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BOREON FIXATION BY ILLITES

ELTON L. COUCH* and RALPH E. GRIM
Department of Geology, University of Illinois, Urbana, Illinois

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Abstract—The mechanism of boron uptake by clays, especially illitic clays, and the factors which control such uptake have long been debated issues. In an attempt to answer some of the questions of the controversy, three illites were treated in solutions containing boron. In the study, boron concentration, salinity, temperature, and time were varied independently over rather wide ranges.

For the illites studied, irreversible uptake of boron was increased by increasing boron concentration, salt concentration, temperature, and time of treatment. The amount of boron which was fixed also varied with the type of illite treated. The amount of fixation was controlled primarily by the specific surface area of the clay and also by the crystallinity, K content, and/or amount of mixed-layer material ("frayed-edge" development?), and apparently was independent of the original boron content of the clay.

A two-step mechanism is proposed for boron fixation by illite, consisting of rapid chemical adsorption of the tetrahedral $B(OH)_4^-$ anion at the "frayed-edge" of the illite flake followed by much slower diffusion of boron into the tetrahedral part of the structure.

INTRODUCTION

THE USE of boron as a paleosalinity index has been debated extensively in the literature in the past 3 decades. The mechanism of uptake and location of boron have been the major aspects of the controversy. Some investigators (e.g. Frederickson and Reynolds, 1960; Walker, 1963) have shown that boron tends to be concentrated in the clay mineral illite, probably proxying for tetrahedral silicon and/or aluminum. Evidence for such substitution has also been observed in dissolution studies (e.g. Goldberg and Arrhenius, 1958), and the possibility of a fit of boron in the tetrahedral part of a mica-type structure has been demonstrated by synthesis (Eugster and Wright, 1960; Stubican and Roy, 1962). However, it remains to be established definitely that boron which is extracted from solutions by detrital clays finds its way into the tetrahedral positions of the structure, and if it does, by what mechanism it enters those positions.

The present research has been undertaken to gain a better understanding of the mechanics of boron fixation by illites. It was felt that a significant approach would be to attempt to isolate some of the factors which influence the irreversible uptake (fixation) of boron by clays and to consider their roles independently over rather wide ranges. Analyses of approximately 200 experimental runs form the basis of the present report.

EXPERIMENTAL

Less-than-2-μ fractions (equivalent spherical diameter) of Beavers Bend, Marblehead, and Fithian illites were treated with boron-bearing solutions. These clays represent appreciable variations in physical and chemical composition, as shown in Table 1.

The relative abundance of 1 M and 2 M polymorph was determined from X-ray powder diffraction patterns and was based on comparison of the 3·66 Å (1 M) and 3·00 Å (2 M) peaks. The crystallinity index for the three illites was arbitrarily assigned as the height of the 10 Å peak divided by its width at one-half the peak height, as shown on oriented-aggregate diffraction patterns published by Gaudette *et al.* (1965). Specific surface measurements were made by Dr. Richard Berger of American Cement Company for Professor James L. Eades of the University of Illinois, and their values were furnished by Professor Eades. These measurements were made by the BET method using nitrogen as adsorbate on $-2\,\mu$ fractions from the same stock of clays as used in this study.

Treatment of samples

Boric acid (H_3BO_3), in concentrations from 10^{-4} to 1 M, was used as the source of boron in solution. For comparison with natural systems, it is recalled that average sea water contains about 4·7 ppm boron, which is equivalent to $4{\cdot}3 \times 10^{-4}$ M H_3BO_3. Because $CaCl_2$ is more effective in increasing the borate-ion activity than most other halide salts (Schafer and Sieverts, 1941), it was used extensively as the salinity agent; also NaCl, KCl, and $MgCl_2$ were used in some experiments. Concentrations of salts in solution varied from 0·01 to 3 M. A wide temperature range (25°–215°C) was used with pressures corresponding approximately to the

*Present address: Gulf Research and Development Co., Pittsburgh, Pennsylvania.

