FIXING CATION INTERACTION WITH BLISTER-LIKE

OSMOTIC SWELLING ON VERMICULITE CLEAVAGES

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For Clays and Clay Minerals

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OSMOTIC SWELLING ON VERMICULITE CLEAVAGES

by

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Abstract--The shrinkage of osmotically swollen natural and artificial blisters on vermiculite cleavages by exchange saturation with fixing cations such as Cs^+ , Rb^+ , NH_4^+ , and K^+ was investigated by replica electron microscopy. Incomplete collapse of either the natural or artificially produced blisters occurred with Cs^+ , Rb^+ , and NH_4^+ saturation, while K^+ saturation completely collapsed the artificially produced blisters but not the natural blisters. The reason for incomplete collapse of the blisters with Cs^+ , Rb^+ and NH_4^+ was the incomplete replacement (trapping in the flakes) of interlayer hydrated cations such as Na^+ , shown by electron probe microanalysis. Much less trapping occurred with K^+ saturation. The amounts of Na^+ entrapment increased with increasing size and decreasing hydration of cations, i.e. $\text{Cs}^+ > \text{Rb}^+ > \text{NH}_4^+ > \text{K}^+$.

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Semiquantitative determination by electron probe microanalysis of Na^+ entrapment in vermiculite flakes near the edge revealed that 1N CsCl entrapped as much as 45.6 percent while 1N KCl entrapped only 7.5 percent. In general, more Na^+ was entrapped by 1N solutions than by dilute solutions. With 0.01N KCl solution, the Na^+ entrapment was only 4.4%. The amount of Na^+ entrapment at the center of the macroflakes was less than at the edge, apparently as a result of more CEC at frayed edges and (or) because of incomplete diffusion of Na^+ to the center. Shrinkage of artificial blisters by K^+ could thus be attributed to its more effective removal of the interlayer hydrated cations, whereas the other fixing cations were less effective. Natural blisters on vermiculite from Libby, MT were not completely collapsed even by K^+ , apparently because the layer charge density was too low in the blister areas.

INTRODUCTION

Electron microscopic studies have shown that blister-like surface configurations occur on micaceous vermiculite (001) cleavage surfaces of a White Mountain, CA soil (Roth et al., 1969). Such configurations result from osmotic swelling of the interlayers and layer lifting into blisters (Sridhar et al., 1970, 1972), a process controlled by the cation charge and hydration properties along with the charge density of layers. Both of these factors control the cation concentration in the electrical double layer, which in turn controls the extent of interlayer swelling in micaceous vermiculite. The blisters form in local regions of lower layer charge density which have resulted from mica weathering. The distribution of blisters appears to be a sensitive measure of the nonuniformity of the charge distribution over (001) cleavage faces (Sridhar et al., 1972). The low charge density areas on the XY plane in vermiculites create wedge zones which are important in cation exchange selectivity (Dolcater et al., 1968).

In X-ray diffraction studies, increasing additions of K^+ to vermiculite resulted in interstratification ($10 + 14 = 12A$) but little edge collapse (Rhoades and Coleman, 1967). Lower concentrations of Cs^+ addition to Na^+ saturated hydrobiotite and vermiculite resulted in largely interstratified Na^+ - and Cs^+ -rich layers with little edge collapse (Sartney, 1967). Edge collapse and Na^+ entrapment (non-exchangeable) occurred, however, with high initial Cs^+ concentrations (Klobe and Gast, 1970).

Electron probe measurements of the Cs^+ sorbed by Transvaal vermiculite showed that the Cs^+ diffused inward from the flake edges, replacing the Ca^{2+} and did not produce interstratified mixtures (Sawhney, 1968). Electron probe scanning profiles over mica flakes showed that diffusion and segregation of different cations occurred at (hk0) edges and cracks over mica flake surfaces (Le Roux et al., 1970).

Micaceous vermiculite is an ubiquitous component of soils generally, because of inheritance from fluvial sediments and accretion from aerosolic dust brought down in rainfall (Jackson et al., 1971). This mineral is extremely important because it has the ability to retain (fix) certain fission products, particularly $^{137}\text{Cs}^+$ (Syers et al., 1972) from fallout and wastes entering natural waters and certain plant nutrients, particularly K^+ and NH_4^+ . Development of a visual model of cation fixation by micaceous vermiculite is essential to a clear understanding of the mechanism involved.

The objectives of the present study were: (a) to investigate by replica electron microscopy the shrinkage induced by fixing cations of osmotically swollen blister-like areas of low charge density on micaceous vermiculite cleavages and (b) to determine with an electron probe the extent of Na^+ entrapment with fixing cations in relation to the shrinkage of the blisters.

