CATION AND LAYER CHARGE EFFECTS ON BLISTER-LIKE OSMOTIC SWELLING OF MICACEOUS VERMICULITE

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ABSTRACT

Osmotic swelling into blister-like configurations was observed by replica electron microscopy (REM) on (001) cleavages of some biotitic and phlogopitic saponitic vermiculites when water was allowed to pass through the 4Å interlayer space and lift low charge areas on the order of 300Å. In those areas, cation dissociation midway between the layers resulted in an osmotic gradient. Some biotitic vermiculites with divalent cation saturation did not show the blistering phenomenon with the natural Ca²⁺ and Mg²⁺ saturation, but did upon Li⁺ saturation and washing, because of greater dissociation of this cation. More numerous blisters were produced by Li⁺ saturation of the biotitic vermiculites with some natural blisters. Exchange saturation with Li⁺ and washing resulted in exfoliation of a phlogopitic saponitic vermiculite and freeing of saponite (18 Å peak) layers from which blisters were previously present. The exfoliated layers were shown to have a lower charge density than the original mica. Na⁺ and Be⁺ saturation resulted in blister formation on Transvaal vermiculite. The density of artificially produced blisters and their relief increased with an increase in hydration of the cation and a decrease in the layer charge density. Therefore, the occurrence of natural blisters on some vermiculites of Mg²⁺ saturation could be explained by the presence of local areas of low charge density, presumably produced by weathering. The swollen configurations on the XY plane create wedge zones at their periphery which may help explain the fixation of radioactive cations such as ¹³Cs⁺ in fallout and wastes. Their occurrence is also important in understanding the mechanism of vermiculite exfoliation and the formation of expansible clay from micas.

INTRODUCTION

The replacement of interlayer K⁺ from biotites and phlogopites by Mg²⁺ produces vermiculite (Walker, 1947; Barshad, 1948; Kulp and Brobst, 1954; Clabaugh and Barnes, 1959; Barnes and Clabaugh, 1961). Biotite and phlogopite weather through vermiculite to minerals of the montmorillonite-saponite (smectite) group (Jackson et al., 1952; Gorbunov and Gradusov, 1954). Such weathering of mica takes place as a result of displacement of K⁺ by large hydrated cations through the process of diffusion (Reed and Scott, 1962). During the transformation in nature, a decrease in layer charge occurs which is essential for production of the interlayer swelling properties of vermiculite, montmorillonite, and saponite. The associated chemical and surface morphological changes of the layers may involve deposition of aluminous (Rich, 1968) or ferruginous coatings (Roth et al., 1968).
Some workers (Walker and Milne, 1950; Norrish, 1954; Norrish and Rausell-Colom, 1963) have reported that, despite a layer charge higher than that of montmorillonite, Li⁺ saturated vermiculite from Kenya exhibited macroscopic swelling similar to that of montmorillonite in many respects. This type of swelling behavior was limited with vermiculites of high layer charge density (Norrish and Rausell-Colom, 1963).

Layer charge decrease and osmotic swelling of interlayers lead to lifting of portions of the 2:1 phyllosilicate layers into blisters, for example, on micaceous vermiculite particles from White Mountain soil (Roth et al., 1969; Sridhar et al., 1970), creating wedge sites (Jackson, 1963) for cation exchange. These crystallographic changes may play an important role in the fixation of radioactive nuclides such as ¹³⁷Cs⁺ in reactor wastes or fallout from nuclear explosions. The colloid chemical processes controlling the lifting of layers into blister-like configurations have not hitherto been clearly established.

The objectives of the present paper are (a) to show that blister-like layer lifting on micaceous vermiculite cleavages from various sources is a function of the charge and hydration properties of the lyotropic cation species used for exchange saturation, and (b) to show that interlayer osmotic swelling occurs in a mosaic of blisters along the XY plane, apparently reflecting a distribution of charge density differences across the micaceous vermiculite crystal layers.