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Table 1. Chemical and physical composition of the illites used in the study

		Beavers Bend illite	Marblehead illite	Fithian illite
Interlayer cations (atoms/cell)*	K^+	1·2130	1·3615	1·1411
	Na^+	0·0372	0·0554	0·0935
	Ca^{2+}	0·0263	0·0989	0·1360
	Total	1·2765	1·5158	1·3706
Tetrahedral cations (atoms/cell)*	Si^{4+}	6·6833	7·0724	6·6605
	Al^{3+}	1·3167	0·9276	1·3395
	Total	8·0000	8·0000	8·0000
Octahedral cations (atoms/cell)*	Al^{3+}	2·5586	2·9974	2·4339
	Fe^{3+}	0·8278	0·0789	0·9014
	Fe^{2+}	0·3804	0·1334	0·4330
	Mg^{2+}	0·3607	0·7174	0·3391
	Ti^{4+}	0·0706	0·0995	0·0707
	Total	4·2281	4·0226	4·1781
Per cent mixed layer*		0	5	10–15
Per cent 1 M polymorph		20	40	45
Crystallinity index		48	38	19
Specific surface area (M^2/g)†		12·0	30·5	20·5
ppm original boron		120	520	155

*Gaudette *et al.*, 1965.

†Eades, J. L., 1966, Personal communication, University of Illinois, Urbana.

particular vapor pressures of the solutions. Experimental runs varied from 12 hr to 210 days.

In each experiment run, 1 g of clay was treated in 100 ml of solution. The runs at temperatures below 100°C were carried out in polyethylene bottles in an appropriate oven and the samples were shaken manually each day throughout the experiments. Runs above 100°C were carried out in stainless steel vessels in an autoclave. As these runs varied from 12 to 24 hr, there was no agitation of the suspensions during the treatment.

Following the treatment, the clay samples were isolated from the solutions and washed in distilled water at room temperature until no boron could be detected in the wash water. Thus, only boron which was fairly rigidly fixed was measured. Prior to chemical analysis, the washed clay samples were dried to constant weight at 110°C.

Chemical analyses

The technique used to analyze boron in clay samples was essentially a combination of the fusion-solution method of Berger and Truog (1944) and the carmine colorimetric method of Hatcher and Wilcox (1950). Duplicate and triplicate analyses of selected samples indicate the results are reproducible within about ± 5 per cent of total boron present for untreated samples and about ± 10 per cent when the additional variables of treatment and washing are introduced.

Comparison of X-ray diffraction patterns from oriented aggregates of treated and untreated samples does not indicate any new phases were formed in the treatment procedure.

ROLE OF VARIOUS FACTORS

Boron concentration

Throughout the range of experiments, the data (Table 2) show that boron uptake is enhanced by a higher concentration of boron in solution. The amount of increase in uptake over a given concentration range, however, varies with the salinity of the solution, temperature of the solution, length of time of treatment, and the particular illite. The Beavers Bend samples contained 120 ppm boron before treatment. Therefore, the negative "increases" shown in Table 2 are within the limits of analytical precision and do not indicate actual loss of boron.

Table 2 indicates that treating Beavers Bend illite for 30 days at 60°C in 0·1 M $CaCl_2$ increased the boron uptake from about zero at 0·001 M

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Table 2. Irreversible boron uptake by the clays for various treatment conditions

Clay	Days treated	$CaCl_2$ (M)	Temp. (°C)	ppm B increase after treatment in: 0·001 M H_3BO_3	0·1 M H_3BO_3	1 M H_3BO_3
Beavers Bend	30	0·1	60	−6	30	56
	30	0·1	90	7	38	80
	120	0·1	60	24	43	69
	30	1·0	60	−1	17	70
	120	1·0	60	18	41	80
	30	3·0	60	17	35	98
	120	3·0	60	24	48	135
Fithian	30	1·0	60	5	60	153
Marblehead	30	1·0	60	11	65	118

H_3BO_3 to 56 ppm at 1 M H_3BO_3. Under similar conditions at 90°C, the range was 7–80 ppm.

Salinity

For a given concentration of boric acid, the amount of boron fixed by a clay generally increased with the concentration of the salt in solution. With a certain amount of data scatter, this is clearly shown in Table 2. For example, 30 days of treatment in 1 M H_3BO_3 of Beavers Bend illite led to an increase of 56, 70, and 98 ppm boron with 0·1, 1·0, and 3·0 M $CaCl_2$, respectively. Similar results were attained by Fleet (1965) with increased salinity of artificial sea water.

