

## CHARGE REDUCTION, OCTAHEDRAL CHARGE, AND LITHIUM RETENTION IN HEATED, Li-SATURATED SMECTITES<sup>1</sup>

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**Abstract**—Reference smectites were examined to determine relationships between Li uptake, cation-exchange capacity (CEC), and octahedral layer charge after Li saturation and heating at 250°C (Hofmann-Klemen effect). Direct measurements of exchangeable Li after heating led to overestimates of charge reduction due to entrapment of Li in collapsed interlayers. Expansion of interlayers by sequential washings with 1 N MgCl<sub>2</sub>, 0.01 N MgCl<sub>2</sub>, and ethanol and subsequent determinations of exchangeable Mg provided accurate measurements of reduced charge. The CEC reductions observed in dioctahedral samples as a result of Li saturation and heating equaled octahedral charge values derived from published mineral formulae, and interlayer charge estimates obtained by alkylammonium exchange confirmed that measured CEC reductions were a consequence of uniform decreases in octahedral layer charge.

Dioctahedral specimens retained 1 to 10 meq/100 g of non-exchangeable Li in excess of CEC reduction and were acidified in direct proportion to their total Fe contents, apparently as a result of the deprotonation of structural hydroxyl groups. Mild acid treatment reprotonated these hydroxyl groups, released excess Li, and resulted in total Li contents comparable to measured CEC reductions. Heating (250°C) Mg-saturated hectorite induced a loss of octahedral Li, acidification, and a reduction of CEC, indicating that Mg had partially replaced octahedral Li. These results suggest that octahedral Li is mobile at low temperatures and that cation movement into or out of the octahedral sheet is favored if the layer charge is reduced.

**Key Words**—Alkylammonium exchange, Cation-exchange capacity, Hofmann-Klemen effect, Layer-charge reduction, Lithium, Octahedral charge.

### INTRODUCTION

Hofmann and Klemen (1950) observed a loss of exchangeable Li and a reduction of layer charge when Li-saturated montmorillonite was heated at low temperatures (200°–300°C). The mechanism of charge reduction advocated by Hofmann and Klemen (and later by Greene-Kelly, 1953) invoked migration of Li ions into vacant octahedral sites until the octahedral charge imbalance was neutralized. Thus, a lower limit to total charge was set by tetrahedral substitution plus terminal edge sites. A number of researchers have since questioned this mechanism. For example, from infrared (IR) spectra of heated, Li-montmorillonites, Tettendorst (1962) concluded that Li moves into the hexagonal cavities of the Si–O network but not into the octahedral sheet. In contrast, Farmer and Russell (1967) interpreted IR data to indicate that part of the Li migrates into the octahedral positions and becomes entrapped, whereas the remainder reacts with interlayer water or structural hydroxyls to liberate protons. This Li reportedly remains in or close to the interlayer region. Calvet and Prost (1971) offered similar interpretations of IR data and suggested that Li remaining in the hexagonal cavities is in a transitional state prior to movement into the octahedral sheet.

Relationships between Li uptake, charge reduction, and octahedral charge have also been disputed. Calvet and Prost (1971) found total charge reduction to be equal to the octahedral charge of Camp Berteau montmorillonite, but measured non-exchangeable Li in excess of that entrapped in the octahedral sheet. Similarly, Lim and Jackson (1986) reported that non-exchangeable Li in excess of the reduction of cation-exchange capacity (CEC) ranged from 4 to 21 meq/100 g in a series of standard smectites. Brindley and Ertem (1971) determined the CEC of a Wyoming montmorillonite (“Volclay”) after Li heat treatment by measuring Li displaced with ammonium acetate. They found no leveling off of CEC at a value corresponding to tetrahedral layer charge. Farmer and Russell (1967) reported that charge reduction and Li retention in heated, Li-montmorillonites could be partially reversed by treatment with NH<sub>3</sub>, and Calvet and Prost (1971) suggested that octahedral sites may not always be the most stable positions for Li retention. Under some conditions, reverse migration may occur from the octahedral sheet to the interlayer region.

Despite widespread use of the Hofmann-Klemen effect in mineralogical investigations, controversy clearly remains concerning the magnitude, specificity, and reversibility of Li uptake by expandable clay minerals having octahedral charge. Because of these conflicting views, the chief objective of this paper is to re-examine

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Table 1. Mineralogy and source of samples.