MATERIALS AND METHODS

Micaceous vermiculites from Transvaal, South Africa (TSA); Libby, Montana (MT); Grouse Creek, Utah (UT) and a saponitic, vermiculitic phlogopite from Woodson, Kansas (KS) were selected for the study. The first two were included because of their contrast in quantities of natural blisters on the (001) cleavage surfaces. TSA vermiculite has a natural cleavage surface without blisters but blisters can be artificially produced upon Li^+ treatment, whereas MT vermiculite has a smooth natural cleavage surface except for the presence of occasional natural blisters and ridges (Sridhar et al., 1972). Macroflakes (16 mm^2) of the several vermiculites were used for Pt-C replica electron microscopy (REM) and Na^+ entrapment studies.

Preparation of samples for electron microscopy

Natural fresh cleavages of MT and TSA vermiculites (soaked in water for 3 hr, then dried) were Pt-C replicated (Sridhar et al., 1972) and examined for blisters by REM. Blisters were artificially produced on TSA vermiculite surfaces by treatment in 1N LiCl for 24 hr, washing free of salts, and allowing the flakes to swell in distilled water.

Collapse of natural blisters on MT vermiculite and Li^+ induced blisters on TSA vermiculite upon cation exchange saturation with fixing cations such as K^+ , NH_4^+ , Rb^+ and Cs^+ was investigated by treatment of the vermiculites with 1N and 0.01N chloride solutions, each treatment involving several changes of solution with at least a 2-hr contact for each. REM observations were then made of the (001) cleavage surfaces.

Preparation of samples for electron probe analysis

To study the Na^+ entrapment by fixing cations in the TSA vermiculite, macroflakes were freshly cleaved to obtain a smooth surface and the flakes were cut with a razor blade. The vermiculite flakes were treated with several changes of Mg^{2+} to replace the natural interlayer cations, followed by treatment with several changes of Na^+ , and removal of salts by water washing. Treatment of each of several flakes with a given fixing cation was carried out by several changes each for at least 2 hr with 1N and 0.01N chloride solutions.

The treated flakes were then mounted on smooth Epoxy discs by means of a double stick tape, and the flakes were coated with carbon to make them conductive. An ARL-EMX electron probe operating at 15 KV was used for analysis. X-ray scanning photographs of each elemental distribution of various treatments were taken after exposure for a constant time for a given element. The exposure times for Cs^+ and Na^+ were 2 and 7 minutes, respectively.

Semiquantitative estimation of Na entrapment was done by the use of a large size beam (65 μm) to prevent heating of the sample, thus reducing Na^+ migration. Counts of Na^+ were recorded with a constant integrated beam current both at 100 μm from edge and approximately at the center of the flakes.

RESULTS AND DISCUSSION

Interaction of K^+ with blisters

Insert
Fig. 1

Treatment of TSA vermiculite showing high and numerous artificially induced blisters (Fig. 1a) with 1N KCl solution for 24 hr largely collapsed the blisters, leaving only slight remnants (Fig. 1b). Six repeated treatments of the vermiculite flakes with 0.01N KCl solution and one final treatment with 1N KCl solution caused complete collapse of the artificially produced blisters (Fig. 1c), leaving a surface that was smooth except for a few wrinkles. The wrinkles probably result because of a misfit of the collapsed layers whose lateral dimensions increased during the blister formation (Sridhar et al., 1972). Treatment of MT vermiculite with either 1N or 0.01N KCl did not result in complete collapse of the natural blisters (Fig. 1d,e,f), a result reflecting a lower charge density of the blister areas (Sridhar et al., 1972).

Insert
Fig. 2

Schematic cross sections of the original blisters as well as of the blisters collapsed with K^+ represented from electron micrographs are given (Fig. 2). The cross section of a Li^+ induced blister on TSA vermiculite shows a high relief (Fig. 2a). The presence of partially collapsed layers after treatment with 1N KCl indicates that the replacement of interlayer hydrated cations is not complete (Fig. 2b). The cross section of almost completely collapsed blisters on TSA vermiculite (Fig. 2c) after treatment with several changes of 0.01N KCl shows a characteristically wrinkled surface (Fig. 1c).