An explanation of the increased boron uptake with salinity, independent of boron concentration can perhaps be found in the role played by neutral salts in boric acid solutions. It has been demonstrated (e.g. Schafer and Sieverts, 1941) that increased concentration of halide salts in solution with a given boric acid concentration, promotes greater dissociation of H_3BO_3. Thus, salinity might play a role in boron fixation by clays by promoting a larger number of borate ions available for reaction.

Temperature

As the temperature of a boric acid solution rises, the activity of the borate ion increases (Kemp, 1956; Nies and Campbell, 1964). Thus, the uptake of boron is likely also to be a function of temperature. Various experiments were set up to test this hypothesis.

Figure 1 illustrates the role of temperature in irreversible uptake of boron by clays. This family of curves shows boron uptake for Beavers Bend illite as a function of boric acid concentration for different temperatures. Boron uptake was enhanced by increased temperature, and the temperature effect was appreciably greater at higher concentrations of boric acid, as shown by the increased spacing between the curves at the high concentration end. Thus, at 0·001 M H_3BO_3, Beavers Bend illite showed essentially no boron fixed at 60°C for 30 days (analyses show 6 ppm less than the untreated clay which is within the limits of precision) and only 15 ppm boron gained at 215°C for 12 hr. However, at 1 M H_3BO_3, treatment for 30 days at 60°C yielded 55 ppm boron increase, whereas 215°C for 12 hr yielded 180 ppm increase.

Time

More treatment time resulted in additional boron fixation as shown in the data for Beavers Bend illite (Table 2). These data show that increasing the treatment time from 30 to 120 days led to additional

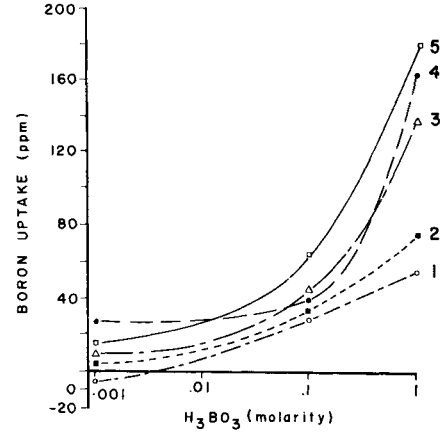


Fig. 1. Boron uptake by Beavers Bend illite for various temperatures and boron concentrations—0·1 M $CaCl_2$. 1. ○—60°C, 30 days; 2. ■—90°C, 30 days; 3. △—185°C, 12 hr; 4. ●—205°C, 12 hr; 5. □—215°C, 12 hr.

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uptake of 7–37 ppm boron. Most similar sets of data show similar relations, and seem to support the generalization that as the treatment time increases, the amount of boron fixed by clays increases. However, following initial rapid uptake, the rate of increase appears to be quite slow, and the effect of additional time is relatively small.

The role of time may be to allow boron to move into the internal structure of the illite following the initial uptake reaction, thus providing additional surface sites.

Character of illite

All the illites did not react the same way to treatment with boron-bearing solutions. For example, the data show that with treatment for 30 days at 60°C in solutions containing 1 M H_3BO_3 and 3 M $CaCl_2$, Beavers Bend illite gained 98 ppm boron; Fithian illite 222 ppm; and Marblehead 243 ppm. Although the data for the Marblehead samples are considerably scattered, the relative uptake by these illites as described here seems to be characteristic of them—i.e., Marblehead tends to fix the greatest amount of boron; Beavers Bend, the least.

Interestingly, the original boron content (Table 1) had little if any effect on the boron uptake by the clays, as Marblehead, with 520 ppm original boron gained over twice as much as Beavers Bend with only 120 ppm original boron. Also, neither crystallinity nor major-element composition (Table 1) placed the principal control on boron uptake by the clays. Instead, the specific surface area of the illite had the strongest effect. Thus, Beavers Bend with the smallest surface area took up the least boron, whereas Marblehead with the greatest surface area took up the most.

The role of specific surface can be even more clearly seen by calculating the boron uptake on a surface area basis. Such calculations produce an interesting change in relative amounts of boron fixed by the three illites. For example, treating the clays for 30 days at 60°C in 1 M H_3BO_3 and 3 M $CaCl_2$ yielded the following data (Table 3).