Sample	Mineralogy <sup>1</sup>	Source
CMS Source Clays		
SWy-1	Na-montmorillonite, minor quartz and calcite	Crook County, Wyoming
SWy-1 <2 μm	Montmorillonite	
STx-1	Ca-montmorillonite, minor silica and calcite	Gonzales County, Texas
STx-1 <2 μm	Montmorillonite, minor silica phase	
SAz-1	Ca-montmorillonite, minor silica phase	Apache County, Arizona
SAz-1 <2 μm	Montmorillonite	
SHCa-1 <2 μm	Hectorite	San Bernardino County, California
CMS Special Clays		
SCa-2	Mg-montmorillonite	Otay, San Diego County, California
SCa-2 <2 μm	Montmorillonite	
SWa-1	Nontronite, minor quartz	Grant County, Washington
SWa-1 <2 μm	Nontronite	
NG-1 <2 μm	Nontronite, minor goethite and quartz	Hohen Hagen, Germany
SapCa-1 <2 μm	Saponite	Ballarat, California
VTx-1	Vermiculite (hand-picked flakes)	Llano County, Texas
Other Clays		
API #23	Ca-montmorillonite	Chambers, Arizona
API #23 <2 μm	Montmorillonite	

<sup>1</sup> Mineralogy of CMS Source Clays from van Olphen and Fripiat (1979). Mineralogy of CMS Special Clays from information supplied by Source Clay Repository and from X-ray powder diffraction. Mineralogy of API clay from Grim and Güven (1978).

relationships between octahedral layer charge, Li-uptake, and cation-exchange capacity in reference clay samples after Li saturation and heat treatment. Specific goals are to determine if charge reduction is: (1) irreversible and equal to non-exchangeable Li obtained by total Li analysis, (2) consistent with layer-charge estimates measured by alkylammonium exchange, and (3) equal to the octahedral charge derived by total chemical analysis. With this information in hand, the mechanism of Li retention and charge reduction that comprise the Hofmann-Klemen effect can be more rigorously evaluated.

## MATERIALS AND METHODS

### Samples

Reference CMS and API samples were obtained from the Source Clays Repository of The Clay Minerals Society and Ward's Natural Science Establishment, Rochester, New York, respectively (Table 1). Most samples were wet sedimented to separate the <2-μm fraction using an automatic fractionator (Rutledge *et al.*, 1967). The clay separates were subsequently saturated with Mg and freeze-dried.

Additional pretreatments were employed on some samples. Specifically, particles of the Llano, Texas, vermiculite (VTx-1) were hand-picked from the sample, treated with pH 5 NaOAc-HOAc buffer to remove residual magnesite, and subsequently ground in ethanol to pass a 60-mesh sieve. Smectites SWy-1 and STx-1 were treated with pH 5 NaOAc-HOAc buffer to remove minor calcite, and CMS special clay samples SCa-2, SWa-1, SapCa-1, and API #23 were ground in ethanol and passed through a 60-mesh sieve. Structural

formulae and calculated charge distributions of selected samples were obtained from the literature and are summarized in Table 2. For comparison, total charge per unit cell was also calculated from CEC data using the relation: total charge = [CEC (meq/100 g)] [formula weight]/10<sup>5</sup>.

### Charge reduction

The general procedure employed for charge reduction was similar to that recently proposed by Lim and Jackson (1986). Samples were saturated with Li by washing them three times with 1 M LiCl solution at pH 7. Subsequently, excess salt was removed by washing four times with ethanol. A centrifuge was used for these treatments. The Li-saturated samples were then placed in silica crucibles, dried at 110°C, and heated at 250°C for 8–12 hr. Materials prepared in this manner are hereafter referred to as Li-250 samples. Silica crucibles were used to avoid exchange of Li for Na in the crucible glass, because Byström-Brusewitz (1976) and Lim and Jackson (1986) found Na contamination to be a significant problem with ordinary soda lime and borosilicate (Pyrex) glass.

Series of reduced-charge specimens were also prepared from the montmorillonite samples by mixing different proportions of air-dried, Li-saturated and Na-saturated materials as described by Brindley and Ertem (1971). The samples were then ultrasonically dispersed in water, allowed to equilibrate, dried at 110°C in silica crucibles, and heated at 250°C for 8–12 hr. Weight loss between 110° and 250°C was recorded for each sample to be able to express subsequent analyses on a 110°C, oven-dry basis.

Table 2. Mineral formulae and charge distribution of selected samples.