**Experimental**

The (001) cleavages of micaceous vermiculites from Transvaal, South Africa (TSA); Grouse Creek, Utah (UT); Libby, Montana (MT); White Mountain, California (CA); Llano, Texas (TX); and weathered phlogopite from the Hills Pond peridotite formation in Woodson County, Kansas (KS) were C-Pt replicated for electron microscopy (REM). The (001) cleavage of CA vermiculite was observed directly under the scanning electron microscope (SEM) after the sample was coated with gold–palladium (60, 40 percent). Osmotic swelling along the Z-axis of these samples following Li⁺ saturation was studied by treatment of flakes with 1N solution of LiCl for two to three hours, washing with water to remove salts, and allowing the flakes to swell (exfoliate) freely in water. Photographs of the natural and Li⁺ treated KS flakes were obtained by a Leitz binocular light microscope before and after exfoliation in water. The Li⁺ exfoliated flakes were prepared for SEM by freezing on a small glass slide and freeze drying.

The (001) cleavage surface micromorphology of flakes (16 mm²) of TSA vermiculite was examined by REM after cation saturation by washing with 1N Cl⁻ or NO₃⁻ solutions of the lyotropic cation series Li⁺, Na⁺, K⁺, Rb⁺, Cs⁺, Be⁺², Mg⁺², Ca⁺², Sr⁺⁶, and Ba⁺⁺ for 24 hours, washing with water until free of salts, and allowing the flakes to swell freely in water for 3 to 4 hr. Other samples were treated with Li⁺, as only this cation induced pronounced morphological changes. As controls, natural flakes were freshly cleaved and kept in distilled water for
about 3 hr so as to wash out salts, if present, and to allow osmotic swelling to take place on the cleavages by passage of water through the 4Å interlayer space of vermiculite to areas of greater swelling, and examined by REM. At least two replicate specimens were examined for each sample material and for each treatment.

Dissolution of the sample for REM in HF at first resulted in precipitates of MgF₂ and CaF₂, occurring as dark cubes impregnating the C–Pt replica. Washing the replica in 12.5 to 20 percent ethanol saturated with boric acid removed the precipitates, indicating that they were fluorides of Mg²⁺ and Ca²⁺ from which the boric acid complexed the fluoride, causing dissolution. Dissolution of the flakes by overnight treatment in 40 percent HF + 2N HCl (final solution basis) did not eliminate the precipitation. Several separate floatings, each for an hour, on the HF + HCl were necessary if the complete sample was allowed to dissolve.

The precipitation problem was also eliminated by initially floating the replica on the 40 percent HF + 2N HCl (final solution basis) for an hour after stripping off the replica from the surface of the macroflakes or from the glass surface on which the microflakes rested. The replica film was finally transferred into the HF + HCl mixture for an overnight washing.

Curling and breaking of the replica sometimes occurred, either while the replica was being stripped or when it was transferred to ethanol, as a result of low surface tension. This problem was overcome by increasing the surface tension through the addition of a little water to the respective ethanol and HF media.

A saponite fraction was separated from the exfoliated KS vermiculite, with slight centrifugal agitation by a vortex mixer, the opalescent supernatant liquid being separated for X-ray diffraction. X-ray diffractograms were made with Ni-filtered CuKα radiation after the flakes were exchange saturated with K⁺, or with Mg²⁺ followed by glycerol solvation (Jackson, 1956).

The total layer charge was obtained by estimating the K⁺ content and by determining the calcium exchange capacity (CaEC). The layer charge values, determined in duplicate, were within a deviation of approximately 2 percent.