Table 3 also demonstrates a common observation: the Marblehead data are considerably more erratic than are those of the other clays. This is probably due to its high original boron content (520 ppm as opposed to 120 ppm for Beavers Bend and 155 ppm for Fithian) which made small changes difficult to detect, and its extemely fine-grained nature which made complete recovery following treatment essentially impossible.

The data of Table 3 seem to be typical for the clays. Although the clays differed markedly in the total amount of boron fixed, all three fixed approximately the same amount when put on a surface area basis. Fithian fixed slightly more than the others.

Table 3. Boron uptake as total boron (ppm B) and as boron/unit of specific surface area (ppm B/SSA) for the three illites at different boric acid concentrations – 30 days at 60°C, 3 M $CaCl_2$

		B increase after treatment in:	
	0·001 M H_3BO_3	0·1 M H_3BO_3	1·0 M H_3BO_3
		(as ppm B)	
Beavers Bend	17	35	98
Fithian	35	123	222
Marblehead	35	11	243
		(as ppm B/SSA)	
Beavers Bend	1·4	2·9	8·2
Fithian	1·7	6·0	10·8
Marblehead	1·2	0·4	8·0

The exact position of Marblehead, however, is rather difficult to establish because of the large amount of scatter in its data.

Thus, the specific surface area of the illite appears to be the most important single property controlling irreversible boron uptake. The fact that Fithian shows relatively more boron fixed on a surface-area basis can probably be attributed to three differences (Table 1): poorer crystallinity, lower potassium content, and greater abundance of mixed-layer material. These three differences of the Fithian clay can perhaps be summarized as greater frayed-edge development (Jackson, 1963).

FIXATION MECHANISM

Evidence for adsorption

Several workers (Landergren, 1964; Fleet 1965; Lerman, 1966; Levinson and Ludwick, 1966) have suggested that adsorption is the initial reaction in boron uptake by clays, and the data of the present study are consistent with this conclusion. The rapidity with which the uptake takes place lends support to an adsorption theory. For example, the present data show that a large amount of boron (up to 180 ppm at 215°C) is fixed in 12 hr of treatment, and Harder (1961) has shown that an appreciable amount of uptake (14 ppm at 15°C) takes place in only 1½ hr of treatment. The principal evidence, however, for an adsorption reaction is the fit of the data to the Freundlich adsorption isotherm. This law stated in one of its forms is:

$x/m = ac^b$, or
$\log (x/m) = \log a + b \log c$, where:
x/m = amount of sorption per mass of sorbent,
c = equilibrium concentration of sorbate in solution,
a and b = empirical constants.

Thus, if adsorption is the initial reaction, a

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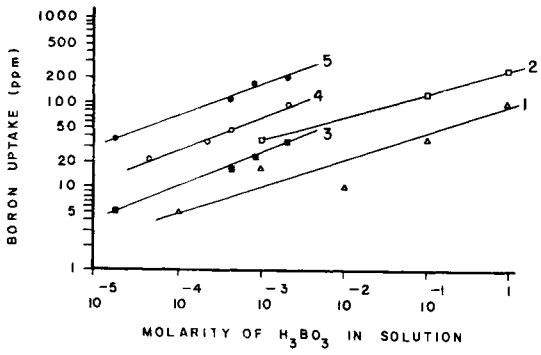


Fig. 2. Boron uptake as function of boric acid concentration for various clays. 1. △—Beavers Bend illite, 3 M $CaCl_2$, 60°C, 30 days; 2. □—Fithian illite, 3 M $CaCl_2$, 60°C, 30 days; 3. □—Montmorillonite no. 19 (Lerman, 1966); 4. ○—illite no. 35 (Fithian illite) (Fleet, 1965); 5. ●—illite no. 36 (Lerman, 1966).

linear relationship should exist between the log of the amount of boron gained per unit mass of clay and that of the equilibrium concentration of boron in solution.