Sample	Reference	Derived unit-cell formula	Charge distribution (mole/unit cell)		
			Tetrahedral	Octahedral	Total
Dioctahedral					
NG-1	1	(Si <sub>7.40</sub> Al <sub>0.60</sub> )(Fe <sup>+3</sup> <sub>3.60</sub> Al <sub>0.26</sub> Mg <sub>0.20</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+0.61</sup>	-0.60	-0.02	-0.62
SWa-1	2	(Si <sub>7.25</sub> Al <sub>0.75</sub> )(Fe <sup>+3</sup> <sub>2.75</sub> Al <sub>0.85</sub> Mg <sub>0.33</sub> Ti <sub>0.05</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+0.98</sup>	-0.75	-0.34	-1.09
SWy-1	3	(Si <sub>7.84</sub> Al <sub>0.16</sub> )(Fe <sup>+3</sup> <sub>0.26</sub> Al <sub>3.22</sub> Mg <sub>0.40</sub> Fe <sup>+2</sup> <sub>0.12</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+0.68</sup>	-0.16	-0.52	-0.68
SAz-1	4	(Si <sub>7.86</sub> Al <sub>0.14</sub> )(Fe <sup>+3</sup> <sub>0.20</sub> Al <sub>2.80</sub> Mg <sub>1.00</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+1.14</sup>	-0.14	-1.00	-1.14
SCa-2	4	(Si <sub>7.90</sub> Al <sub>0.10</sub> )(Fe <sup>+3</sup> <sub>0.20</sub> Al <sub>2.72</sub> Mg <sub>1.08</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+1.18</sup>	-0.10	-1.08	-1.18
API #23	4	(Si <sub>7.96</sub> Al <sub>0.04</sub> )(Fe <sup>+3</sup> <sub>0.16</sub> Al <sub>2.92</sub> Mg <sub>0.92</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+0.96</sup>	-0.04	-0.92	-0.96
Trioctahedral					
SHCa-1	5	(Si <sub>8.00</sub> )(Al <sub>0.04</sub> Mg <sub>5.30</sub> Li <sub>0.66</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+0.66</sup>	0	-0.62	-0.62
SapCa-1	6	(Si <sub>7.54</sub> Al <sub>0.46</sub> )(Fe <sup>+3</sup> <sub>0.12</sub> Al <sub>0.30</sub> Mg <sub>5.22</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+0.74</sup>	-0.46	-0.30	-0.76
VTx-1	7	(Si <sub>5.79</sub> Al <sub>2.21</sub> )(Fe <sup>+3</sup> <sub>0.13</sub> Al <sub>0.16</sub> Mg <sub>5.62</sub> Ti <sub>0.04</sub> Mn <sub>0.01</sub> )O <sub>20</sub> (OH) <sub>4</sub> X <sup>+1.89</sup>	-2.21	+0.31	-1.90

1. Schneiderhörn (1965); nontronite from Hohen Hagen, Germany.
2. Rozenson and Heller-Kallai (1976); CMS Special Clay SWa-1.
3. Knechtel and Patterson (1962); olive green Clay Spur, Crook County, Wyoming.
4. Grim and Güven (1978); Cheto, Arizona; Otay, California; Chambers, Arizona.
5. Ames *et al.* (1958); hectorite from Hector, California.
6. Post (1984); CMS Special Clay SapCa-1.
7. Norrish (1973); vermiculite from Llano County, Texas.

### Cation-exchange capacity

CEC values for the unheated samples (CEC<sub>0</sub>) were obtained using a mechanical extractor as described by Jaynes and Bigham (1986). Reduced exchange capacities (LiEC<sub>R</sub>, MgEC<sub>R</sub>) resulting from Li-saturation and heating of the clays were also measured with a mechanical extractor following two different procedures. In the first procedure, readily exchangeable Li was displaced by an overnight extraction of 0.5–2 g of the Li-250 sample with 50 ml of 1 N MgCl<sub>2</sub> at pH 7. Such an extraction has been shown to be comparable to multiple salt washings using standard, centrifuge-based techniques (Jaynes and Bigham, 1986). The extract was then made to 100-ml volume with 1 N MgCl<sub>2</sub>, and Li was determined on a diluted portion of the extract using flame emission spectroscopy. Based on this determination, a LiEC<sub>R</sub> value was calculated.

Following the LiEC<sub>R</sub> determination, a reduced magnesium-exchange capacity (MgEC<sub>R</sub>) was measured as follows: The Mg-washed (1 N MgCl<sub>2</sub>) sample remaining from the LiEC<sub>R</sub> determination was extracted once with 50 ml of dilute (0.01 N) MgCl<sub>2</sub> and once with 50 ml of ethanol to remove excess salt. Washing with a dilute salt solution of the saturating cation (Mg) facilitated the expansion of collapsed interlayers and the removal of otherwise slowly exchangeable Li; similar effects have been reported for the displacement of intercalated salts in kaolinite and halloysite (Wada and Harada, 1969). The sample was then extracted overnight (~8 hr) with 50 ml of 1 N CaCl<sub>2</sub> at pH 7 to displace exchangeable Mg. The resulting extract was made to 100-ml volume with 1 N CaCl<sub>2</sub>, and the Mg content of a diluted portion of the extract was determined using atomic absorption spectroscopy. All ex-

change capacities were expressed on a 110°C, oven-dry basis.