**Results and Discussion**

**Blister–like swelling on natural vermiculite cleavages**

Blister– or bubble–like configurations are present (Fig. 1, a, b, and c) on the natural (001) crystallographic cleavages of KS, MT, and CA vermiculites. The blisters occur in clusters over certain areas on the KS flakes (Fig. 1, a), unlike the MT and CA vermiculites on which they are present singly or in twos. Direct observation of the blisters on CA vermiculite was made by SEM (Fig. 1, c), with results confirming REM. The formation of the blisters appears to be a result of osmotic swelling, since the blisters are not formed upon cation exchange saturation alone in the presence of the 1N salt solution. They form subsequent to washing, as water passes by osmosis through the 4Å interlayer space of vermiculite and accumulates in low charge areas, as discussed later in this paper. A mechanical stretching of the
Fig. 1. Electron micrographs of the (001) surface of freshly cleaved natural (water treated) micaceous vermiculites showing (a) clusters of blisters on Woodson, KS phlogopite, saponitic vermiculite by Pt-C replica; (b) irregularly shaped blisters present on the basal cleavages of Libby, MT vermiculite by Pt-C replica; (c) blisters in singles or twos present on the surface of White Mountain, CA vermiculite by scanning electron microscopy; (d) particulate phase coating the surface of Transvaal (TSA) vermiculite, with no blisters by Pt-C replica; (e) surface of Grouse Creek, UT vermiculite with ridges (arrow) but no blisters by Pt-C replica; (f) surface of Llano, TX vermiculite, with ridges (arrow) but no blisters, by Pt-C replica. Bar = 1 μm.
Fig. 2. Schematic cross sections of some morphological features represented from Pt–C replica electron microscopy showing (a) over-lapping blisters with many osmotically swollen layers; (b) broken blisters with platelets of clay size left over on the surfaces; and (c) a ridge formed by natural lifting of layers on the (001) cleavage surface.

layers by an increase in the $b$-dimension (Low et al., 1970) apparently occurs, which stabilizes the blister configurations, since they remain intact even after evacuation to $5 \times 10^{-6}$ torr of pressure during Pt–C replica preparation.

The blisters on KS vermiculite have a higher relief (the highest blister is about 2,800 Å high; Fig. 1, a) than those on MT and CA vermiculites (on the order of 300Å). On the other hand, TSA, UT, and TX vermiculites do not have blisters in the natural state (Fig. 1, d, e, and f), although some form after exchange saturation with highly hydrated cations (discussed below).

A schematic cross section of the blisters is given (Fig. 2, a) to provide a better illustration of the blistering phenomenon, showing the relief and that the blisters are multilayered, as deduced from the high relief of the margins remaining after the breaking–off of blisters (Figs. 1, c and 3, d).

Some of the natural cleavages of TSA vermiculite have a particulate coating (Fig. 1, d) which has considerable relief. This coating is of
unknown composition and is not removed by deferration treatment. Most frequently, the fresh cleavages of this vermiculite are smooth and devoid of particulate material; care must therefore be exercised in interpreting the effect of different treatments on its removal. The basal cleavages of the UT and TX vermiculites (Fig. 1, e and f) are mostly smooth, excepting for ridges (arrows) and slight coatings.

Exchange saturation with Li⁺ and washing frees layers

Washing of the Li⁺ saturated vermiculites enhances swelling (Fig. 3), enlarging the blisters. With KS flakes, the smooth areas following treatment presumably represent more micaceous surfaces (Fig. 3, a). A few layers that previously showed the natural blisters (Fig. 1, a) were removed by the strong swelling force (Fig. 4, a) developed by the extensive hydration of exchangeable Li⁺ when the flakes were washed free of LiCl and allowed to freely swell in water, but not before washing (Fig. 4, c). Some layers were exuded (Fig. 4, d) from the cleavages. After vortex mixing, free-floationg, slowly settling saponite layers appeared in the supernatant liquid. These gave a strong 18.4 Å peak in the X-ray diffractogram (Fig. 5). The sample had previously been treated with distilled water and agitated to remove any fine particles on the exterior of the flakes, but no 18 Å peak was obtained (Fig. 5, control). Thus, the fine fraction obtained after exfoliation following Li⁺ treatment is attributable to the freeing of the blister-forming layers of the mixed-layer assemblages from throughout the flake (Fig. 4, b). When the time allowed for settling was less than 5 minutes, a few coarser particles (approximately 20 to 50 µm) were also present in the supernatant, which gave an irregularly interstratified mica/vermiculite (11.5 Å) peak and a small phlogopite (10.2 Å) peak in addition to the peak for the most abundant dispersed mineral, saponite (18.4 Å). The coarse residue after Li⁺ treatment consisted of abundant irregularly interstratified mica/vermiculite (11.9 Å) and phlogopite (10.2 Å) (Fig. 5).