The present experimental studies were not of such design to allow a Freundlich adsorption test. The intent was to measure irreversible boron uptake (fixation) and thus the clay samples were isolated from the solutions following treatment and equilibrated with distilled water. However, the measurements of boron uptake in the experimental studies of Fleet (1965) and Lerman (1966) were presumably made at equilibrium concentrations. As these authors have shown, their data fit the Freundlich law quite well. Figure 2 shows the adsorption isotherms for Fleet's (1965) and Lerman's (1966) data and also summarizes some of the present data (curves 1 and 2). It is interesting that the irreversible boron uptake data of the present study as shown in curves 1 and 2 also conform to a log–log relationship rather well. However, the slopes of those curves are somewhat lower than that of the adsorption isotherms of Fleet and Lerman.

Chemical species adsorbed

According to Kemp (1956), at relatively low concentrations boric acid dissociates and hydrates according to:

$$H_3BO_3 + 2H_2O \rightleftarrows H_3O^+ + B(OH)_4^-$$

Nies and Campbell (1964) noted that in boric acid solutions of less than 0·1 M concentration, the $B(OH)_4^-$ ion is essentially the only ionic species present. However, at higher concentrations, polyborate ions became important and above about 0·5 M, one finds an appreciable population of the various complex ions.

Lerman (1966) proposed that the major chemical species adsorbed by clays from seawater is the $NaB(OH)_4^0$ complex with lesser amounts of $H_3BO_3^0$ and $B(OH)_4^-$ being adsorbed. In the present study, the clays were treated with 0·1 M H_3BO_3 in solution with Ca-, Mg-, Na-, and K-chloride salts in concentrations from 0·01 to 1 M. This set of experiments showed that Na was not needed for the uptake as Ca, Mg, and K in solution led to essentially the same boron uptake as did Na. This observation tends to oppose the view that $NaB(OH)_4^0$ is an important species in the adsorption process.

Furthermore, the present data indicate that conditions which lead to increased borate-ion activity (increased H_3BO_3 concentration, salinity, and temperature) also lead to increased boron uptake by illites. These data suggest that the various borate ions are the chemical species being adsorbed. At low to moderate concentrations, the $B(OH)_4^-$ ion is expected to be the principal species.

Type of adsorption

Adsorption phenomena are classed as physical adsorption, in which the adsorbate is held to the surface of the adsorbent by van der Waals bonds, and chemical adsorption (or chemisorption) in which the bonding is essentially ionic and/or covalent in nature.

The available data as previously described indicate that fixation takes place very soon following initial adsorption and may be simultaneous with it. Furthermore, while the different sets of data shown in Fig. 2 are not directly comparable, the similarity of curves 2 and 4 (Fithian illite) *suggests* that most of the adsorbed boron becomes fixed. The somewhat lower slope of the fixation curve (curve 2) indicates that a larger fraction of the adsorbed boron is fixed at lower concentrations of boric acid than at higher concentrations where increased complexing of borate ions is found (Nies and Campbell, 1964). Thus, it is suggested that early fixation is primarily through chemical bonding of adsorbed borate ions, especially the $B(OH)_4^-$ ions, to the clay mineral surface.

Other aspects of the available data are consistent with chemisorption being the initial reaction leading to fixation (compare, e.g. Barrow, 1961, p. 623). First, uptake is enhanced by increased temperature up to at least 215°C. Second, the illites of this study played major roles in determining the amount of boron gained; data of Harder (1961), Fleet (1965), and Lerman (1966), which show even greater differences among the different clay minerals, also demonstrate that the amount of adsorp-

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tion is characteristic of the adsorbent, as well as of the adsorbate. Third, the maximum uptake observed in the present study was about 1 borate ion/100 Å^2. This value is consistent with a monolayer limit to the adsorption.

Location of adsorbed ions

Van Olphen (1963) has presented convincing arguments that the edge of a clay flake, where Si—O, Al—O, etc. bonds are broken leaving a net positive charge, is the place one expects anions to be adsorbed. Furthermore, he quotes direct evidence, including an electron micrograph, from Thiessen (1942) which shows that negative gold ions are indeed adsorbed at the edges of kaolinite flakes.

This "edge activity" of clays (especially illites) for various reactions has been observed in many studies and a "frayed-edge" or "core-rind" model of illite has developed (Jackson, 1963; Gaudette *et al.*, 1966). Because of increased disorder and greater abundance of broken bonds at these frayed edges, they represent likely places for chemisorption of the type proposed here to take place.