Osmotic swelling in low charge areas (montmorillonite-like) of the vermiculite results in blisters on the order of a few hundred Å high (Sridhar et al., 1972). Therefore, the blister areas contain far more than the four molecular layers of water (Kittrick, 1966) in 15Å vermiculite interlayers under wet conditions. The blister configurations remain intact even under vacuum during Pt-C replica preparation, probably because the ditrigonal rotation of tetrahedra and stretching of lateral (ab) dimensions of the layers during swelling are not readily reversible. The layers and interlayer cations apparently interlock to stabilize the blister configurations under dehydration in the vacuum, thus making possible a study of the fixing cation interactions. The blisters apparently have collapsed incompletely upon treatment with 1N KCl because of a rapid closure (Sawhney, 1969) of layer edges at this high salt concentration, leading to the incomplete replacement (i.e. trapping) of hydrated cations, as discussed below.

Na⁺ entrapment studies with fixing cations and relation to blister collapse

Insert Table 1 The extent of Na⁺ entrapment in TSA vermiculite by different fixing cations was estimated in a semiquantitative way by electron probe microanalysis (Table 1). Since Li⁺ cannot be analyzed by the electron probe, Na⁺, which is the next most hydrated monovalent cation was used. The control consisted of flakes treated repeatedly with 0.5N MgCl₂ to replace all the interlayer cations other than K⁺ and the small amount of Na⁺ remaining (the same at flake center and edge, Table 1). The flakes repeatedly treated with 0.5N NaCl for exchange saturation with Na⁺, gave 892 counts at 100 μm from edge (Table 1). Subsequent treatment with the various fixing cation solutions showed that Na⁺ entrapment increased with increasing size and decreasing hydration of cation, i.e., Cs⁺ > Rb⁺ > NH₄⁺ > K⁺ (Table 1). In general, more Na⁺ was entrapped by concentrated solutions (1N) than by diluted solutions (0.01N), except with NH₄⁺. Thus, entrapment of hydrated cations is indicated as the reason for the incomplete collapse of the blisters treated with 1N KCl.

Insert Table 2 The finding that Na⁺ entrapment decreased gradually from edge to center (Table 1) can be explained as follows: The presence of more Na⁺ and less K⁺ at the edge and vice versa at the center of the 0.5N NaCl-treated samples (Table 2) suggests the formation of more interlayer openings near the flake margin ("frayed edges") because of various salt treatments. The relatively small increase in K⁺ from edge to center may

reflect slightly more mica impurity at the flake centers. There may also be an incomplete diffusion of Na^+ into the wedge shaped interlayer spaces of the vermiculite-mica transition (Le Roux et al., 1970).

Distribution of entrapped Na^+ and entrapping Cs^+ . To determine

Insert the distribution of entrapped Na^+ in the TSA vermiculite flakes, x-ray
Fig. 3 scanning photographs of the distribution of Na^+ and Cs^+ were taken (Fig. 3). The flake that was repeatedly treated with 0.5N MgCl_2 to replace the interlayer cations revealed the presence of a small amount of uniformly distributed Na^+ both at the edge and center (Fig. 3 a,b), which represents Na^+ in interlayers of the mica impurities (see K^+ content, table 2). Treatment with NaCl to exchange saturate the vermiculite phase resulted in a greater amount of Na^+ at the edge than at the center (Fig. 3c,d). Treatment for 24 hr of the flake with several changes of the fixing cation, Cs^+ , resulted in more entrapment of Na^+ at the edge than the center (Fig. 3e,f), as compared with the controls (Fig. 3a,b). The distribution pattern of Cs^+ in the above flakes in the same spots as those of Na^+ reveals that the amount of Cs^+ present at the edge was greater than at center (Fig. 3g,h). These observations indicate that entrapment of Na^+ occurred throughout the flakes not just in the center.

Reasons for complete collapse of blisters with dilute KCl solution.

The entrapment of Li^+ by 0.01N KCl should have been remarkably lower (comparable to the Na^+ entrapment by 0.01N KCl in Table 1) and this is partly the reason for the complete collapse of blisters (Fig. 1c) with 0.01N KCl solution. The Li^+ was apparently almost completely replaced by K^+ and

the initial collapse of blisters occurred by double layer compression (Norrish, 1954) followed by electrostatic forces of attraction between the vermiculite layers and the cations.

Differences in shrinkage of the natural and artificial blisters with K^+ . The complete collapse of blisters on TSA vermiculite with K^+ saturation (Fig. 1c) indicates that these blisters, though having a sufficiently low layer charge density for swelling, have high enough layer charge for dehydration of the K ions. A high layer charge is essential for dehydration of the cations according to Shainberg and Kemper (1966). In contrast, the lower layer charge of the naturally swollen blisters on MT vermiculite prevented complete blister collapse with K^+ (Fig. 1d,e,f) as discussed above. When the layer charge is too low, the electrostatic forces of cation-layer attraction are ineffective in bringing the swollen layers together and therefore, the natural blisters do not shrink to a great extent. An interpretation of the blister behavior in different vermiculites, as reflecting different layer charge densities in various areas, is consistent with earlier results (Sridhar et al., 1972) and with the usual x-ray diffraction finding that not all of the vermiculite interlayers collapse to $10\text{\AA}$ upon treatment with K^+ at 25C.