A comparison of CaEC and K⁺ contents reveals that the Li⁺ exfoliated fraction had a higher CaEC and lower K⁺ content, the reverse of the composition of the original material (Table 1). The Li⁺ exfoliated fine fraction had a lower average layer charge (161 meq/100 g) than the original material which had an average (phlogopite + vermiculite + saponite) layer charge of 188 meq/100 g. The layer

1 The (006) spacing of 1.54 Å of the clay fraction of KS vermiculite (to be reported in detail in a separate paper) identifies the clay as saponite of the saponite-montmorillonite (smectite) group.
Fig. 3. Electron micrographs of Pt-C replicas of Li⁺ treated vermiculite (001) cleavage showing (a) relatively smooth surface (arrow indicates a low ridge) resulting after exfoliation of a few layers from KS phlogopite, saponitic vermiculite (Fig. 5) which had natural blisters (Fig. 1, a); (b) more numerous blisters produced on MT vermiculite cleavage; (c) frequent low blisters on the CA vermiculite (arrows); (d) extensive lifting of layers into blisters produced on TSA vermiculite (a large blister has completely broken off, leaving a smooth area and small clay platelets, arrows); (e) groups of blisters produced on UT vermiculite; (f) very few blisters (arrows) produced on TX vermiculite. Bar = 1 μm.
charge of the non-mica layers of the original and Li⁺ exfoliated fractions averaged 127 to 130 meq/100 g, based on a phlogopite charge of 210 meq/100 g. Thus, the saponitic fine fraction freed by Li⁺ exfoliation of the large sample has a lower layer charge than the material from which it is freed. Blister-forming layers were also freed from TSA and some other vermiculite flakes (discussed later), although not obtained in sufficient quantities for layer charge determinations. Since Li⁺ was shown to selectively exfoliate low charge density layers, one can conclude that the blisters are likewise areas with low charge density, scattered on the XY cleavages of micaceous vermiculites. In addition to the layer charge variations along the Z-axis (differences

Fig. 4. Photomicrographs (Bar = 100 μm) of Li⁺ treated KS phlogopitic saponitic vermiculite showing (a) exfoliated particle on edge side, with dark and light bands representing unweathered mica cores and vermiculite zones, respectively, after Li⁺ saturation, washing free of salts and standing in distilled water; (b) natural fresh cleavage (control); (c) no exfoliation (control) in 1N LiCl solution. (d) scanning electron micrograph (Bar = 1 μm) of Li⁺ exfoliated and freeze dried flake on edge, showing exuding curtains of saponite.
between that of mica and expansible layers) present in all six samples, variation among the vermiculites in frequency of low charge spots (blisters) along the XY planes apparently determines whether the samples exfoliate in water (Fig. 4, a).