The nature of the $B(OH)_4^-$ ion itself makes an edge-adsorption mechanism attractive. With its negative charge, tetrahedral geometry, and proper size, it would fit nicely as a simple extension of the already-present tetrahedral layer of the clay.

Incorporation of boron into the structure

Fairly rigorous chemical treatment of ancient clays, which probably dissolves some of the outer parts of the clay flakes, does not substantially reduce their boron contents, as shown by several studies (e.g. Frederickson and Reynolds, 1960). Such observations are inconsistent with the notion of borate ions being held rather loosely at the edge of the clay flakes. Thus, after the initial adsorption and "edge fixation" of boron, some process seems operative by which the boron migrates to the interior of the clay mineral structure. At least two processes for such incorporation present themselves as possibilities:

(i) Boron is incorporated in authigenic illites as suggested by Goldberg and Arrhenius (1958). Probably such incorporation occurs in marine and perhaps diagenetic environments. The mechanism could also operate in detrital clays by growing new mineral matter about a detrital core, thus incorporating adsorbed boron.

(ii) After chemisorption of the borate ion at the mineral edge, boron may migrate into the interior of the crystal by intracrystalline diffusion. This possibility will be considered further.

Evidence for diffusion. The present data, as well as that of Harder (1961), indicate that following an initial rapid uptake, boron uptake proceeds very slowly with no evidence of reaching equilibrium after several months of treatment. Such data suggest a fast, initial adsorption followed by diffusion of boron into the structure, so that diffusion quickly becomes the rate-determining step.

This model can be further tested by checking the fit of the data to the "parabolic diffusion law", one of several statements of which is:

$x/m = at^{1/2} + b$, where:
x/m = amount of uptake/unit mass of clay,
t = time,
a and b = empirical constants.

Thus, if the model is correct, a plot of boron uptake versus the square root of time of treatment should be linear. Figure 3 shows some of the present data so plotted.

Since the continued uptake of boron following initial rapid uptake is quite slow, and since the "zero point" is 120 ppm original boron, analytical error makes it very difficult to get meaningful data.

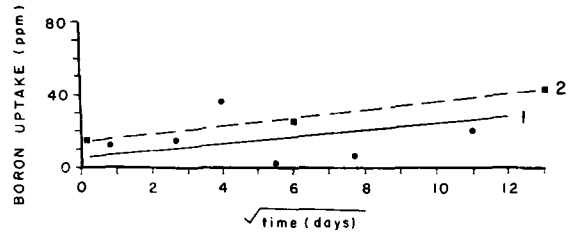


Fig. 3. Boron uptake as a function of time. 1. ● – Beavers Bend illite, 60°C, 2 M $CaCl_2$, 0·001 M H_3BO_3; 2. ■ – Data of Harder (1961) for an illite clay.

Thus, the present data are much too scattered to permit any firm conclusions regarding adherence to a parabolic law. However, Harder (1961) worked with an illitic clay containing only 34 ppm original boron, and his time data, while there are only three points, fit a parabolic law quite well (Fig. 3).

With some reservation, then, it is suggested that fixation of boron by detrital illites is at first by edge fixation of the $B(OH)_4^-$ anion forming an electrostatic bond with the positive edge charge of the clay, followed by intracrystalline diffusion. By such a mechanism, boron atoms can migrate from surface sites into tetrahedral sites of the illite structure replacing silicon and/or aluminum. This suggestion is consistent with the more general suggestions regarding fixation made by Fleet (1965).

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Proposed mechanism for boron fixation by illites

In summary, it is suggested that the sorption-fixation mechanism for boron by detrital illites is a two-step process, beginning with chemical adsorption of the tetrahedral $B(OH)_4^-$ anion at the tetrahedral part of the "frayed edge" of the illite flake. At that location, the anion gains stability (becomes "fixed") through a weak ionic bond with the net positive charge expected there and through epitaxial fit due to the tetrahedral geometry of the units in that layer. The second step is diffusion of boron into the interior of the crystal.