### Li retention

To compare CEC reduction directly with the incorporation of Li into the mineral structures, total Li contents were determined on both untreated and Li-250 specimens. Exchangeable Li was removed from the latter by sequentially washing the samples with 1 N MgCl<sub>2</sub>, 0.01 N MgCl<sub>2</sub>, and ethanol as described above. To determine if any non-exchangeable Li could be displaced with mild acid treatment, a second set of Mg-saturated, Li-250 clays (~0.1 g) were washed twice with 5-ml aliquots of pH 5 NaOAc-HOAc buffer solution. A third 5-ml aliquot of acetate buffer was added, and the samples were placed in a 65°C oven for 8 hr. The samples were then re-saturated with Mg, washed with ethanol, and dried.

About 50 mg of the untreated, Li-250, and Li-250-acid-washed clays were weighed, transferred to Teflon-lined decomposition bombs, and decomposed with HF and H<sub>2</sub>SO<sub>4</sub>. Following acid dissolution, the digests were analyzed for Li using flame emission spectroscopy. The difference in total Li between the untreated and treated samples (Li retention) was expressed in meq/100 g on a 110°C, oven-dry basis.

### Titrateable acidity

Oven-dried, Li-saturated samples (0.5–1.2 g) were weighed, transferred to silica crucibles, and heated at 250°C for 8–12 hr. The heated samples were then quantitatively transferred to plastic beakers using 10 ml of ethanol. The sample slurries were stirred and larger aggregates were crushed using a glass rod. The slurries

were equilibrated for 1 hr to permit expansion of collapsed layers. Subsequently, the slurries were brought to 100 ml volume with distilled water and titrated to pH 7 using 0.01 N NaOH, a magnetic stirrer, and a pH meter. The results were then expressed as meq/100 g acidity on a 110°C, oven-dry basis.

#### *Alkylammonium exchange*

Alkylammonium complexes of untreated and Li-250 samples were prepared to estimate layer-charge reductions due to the Hofmann-Klemen effect. The Li-250 clays were saturated with Mg and washed with ethanol as described above to enhance expansion of collapsed layers. All samples were then saturated with Na prior to alkylammonium exchange. Alkylammonium chlorides were synthesized by HCl treatment of the corresponding amines, and alkylammonium-clay complexes were subsequently prepared as oriented aggregates on glass slides using a modification of the method of Rühlicke and Kohler (1981). All samples were stored under vacuum until immediately prior to analysis. Basal X-ray diffraction spacings were then recorded using  $\text{CuK}\alpha$  radiation and a Philips PW 1316/90 wide-range goniometer fitted with a theta-compensating slit, a 0.2-mm receiving slit, and an AMR diffracted-beam graphite monochromator. A cholesterol standard (Kittrick, 1960) was used to correct the  $2\theta$  values to ensure accurate  $d$ -values.

Mean layer charge was calculated from  $d$ -values of the alkylammonium-clay complexes in the monolayer (13.6–13.8 Å) to bilayer (17.5–17.7 Å) transition range using the method of Lagaly and Weiss (1976). Because most smectites have a heterogeneous charge distribution, Méring's (1949) method was used to determine the proportion of monolayer to bilayer complexes from the  $d$ -values. Stul and Mortier (1974) employed a similar procedure to calculate the mean layer charge of heterogeneous montmorillonites. The ratio of monolayers to monolayers + bilayers was then used to calculate the proportion of layers at each critical carbon chain length ( $N_c$ ). The layer charge for each  $N_c$  was obtained from Lagaly and Weiss (1976, Table 2, p. 160), whose charge values were based on an assumed particle diameter of 250–600 Å and a dioctahedral structure and charge distribution. No additional corrections were made for differences in structure, particle size, or charge distribution. The mean layer charge was then determined by summing the relative contribution of each layer charge.

## RESULTS AND DISCUSSION

Lithium saturation and heating caused the color of all dioctahedral minerals to darken. The montmorillonite samples changed from nearly white to dark gray; they also developed hydrophobic characteristics. The color of the German nontronite, NG-1, changed from

bright yellow to dark red (indicating the presence of goethite), whereas only a slight reddening of the Washington nontronite, SWa-1, was observed. In contrast, no change in color or physical properties was noted for the trioctahedral minerals.

#### *Cation-exchange capacity*

Natural and reduced CECs for all clay samples are presented in Table 3. As expected, the montmorillonites (SWy-1, STx-1, SAz-1, SCa-2, API #23) showed the greatest charge reduction following Li-saturation and heating; however, the trioctahedral clay minerals also exhibited substantial reductions in CEC if readily exchangeable Li ( $\text{LiEC}_R$ ) was employed as an indicator of residual layer charge. Differences between the reduced CEC values ( $\text{LiEC}_R$  vs.  $\text{MgEC}_R$ ) for each sample can be attributed to entrapment of Li in the interlayer region in a manner similar to the K "fixation" observed in heated, K-saturated smectites and vermiculites (i.e., collapsed interlayers). Lithium "fixation" probably affected the results of Brindley and Ertem (1971) who reported charge reductions in montmorillonite (based on exchangeable Li) that exceeded the octahedral charge.