Interaction of natural and artificial blisters with Cs^+ , Rb^+ and NH_4^+

Treatment with a less hydrated cation such as Cs^+ did not completely collapse the natural blisters present on the fresh cleavages of either MT or KS vermiculite (Fig. 4a,b), attributable to the entrapment of Li^+ (based on the Na^+ entrapment by different fixing cation solutions, Table 1).

Insert Likewise, the artificially produced blisters on the cleavage surfaces of
Fig. 4 TSA and UT vermiculites were not collapsed (Fig. 4c,d). Nevertheless, the blisters have a lower relief in most Cs^+ treated samples than the original blisters, natural or artificial (produced by Li^+ saturation and washing), indicating partial shrinkage of the circum-blisters wedges by Cs^+ . Treatment with 1N or 0.01N solutions of Rb^+ and NH_4^+ also resulted in only partial collapse of the blisters.

Comparison of fixing cations in blister collapse

Blisters produced artificially by Li^+ saturation and water washing of TSA vermiculite were treated with 0.01N solutions of the fixing cations.

Insert
Fig. 5 Apparently, there is an increase in the collapse of blisters with decreasing size of the cations (Fig. 5a,b,c, and d). K^+ being the smallest, displaced most of the interlayer hydrated Li^+ and collapsed the blisters completely, leaving a smooth surface (Fig. 5d) as explained before.

Insert
Fig. 6 As the diameter of the fixing cations decreased and the hydration increased, a qualitative increase in the shrinkage or collapse of blisters occurred (Fig. 6). On the other hand, as the diameter of the nonfixing cations decreased (hydration increased), the swelling into blisters increased (Sridhar et al, 1972).

CONCLUSIONS

1. Na^+ entrapment in Transvaal vermiculite increased with increasing size and decreasing hydration of the fixing cations used for its replacement, in the order:

Blister shrinkage increased in the opposite order, i.e., shrinkage was greatest with K^+ because Na^+ entrapment was minimal.

2. K^+ completely collapsed the artificial blisters on Transvaal, South Africa vermiculite but failed to collapse the natural blisters on the Libby, MT vermiculite, an effect attributed to too low a layer charge density of the layers forming the blisters in the latter.
3. Concentrated fixing solutions entrapped more Na^+ than did dilute solutions because of greater edge collapse on treatment with concentrated solutions.
4. The primary cause of blister collapse with dilute KCl solution was therefore attributed to the nearly complete removal of the interlayer hydrated cations, whereas other fixing cations or even concentrated KCl solutions failed to do this.
5. Entrapment of hydrated cations was hypothesized to occur in the low layer charge density areas, i.e. in blisters, because the cations are more hydrated (occur in a thicker electrical double layer) in these areas and therefore do not come out rapidly along the collapsed interlayers upon treatment with fixing cations. Thus, the low charge density areas may be important in conserving some of exchangeable cations such as

$^{90}\text{Sr}^{2+}$ in fallout or Ca^{2+} and Mg^{2+} after soil treatment with potassium
or ammonium.

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Table 1. Semiquantitative determination of Na^+ entrapment in vermiculite flakes upon treatment with fixing cations

Table 2. Distribution of Na^+ and K^+ at edge and approximate center of 0. 5N NaCl treated sample

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Fig. 1. Electron micrographs of Pt-C replicas of (001) cleavage of vermiculites after various treatments showing (a) high Li^+ produced blister on Transvaal (TSA) vermiculite cleavage; (b) largely collapsed Li^+ produced blisters (arrows) on TSA vermiculite cleavage upon treatment with 1N KCl for 24 hr; (c) completely collapsed, except for wrinkles (arrow), Li^+ produced blisters on TSA vermiculite cleavage upon treatment with several changes of 0.01N KCl; (d) high natural blisters on Libby, MT vermiculite cleavage; (e) partially collapsed natural blisters (arrows) on MT vermiculite cleavage after 24-hr treatment with 1N KCl; (f) partially collapsed natural blister (arrow) on MT vermiculite cleavage after treatment with several changes of 0.01N KCl. Bar = $1\text{ }\mu\text{m}$.

Fig. 2. Schematic cross sections of Li^+ produced blisters on TSA vermiculite cleavage represented from electron micrographs of Pt-C replicas showing (a) blister with high relief; (b) largely collapsed blister after 1N KCl treatment; (c) virtually completely collapsed (with few wrinkles) blister after 0.01N KCl treatment.