The migration of boron from the chemisorbed $B(OH)_4^-$ anion through the structure is envisioned as taking place through the formation of Frenkel and Schottky crystal defects. The boron concentration gradient for diffusion would be from surface adsorption sites inward. The mechanics of this type of migration of ions is discussed in some detail by Azaroff (1960, Chap. 5 and 12) and Jost (1952, Chap. 2 and 3).

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Résumé—Le mécanisme de fixation du bore par des argiles, et surtout par les argiles illitiques, et les facteurs qui contrôlent une telle fixation sont depuis longtemps un sujet controversé. Pour tâcher d'apporter une résponse à quelques-uns de ces problèmes, on a traité trois illites dans des solutions qui contenaient du bore. L'étude a fait varier indépendamment et substanciellement la concentration du bore, la salinité, la température et le temps.

Pour les illites qui ont fait l'objet de ces tests, on a constaté qu'il était possible d'obtenir une fixation irréversible du bore en augmentant la concentration du bore, la concentration saline, la température et la période de traitement. La quantité de bore fixée dépendait également du type d'illite traitée; cependant elle était avant tout fonction de la surface spécifique de l'argile, ainsi que de la cristallinité, de la teneur en K, et/ou de la quantité de matériaux de couche mixte (développement par "bord éraillé" ?), mais semblait être indépendante de la teneur en bore initiale de l'argile.

On propose un mécanisme à deux temps pour la fixation du bore par l'illite-en premier lieu l'absorb-

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tion chimique rapide de l'anion tétrahédrique $B(OH)_4^-$ au "bord éraillé" du flocon d'illite, suivi en second lieu par la diffusion beaucoup plus lente du bore dans la partie tétrahédrique de la structure.

Kurzreferat – Der Mechanismus der Aufnahme von Bor durch Tone, besonders durch illitische Tone, und die diese Aufnahme bestimmenden Faktoren, stellen schon seit vielen Jahren ein umstrittenes Problem dar. In dem Bestreben eine Antwort zu finden, wurden drei Illite in borhaltigen Lösungen behandelt. In den Versuchen wurden die Borkonzentration, die Salzhaltigkeit, die Temperatur und die Zeit unabhängig voneinander in weiten Bereichen variiert.

In den drei untersuchten Illiten wurde die irreversible Boraufnahme durch Erhöhung der Borkonzentration, der Salzkonzentration, der Temperature und der Behandlungszeit gesteigert. Die aufgenommene Bormenge änderte sich ferner je nach der Art des behandelten Illits. Die Menge wurde in erster Linie durch die spezifische Oberfläche des Tones sowie durch die Kristallinität, den K-Gehalt bzw. die Menge von Mischschichtmaterial ("Fransenrand"-Entwicklung?) bestimmt und war scheinbar unabhängig vom ursprünglichen Borgehalt des Tones.

Es wird ein zweistufiger Mechanismus für die Bindung des Bors an Illit vorgeschalgen, wobei schnelle chemische Adsorption des tetrahedrischen $B(OH)_4^-$ Anions am "Fransenrand" des Illit Blättchens stattfindet, gefolgt von einer viel langsameren Diffusion des Bors in dem tetrahedrischen Teil des Gefüges.

Резюме—Механизм поглощения бора глинами, особенно иллитовыми глинами, а также факторы, которые регулируют такое поглощение, представляют собой уже издавна обсуждаемые проблемы. При попытке ответить на некоторые вопросы, возникшие в ходе прений, три иллита подвергались обработке в растворах, содержащих бор. При этом исследовании, концентрация бора, соленость, температура и время самостоятельно менялись в довольно крупных диапазонах.

Для исследуемых иллитов, необратимое поглощение бора повысилось увеличением концентрации бора и соли, а также времени обработки. Количество фиксируемого бора было тоже разным, в зависимости от подвергаемого обработке иллита. Объем фиксации регулируется преимущественно удельной площадью поверхности глины, а также кристаллличностью, содержанием K, и/или количеством материала смешанного слоя (рост истертой кромки?) и повидимому не зависит от исходного содержания бора в глине.

Предлагается двухступенчатый механизм для фиксации бора иллитом, состоящий из быстрой химической адсорбции четырехгранного $B(OH)_4^-$ аниона на истертой кромке чешуйки иллита с последующей намного более медленной диффузией бора в четырехгранную часть структуры.

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