Due to its high layer charge, the vermiculite employed in the present study (VTx-1) exhibited more Li "fixation" than did the other clay samples even though no charge reduction should have occurred because the mineral is trioctahedral and has a net positive charge on the octahedral sheet (Table 2). In contrast to its low  $\text{LiEC}_R$ , sample VTx-1 yielded a  $\text{MgEC}_R$  that was essentially equal to its natural CEC, indicating that collapsed interlayers were effectively re-expanded and entrapped Li was released by extended washing with dilute  $\text{MgCl}_2$  solution. The  $\text{MgEC}_R$  values obtained in the present study therefore appear to be reliable and reasonably quantitative indicators of CEC for the Li-250 clays. Consequently, the difference between  $\text{CEC}_0$  and  $\text{MgEC}_R$  (Table 3) is henceforth used as a measure of net charge reduction following Li saturation and heating.

#### *Li retention and CEC reduction*

If all non-exchangeable Li compensates for octahedral charge, Li retention should equal CEC reduction as defined in Table 3. Figure 1 is a plot of Li retention vs. CEC reduction and includes data from all  $<2\text{-}\mu\text{m}$  samples. Because the line in this plot has a slope of one, any point on the line denotes equivalence between Li retention and CEC reduction. All the dioctahedral samples plot above the line, indicating that Li retention exceeded CEC reduction by 1 to 10 meq/100 g. The effect was most pronounced in the two nontronites. A possible explanation for this excess Li retention is suggested by the work of Russell (1979). Using IR spectroscopy, Russell observed that: (1) hydroxyl groups coordinated to Fe were deprotonated when dioctahedral

Table 3. Cation-exchange capacities<sup>1</sup> of untreated and Li-250<sup>2</sup> samples.

Sample	Untreated	Li-250		CEC reduction
	CEC <sub>0</sub> (meq/100 g)	LiEC <sub>R</sub> (meq/100 g)	MgEC <sub>R</sub> (meq/100 g)	CEC <sub>0</sub> - MgEC <sub>R</sub> (meq/100 g)
Nontronites				
NG-1 <2 μm	97.0	64.6	83.8	13.2
SWa-1	101	50.3	69.8	31.2
SWa-1 <2 μm	107	51.9	73.3	33.7
Montmorillonites				
SWy-1	79.8	8.9	19.7	60.1
SWy-1 <2 μm	87.0	8.3	15.1	71.9
0.5Li, 0.5Na	—	—	50.2	36.8
0.2Li, 0.8Na	—	—	67.3	19.7
STx-1	84.2	7.5	9.5	74.7
STx-1 <2 μm	88.3	6.6	10.5	77.8
0.5Li, 0.5Na	—	—	51.5	36.8
0.2Li, 0.8Na	—	—	67.0	21.3
SAz-1	125	2.2	19.1	106
SAz-1 <2 μm	130	2.1	14.6	115
0.5Li, 0.5Na	—	—	71.6	58.4
0.2Li, 0.8Na	—	—	105	25.0
SCa-2	123	3.6	13.9	109
SCa-2 <2 μm	125	7.3	13.4	112
0.5Li, 0.5Na	—	—	68.9	56.1
0.2Li, 0.8Na	—	—	103	22.0
API #23	127	5.4	9.8	117
API #23 <2 μm	127	4.3	10.4	117
Trioctahedral (hectorite, saponite, vermiculite)				
SHCa-1 <2 μm	89.2	81.4	78.1	2.1
SapCa-1 <2 μm	80.4	67.2	75.9	4.5
VTx-1	212	92.2	210	2.0

<sup>1</sup> CEC<sub>0</sub> = CEC of original (natural) clay; LiEC<sub>R</sub> = Reduced CEC obtained by measuring Li displaced from heated (250°C) samples with 1 N MgCl<sub>2</sub>; MgEC<sub>R</sub> = Reduced CEC obtained by saturating heated (250°C) clays with Mg and measuring Mg displaced with 1 N CaCl<sub>2</sub>; CEC reduction obtained by subtracting MgEC<sub>R</sub> from CEC<sub>0</sub>.

<sup>2</sup> Li-250 samples prepared by heating Li-saturated clays at 250°C for 8–12 hr in silica crucibles. Montmorillonites with partial charge reduction similarly prepared by heating (Li<sub>x</sub>Na<sub>1-x</sub>)<sub>2</sub>-saturated montmorillonites.

dral smectites were treated with alkalis, (2) alkali cations were retained in the clay mineral structure, and (3) hydroxyls were reprotonated if the clays were treated with acetic acid.

