of the experiments and is shown in Fig. 4. It is evident that only a small fraction of the added Si remained in solution for both types of clay minerals.

It thus appears that silicate was able to adsorb on a set of sites that was unavailable to B. It is surprising that despite the large amount of silicate adsorption, the amount of B adsorption was reduced only slightly or not at all. This result indicates that the majority of the B adsorption is occurring on B specific sites, a
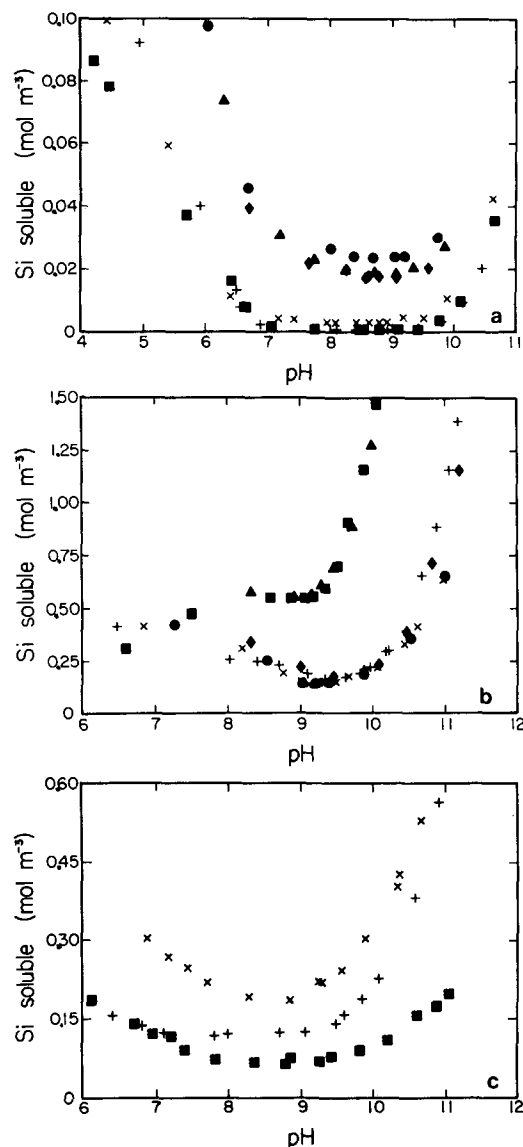

Fig. 4. Soluble silicon for clay minerals: (a) kaolinites, (b) montmorillonites, and (c) illites. Crosses represent KGa-1, well crystallized kaolinite, SAz-1, Ca-montmorillonite, and IMt-1, illite; squares represent KGa-2, poorly crystallized kaolinite, STx-1, Ca-montmorillonite, and Fithian illite; plusses represent Georgia kaolinite, SWy-1, Na-montmorillonite, and Morris illite in the absence of added silicon. Circles represent KGa-1, well crystallized kaolinite and SAz-1, Ca-montmorillonite; triangles represent KGa-2, poorly crystallized kaolinite and STx-1, Ca-montmorillonite; diamonds represent Georgia kaolinite and SWy-1, Na-montmorillonite in the presence of added Si.

phenomenon that had been previously observed by Bingham and Page (1971). Alternatively, it is possible that the amount of solution Si was controlled by the precipitation of kaolinite. If precipitation were occurring, it would not be surprising that B adsorption was reduced only slightly in the presence of Si. We consider kaolinite precipitation to be unlikely after 20 h. Linares and Huertas (1971) have indicated that Al must be present as a six-fold coordinated complex in solution in order for kaolinite precipitation to be possible at room temperature.

Since many illites are natively high in B, we studied the release of B and Si from the illites to equilibrating

solutions not containing B. Silicon release behavior under these conditions was essentially identical to that found during the B adsorption experiments (data not shown). Boron release from the illite minerals was low. However, the curves (Fig. 3) were similar in shape to the Si release curves (Fig. 4c) showing a minimum in the pH range 8 to 9. This behavior suggests that B and Si may be dissolving from the clay lattice. Fusion analysis results of the Morris illite indicate, however, that B is concentrated at the surface of the material. The amount of total B in the leached material (47.7 ± 0.8 mmol kg^{-1}) is significantly (95% confidence) lower than that in the starting material (55.6 ± 1.4 mmol kg^{-1}). Additional evidence for native adsorbed B was provided by the fact that the leached residue adsorbed markedly more B than the starting material (data not shown). However, greater scatter is present in these data and is probably due to the successive leachings.

The B adsorption values were corrected for B release from the illites. However, with this correction the fit of the model to the data was less good. This effect is perhaps due to the scatter present in the B release data. Nevertheless, conclusions regarding significance of the surface complexation constants are unchanged by this correction.

ACKNOWLEDGMENT

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