**Osmotic swelling in relation to cation hydration and layer charge**

Macroswelling, enhancement of blister size and freeing of layers (Fig. 3) caused by Li⁺ as compared to the natural Ca²⁺ and Mg²⁺ saturation result from the (a) higher hydration energy of Li⁺ as well as (b) layer charge effects.
Cation hydration effect

The fraction of adsorbed cations that occurs in a hydrated form can be calculated from the Boltzmann distribution law (Shainberg and Kemper, 1966b):

\[ f = \frac{1}{1 + \exp \left(-\frac{\Delta E_A}{RT}\right)} \]

\[ = \frac{1}{1 + \exp \left(\frac{(-E_\omega + E_\sigma^*)}{RT}\right)} \]  

(1)

- **f**: fraction of fully hydrated cations,
- **\Delta E_A**: net change in energy when water molecules become part of the primary hydration shell of the cations,
- **R**: gas constant,
- **T**: absolute temperature,
- **E_\omega**: \(-2300\) cal/mole, the energy of association of water molecules with their neighbors, and
- **E_\sigma^***: energy of adsorption of water molecules on the cations after correction for the repulsive forces between two dipoles adsorbed on opposite sides of the same cation.

For example, the fraction of cations that become hydrated and dissociated from a montmorillonite surface is 0.84 for Li\(^+\), 0.64 for Na\(^+\), 0.51 for K\(^+\), 0.47 for Cs\(^+\), and 0.63 for Ca\(^{2+}\) (Shainberg and Kemper, 1966a, from equation 1). Thus, the fraction of Li\(^+\) which becomes hydrated is greater than that for Na\(^+\) or Ca\(^{2+}\) and presumably for Mg\(^{2+}\) (value unavailable). When ions are completely hydrated, the Coulombic forces between the ions and the clay exchange sites are small and a greater cation concentration occurs midway between the plates. The excess cation concentration \((u)\) midway between the layers (van Olphen, 1963) is given in the equation:

\[ n(e^+ - 1) + n(e^- - 1) = 2n(\cosh u - 1) \]

(2)

in which **n** = local ion concentrations in number of ions/cm\(^3\) and **e** = charge of an electron \((4.77 \times 10^{-19}\) esu). From this equation, the osmotic swelling pressure \((p)\), which is directly proportional to the excess ion concentration midway between the layers and effective in expanding the layers to form blisters, is given (van Olphen, 1963) by,

\[ p = 2nkT (\cosh u - 1) \]

(3)

in which **k** = the Boltzmann constant and **T** = absolute temperature. A greater osmotic swelling force is therefore apparent from equation 3 for Li\(^+\) than for the natural Ca\(^{2+}\) and Mg\(^{2+}\) saturation, corresponding to the higher fraction dissociated (equation 1).
TABLE I. CATION EXCHANGE CAPACITY, K⁺ CONTENT AND LAYER CHARGE OF FOUR VERMICULITES

<table>
<thead>
<tr>
<th>Source</th>
<th>Size fraction (µm)</th>
<th>Meq/100 g</th>
<th>Layer charge</th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>CaEC</td>
<td>K⁺</td>
<td>Average</td>
<td>Expanded*</td>
</tr>
<tr>
<td>Micaceous vermiculites that show macroscopic flake swelling with Li⁺ saturation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Woodson, KS original†</td>
<td>&gt;500</td>
<td>35</td>
<td>153</td>
<td>188</td>
<td>130</td>
</tr>
<tr>
<td>Woodson, KS Li⁺ exfoliated fraction</td>
<td>&lt;20</td>
<td>75</td>
<td>86</td>
<td>161</td>
<td>127</td>
</tr>
<tr>
<td>Libby, MT</td>
<td>&lt;2</td>
<td>137‡</td>
<td>60‡</td>
<td>197</td>
<td>192</td>
</tr>
<tr>
<td>Micaceous vermiculites that do not show macroscopic flake swelling on Li⁺ saturation</td>
<td></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Transvaal, S. Africa</td>
<td>&lt;2</td>
<td>106‡</td>
<td>86‡</td>
<td>192</td>
<td>180</td>
</tr>
<tr>
<td>Llano, TX</td>
<td>&lt;50</td>
<td>151‡</td>
<td>2‡</td>
<td>153</td>
<td>153</td>
</tr>
</tbody>
</table>

*Layer charge of the non-mica layers calculated by assigning all the K⁺ content to mica with 210 meq/100 g and the CaEC to the remaining, weathered fraction. Use of 210 for the mica layer charge gave approximately equal charge for the expanded layers (original and exfoliated); use of 225 gave 110 and 121, respectively.