To evaluate whether deprotonation was a factor in the present study, the titratable acidity produced on heating Li-saturated clays was plotted against the total structural Fe content (Figure 2). The dioctahedral minerals were acidified, whereas the trioctahedral clay minerals remained alkaline. The nontronites, having high total Fe contents, were clearly the most affected lending support to the hypothesis (Russell, 1979) that hydroxyls coordinated to octahedral ferric iron are easily destabilized. Some acidification (especially in low-Fe samples) may also be a direct consequence of the Hofmann-Klemen effect due to the ionization of structural hydroxyls overlying cations that have migrated into the octahedral sheet (Farmer and Russell, 1967).

If excess Li is retained primarily as a consequence of hydroxyl dissociation, reprotonation of the hydroxyls should release additional Li. To evaluate this possibility, Li contents were determined on the Li-250 clays after a mild acid wash with pH 5 NaOAc-HOAc

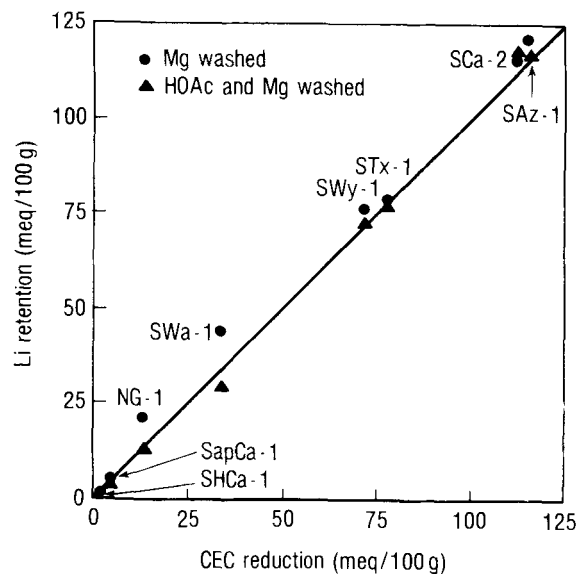


Figure 1. Lithium retention vs. reduction of cation-exchange capacity (CEC<sub>0</sub> - MgEC<sub>R</sub>). Li retention in the vermiculite (VTx-1) was zero.



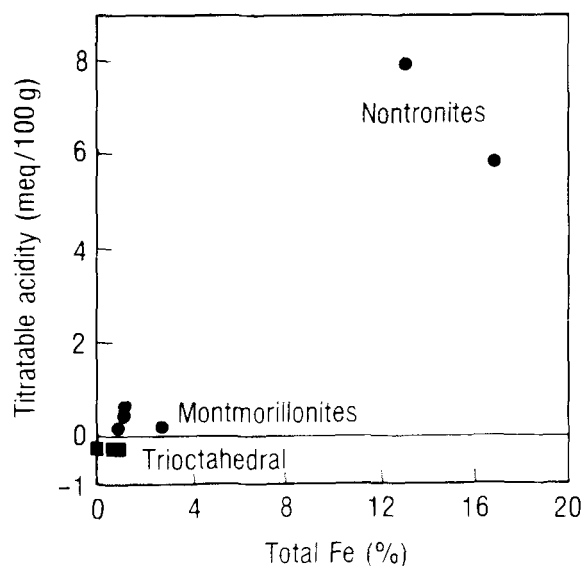


Figure 2. Titratable acidity of heated, lithium-saturated samples vs. total iron content.

buffer. When Li contents after acid-washing are plotted against CEC reduction (triangular points in Figure 1), better agreement is achieved than before washing. The data indicate that some non-exchangeable Li was, indeed, retained in compensation for deprotonated hydroxyls and that washing with acetic acid reprotonated the hydroxyls and released excess Li. The resistance of the remaining Li to removal by acid and multiple salt washes suggests that it was retained in structurally remote octahedral positions.

The foregoing data indicate that if Li-saturated dioctahedral clays are heated, Li may be retained: (1) in collapsed interlayers due to Li "fixation," (2) in octahedral cation sites due to the Hofmann-Klemen effect, and (3) in compensation for deprotonated hydroxyl groups with no net alteration in charge. Processes one and three probably account for most reported discrepancies between Li retention and charge reduction (see, e.g., Calvet and Prost, 1971; Brindley and Ertem, 1971; Lim and Jackson, 1986).

#### Alkylammonium exchange

Alkylammonium complexes were prepared from the untreated and Li-250 clays to determine if measured

Table 4.  $d(001)$  values of alkylammonium-treated samples.