Fig. 3. X-ray scanning (electron probe) photographs of the distribution of entrapped Na^+ and entrapping Cs^+ in a $1600\text{ }\mu\text{m}^2$ area of TSA vermiculite flakes representing (a,b) Na^+ in interlayers of the mica impurities near the edge and center, respectively, after repeated treatments with

0.5N MgCl_2 ; (c,d) Na^+ at the edge and center, respectively, after exchange saturation of the flakes with Na^+ ; (e,f) entrapped Na^+ at the edge and center, respectively, after repeated treatment with 1N CsCl ; and (g,h) entrapping Cs^+ at the edge and center, respectively, in the same spots as (e) and (f).

Fig. 4. Electron micrographs of Pt-C replicas of (001) cleavage of vermiculites with blisters incompletely shrunken by treatment with Cs^+ showing (a) partially collapsed natural blisters (arrows) on the MT vermiculite; (b) largely collapsed natural blisters (arrows) on KS phlogopitic saponitic vermiculite; (c) incompletely collapsed Li^+ swollen blisters on TSA vermiculite; (d) partially shrunken Li^+ produced blisters on UT vermiculite. Bar = 1 μm .

Fig. 5. Electron micrographs of Pt-C replicas of TSA vermiculite cleavage with Li^+ produced blisters after treatment with 0.01N solutions of fixing cations, showing (a) little affected blisters upon treatment with Cs^+ ; (b) incompletely collapsed blister (arrow) and broken off blister (arrow) after treatment with Rb^+ ; (c) largely collapsed blisters (arrows) upon treatment with NH_4^+ ; (d) virtually completely collapsed blisters after treatment with K^+ , with prominent ridges (arrow).

Bar = 1 μm .

Fig. 6. Qualitative comparison of the vermiculite response to cations causing swelling and to fixing cations, in relation to cation diameter.

Table 1. Semiquantitative determination of Na^+ entrapment in vermiculite flakes upon treatment with fixing cations.

Replacing* solution	Na^+ entrapped, near edge (100 μm from edge)		Na^+ entrapped approximately at center	
	counts**	%	counts**	%
Control	48 $\pm$ 2 [#]	0.0	48 $\pm$ 2	0.0
0.5N NaCl	892 $\pm$ 44	100	347 $\pm$ 22	35.4
1N CsCl	433 $\pm$ 15	45.6	185 $\pm$ 9	16.2
0.01N CsCl	262 $\pm$ 18	25.4	115 $\pm$ 4	7.9
1N RbCl	314 $\pm$ 7	31.5	324 $\pm$ 9	32.7
0.01N RbCl	227 $\pm$ 26	21.2	181 $\pm$ 12	15.8
1N NH_4Cl	148 $\pm$ 11	11.8	144 $\pm$ 10	11.4
0.01N NH_4Cl	157 $\pm$ 12	12.9	139 $\pm$ 14	10.8
1N KCl	111 $\pm$ 7	7.5	101 $\pm$ 7	6.3
0.01N KCl	85 $\pm$ 6	4.4	60 $\pm$ 5	1.4

* Control consists of the flakes treated with 0.5N MgCl_2 to replace all interlayer cations so as to determine interlayer Na. All the flakes are then treated with several changes of 0.5N NaCl to saturate the exchange sites. Fixing cation solutions of 1N and 0.01N are used to replace the Na^+ with 0.01N solutions, the samples were first treated 6 times with 0.01N solution and finally once with 1N solution.

[#] $\pm$ standard deviation from mean.

** With a constant integrated beam current.

Table 2. Distribution of Na^+ and K^+ at edge and approximate center of
0.5N NaCl treated sample

Counting region	Na^+		K^+	
	counts*	%	counts*	%
100 μm from edge	892 $\pm$ 44	100	18,162 $\pm$ 1029	90.5
Approximate center	347 $\pm$ 22	48.5	20,058 $\pm$ 190	100

* With a constant integrated beam current.

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Li^+ SWOLLEN BLISTERS (TRANSVAAL VERM)

Fig. 2. Schematic cross sections of Li^+ produced blisters on TSA vermiculite cleavage represented from electron micrographs of Pt-C replicas showing (a) blister with high relief; (b) largely collapsed blister after 1N KCl treatment; (c) virtually completely collapsed (with few wrinkles) blister after 0.01N KCl treatment.

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Fig. 6. Qualitative comparison of the vermiculite response to cations causing swelling and to fixing cations, in relation to cation diameter.