+Saponitic, vermiculitic phlogopite from Woodson County, KS.

†Data from Alexiades and Jackson (1965).

Layer charge effect

In addition to the inherent hydration differences between the cations, the hydration of any particular exchangeable cation, and therefore the osmotic swelling, is affected by the layer charge density of the exchanger. Partial dehydration of the exchangeable cations occurs with a higher layer charge density (Shainberg and Kemper, 1966b) and results in a small fraction of the cations in the diffuse double layer (Heald et al., 1964). For example, the number of dissociated
cations is higher in a low charge area of the vermiculite compared to that in a high charge area in the same vermiculite and so a greater cation concentration occurs midway between layers in the former than the latter. The osmotic pressure is consequently greater for low charge than for high charge areas in the same vermiculite, according to equations 2 and 3.

The fact that layers fan out at the edges and that the swelling is less at the center of the particle (Fig. 4, a) suggests that more K\(^+\) loss and lower layer charge occur at the edge of the flake. This supports the diffusion model proposed for the weathering of mica (Reed and Scott, 1962). The presence of regular alternating dark and light bands reveals the pattern of weathering in that the dark bands would represent the less swollen micaceous portions (a higher K content and higher layer charge).

**Differences among the vermiculites**

Greater frequency of blisters on the basal cleavages of MT and CA vermiculites after Li\(^+\) treatment, compared to that on the natural cleavages, shows that additional layers were raised upon Li\(^+\) treatment besides those present naturally (Fig. 3, b and c). Exchange saturation with Li\(^+\) produced pronounced lifting of layers into blisters (Fig. 3, d and e) on the cleavages of TSA and UT vermiculites on which no blisters were observed in the natural state. On the other hand, TX vermiculite produced blisters very rarely (Fig. 3, f).

Overlapping of the blisters can be seen (Fig. 3, d) where a large blister was present on a small blister (diagrammed, Fig. 2, a). The large blister was broken off from the cleavage with particulate coating, as a result of the swelling force created by extensive hydration of the Li\(^+\) ion, leaving a smooth area without particulate coatings (Fig. 3, d). The smooth surface has small epitaxial clay platelets (arrows), presumably formed by the shattering of the broken off layers (Fig. 2, b). Thus, the fracture of swelling layers into very fine clay particles appears to be one of the mechanisms of clay formation during weathering of micaceous vermiculite. Occasional ridges (Fig. 1, e) are believed to be formed by natural lifting and mis-fit on the collapse of layers on the basal cleavages, a schematic cross section of which is given (Fig. 2, c).

When TSA vermiculite was treated with 1N LiCl but not allowed to swell freely in water, then treated with 1N CsCl and allowed to swell in water, only a very few blisters were produced. This result suggests that if osmotic swelling is not allowed to take place after saturation of the exchange sites with Li\(^+\), subsequent Cs\(^+\) saturation can
largely prevent blister formation. The few blisters present may result from some Li⁺ entrapment by Cs⁺ (details are to be reported in a separate paper). These observations indicate that osmotic swelling, which is over and beyond the 14 Å intracrystalline swelling of vermiculite, is responsible for blister production.

When the TSA vermiculite was treated with LiCl for 24 hours, allowed to swell freely in water, and agitated with a vortex mixer, a few layers carrying blisters were completely exfoliated. An almost smooth surface, except for a few blisters and broken edges, remained. A similar phenomenon was observed with KS vermiculite after treatment with LiCl, except that the vortex mixing force was not required with the latter material. The blister forming areas in TSA vermiculite thus appear to have a higher charge than those of KS vermiculite, consistent with the absence of natural blisters in the former. Absence of natural blisters and their sparse induction by artificial treatment in TSA and TX vermiculites indicate the lack of a sufficient number of very low charge density areas along XY planes to cause exfoliation. Macroswelling of vermiculites thus appears to be controlled by the frequency of low-charge areas along the XY planes rather than by the average layer charge or the layer charge of expanded layers (Table 1).