Sample <sup>1</sup>	d-values (Å)											
	C6 <sup>2</sup>	C7	C8	C9	C10	C11	C12	C13	C14	C15	C16	C18
Ng-1 <2 μm	—	13.8	14.0	15.0	15.8	16.7	17.3	17.7	17.9	18.2	18.6	20.6
Li-250	—	13.6	14.0	14.2	15.8	16.1	17.3	17.7	17.9	18.2	18.6	20.1
SWa-1 <2 μm	—	13.6	14.0	14.2	15.5	16.1	17.0	17.7	17.7	18.0	18.2	19.6
Li-250	—	13.6	13.8	13.8	14.2	14.7	16.4	16.7	17.2	17.3	17.9	18.2
SWy-1 <2 μm	—	—	13.6	13.4	13.6	13.8	14.5	15.2	15.5	15.8	15.8	17.7
0.2Li, 0.8Na-250	—	—	—	—	—	—	—	—	14.0	—	—	15.2
0.5Li, 0.5Na-250	—	—	—	—	—	—	13.4	13.4	13.4	13.6	13.4	13.6
Li-250	—	—	11.3	—	—	—	12.6	—	—	—	—	12.6
STx-1 <2 μm	—	—	13.8	14.5	15.2	15.8	16.4	17.0	17.0	17.7	17.7	19.0
0.2Li, 0.8Na-250	—	—	—	13.6	13.4	13.8	15.2	15.5	15.5	15.8	17.3	17.7
0.5Li, 0.5Na-250	—	—	—	—	—	—	13.4	13.6	13.6	13.8	13.8	14.0
Li-250	—	—	9.9	—	—	—	9.7	—	—	—	—	9.9
SAz-1 <2 μm	13.6	13.8	14.7	17.0	17.3	17.3	17.7	17.7	17.7	18.4	18.8	20.8
0.2Li, 0.8Na-250	13.6	13.6	13.8	14.5	15.5	15.8	17.3	17.3	17.3	17.7	18.0	18.8
0.5Li, 0.5Na-250	—	—	13.4	13.4	13.4	13.6	13.6	13.8	14.0	14.2	14.7	14.7
Li-250	—	—	9.9	—	—	—	9.9	—	—	—	—	9.9
SCa-2 <2 μm	13.8	13.8	15.0	17.0	17.3	18.0	18.0	18.0	18.0	18.4	19.2	21.3
0.2Li, 0.8Na-250	13.6	13.8	13.8	14.5	15.2	16.1	17.3	17.7	17.7	18.0	18.0	19.2
0.5Li, 0.5Na-250	—	—	13.4	13.6	13.6	13.6	13.6	14.0	14.2	14.2	14.7	14.5
Li-250	—	—	10.0	—	—	—	10.0	—	—	—	—	10.0
API #23 <2 μm	13.4	13.6	14.7	15.9	16.7	17.3	17.7	17.7	17.3	18.0	19.2	21.0
Li-250	—	—	9.7	—	—	—	9.9	—	—	—	—	9.9
SHCa-1 <2 μm	—	—	13.7	13.6	13.6	13.8	14.2	15.2	15.5	16.1	17.0	17.5
Li-250	—	—	13.7	13.6	13.6	13.8	14.2	14.7	15.5	15.8	17.0	17.5
Mg-250	—	—	—	—	13.6	13.8	14.0	14.6	15.2	15.5	16.7	17.3
SapCa-1 <2 μm	—	—	13.7	13.6	13.8	15.0	15.8	15.8	16.7	17.3	17.7	17.9
Li-250	—	—	13.7	—	13.8	—	15.8	15.8	16.7	17.3	17.7	17.9
VTx-1	17.3	18.0	19.2	20.1	21.0	22.7	23.6	24.5	24.5	26.8	26.8	28.5
Li-250	17.3	18.0	19.2	—	21.0	—	23.6	—	24.5	—	26.8	28.5

<sup>1</sup> Reduced charge clays obtained by heating (250°C) Li-saturated (Li-250) or partially Li-saturated (Li<sub>x</sub>Na<sub>1-x</sub>-250) samples for 8–12 hr in silica crucibles.

<sup>2</sup> Number of carbon atoms in alkyl chain. The seventeen-carbon amine (heptadecylamine) was unavailable.