Lyotropic series cation effects on surface morphology

The blistering phenomenon was observed on TSA vermiculite basal cleavages only with Li⁺ and Na⁺ of the monovalent lyotropic cations and Be²⁺ of the divalent lyotropic cations (Fig. 6). Li⁺ produced blisters on TSA and UT vermiculites while Na⁺ produced blisters on the former. The inability of Na⁺ to produce blisters on UT vermiculite can be attributed to the absence of local spots of sufficiently low charge density to be osmotically swollen.

The density (number of blisters per unit area) and relief (height) of artificial and natural blisters tends to increase as follows:

\[
\text{Li}^+ > \text{Na}^+ \geq \text{Be}^{2+} > \text{Mg}^{2+} > \text{Ca}^{2+}
\] (4)

The above is consistent with the hydration energy differences of these cations. The sparse production of blisters by Na⁺ and Be²⁺ unlike Li⁺ indicates that there are some local areas of intermediate layer charge which can be raised by Li⁺ but not by Na⁺ or Be²⁺. Therefore, it is possible to explain the occurrence of natural blisters even with Mg²⁺ (Fig. 1, a, b, and c), when the charge density in certain areas is sufficiently low for osmotic swelling to have taken place.

The differences among the lyotropic cations in inducing the osmotic swelling of vermiculite layers can be explained by the fact that the
Fig. 6. Electron micrographs of Pt–C replicas of artificially produced blisters on TSA vermiculite cleavages by different cations showing (a) high relief with Li⁺; (b) intermediate relief with Na⁺; and (c) low relief with Be⁺. Bar = 1 μm.
fraction of Li⁺, Na⁺, and Be²⁺ which becomes hydrated is greater than that of the other lyotropic cations (equation 1). Therefore, the osmotic pressure exerted by the former cations is greater than that exerted by the latter (equations 2, 3).

Conclusions

1. Some natural micaceous vermiculites show blister-like configurations on their (001) cleavages (Fig. 1) observed by both scanning and replica electron microscopy. These configurations are artificially produced on micaceous vermiculite surfaces by exchange saturation with Li⁺, Na⁺, or Be²⁺ treatment (Figs. 3 and 6).

2. Osmotic swelling between the layers, responsible for formation of the blisters, is controlled by hydration energy of the cation (equations 1, 2, and 3) and the charge density of the layers (Heald et al., 1964; Shainberg and Kemper, 1966b). Osmotic swelling is greater than the intracrystalline swelling of vermiculite to 14 Å.

3. Exchange saturation with a highly hydrated cation such as Li⁺ frees the blister-forming layers (Fig. 3, a and d) if the layer charge is sufficiently low (saponitic). Low charge density layers scattered along the Z-axis (charge differences between expansible layers as contrasted with mica layers) cause macroscopic exfoliation of Li⁺ saturated, washed vermiculites (Fig. 4, a). Fracture of such layers is probably one mechanism of clay formation (Fig. 5).

4. Variations in charge density in different areas of the XY planes appears to cause the blisters to form and thus their presence may be a sensitive way to measure the distribution of low charge areas over the XY planes of the (001) cleavage. In contrast, X-ray diffraction and exfoliation measure non-uniformity of charge along the Z-axis. The mosaic of these blisters (low charge density areas) on the layers of micaceous vermiculites creates wedge zones (Dolcater et al., 1968) important in cation exchange capacity, selectivity, and fixation of K⁺, Rb⁺, and ¹³⁷Cs⁺.

Acknowledgments

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