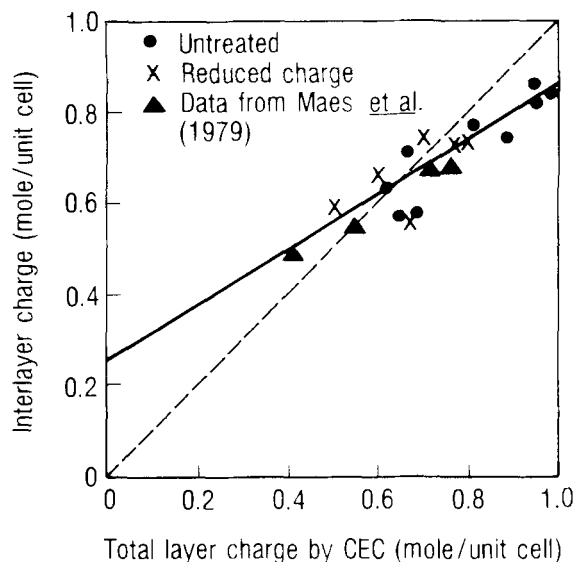


Figure 3. Total layer charge vs. interlayer charge. Dotted line designates equality between the two measures of charge.

CEC reductions were consistent with interlayer charge as estimated by the alkylammonium method (AAM). The  $d(001)$  values of the complexes are presented in Table 4. All full-charge smectites showed a gradual expansion from monolayer to bilayer complex and are, therefore, heterogeneous in charge distribution (Lagaly and Weiss, 1969). Alkylammonium complexes prepared from the dioctahedral smectites after Li saturation and heating (Table 4) yielded smaller basal spacings, thereby confirming that charge reduction had occurred. Except for sample SWy-1, which yielded  $d(001)$  values of 11.3–12.6 Å, the Li-250 montmorillonites showed no expansion, even with the larger alkylammonium cations. Clementz and Mortland (1974) also found that heated, Li-saturated Wyoming montmorillonite (API H-25) expanded with alkylammonium treatment to basal spacings intermediate between those of expanded and collapsed layers. They suggested that the intermediate spacings may have been due to random interstratification between tetrahedrally charged and uncharged layers.

The montmorillonites with partial charge reduction ( $\text{Li}_x\text{Na}_{1-x}$ -250) had basal spacings intermediate between those of the untreated and Li-250 samples and proportional to the amount of Li initially on the exchange complex. These results suggest that layer-charge reduction was a systematic and spatially uniform process. The German nontronite, which derives most of its charge from the tetrahedral sheet, showed only minor reductions in basal spacings after Li saturation and heating. Similarly, no significant differences between spacings of the Li-250 and the untreated trioctahedral samples were noted, indicating little or no charge reduction.

A mean interlayer charge was calculated from the alkylammonium data (Table 4) for all untreated and reduced-charge smectites that expanded to a bilayer complex. These data are presented in Figure 3 as a plot of interlayer charge vs. total layer charge calculated from the corresponding CEC ( $\text{CEC}_0$  or  $\text{MgEC}_R$ ). The interlayer charge was generally lower than the total charge due to the inclusion of crystal edge sites in the latter that were not measured by AAM. Most samples had interlayer to total layer charge ratios of about 0.8 to 0.9, consistent with previously reported results (Lagaly, 1981). In a few samples, interlayer charge slightly exceeded the total charge due to inert impurities in the sample or, more likely, to experimental errors associated with AAM. Because the number of alkylammonium complexes is limited, errors in layer-charge calculations by AAM can be as much as 13% (Lagaly and Weiss, 1969). Similarly, Maes *et al.* (1979) found that differences in charge density of as much as 20% could be accounted for by alkyl chains extending beyond the edges of clay particles.

The plot in Figure 3 was fitted to data collected in the present study using linear regression. Triangular points, from a study of reduced-charge montmorillonites by Maes *et al.* (1979), show good agreement with these data. Extension of the regression line to the y-axis gives a positive intercept, indicating a residual interlayer charge when the total charge is zero. Maes *et al.* (1979) interpreted this anomaly as an indication that the alkylammonium method may overestimate the interlayer charge at low values of total charge. Alternately, the data are not linear at total layer-charge values  $<0.4$  mole/unit cell. In any case, the strong correlation between the two charge determinations suggests that observed CEC reductions reflect true decreases in the layer charge of heated, Li-smectites.

#### Comparison of CEC reduction and octahedral charge

Correspondence between CEC reductions ( $\text{CEC}_0 - \text{MgEC}_R$ ) measured in the present study and octahedral charge values obtained from published mineral formulae is indicated in Figure 4. Any points on the line reflect perfect agreement between experimental measurements and mineral formulae. Data for samples SCA-2, SAz-1, SWy-1, SWa-1, and API #23 are consistent with published results. The agreement is not so good for sample NG-1, but other data (alkylammonium exchange and CEC) suggest that the formula of this sample may be erroneous. Ratios plotted in Figure 4 indicate the proportion of lost exchange capacity after heating Li-saturated, dioctahedral smectites. This method of evaluating the source of charge reduction is similar to that employed by Glaeser *et al.* (1972) for estimating tetrahedral charge by extrapolation of CEC data from a series of reduced-charge samples. In the

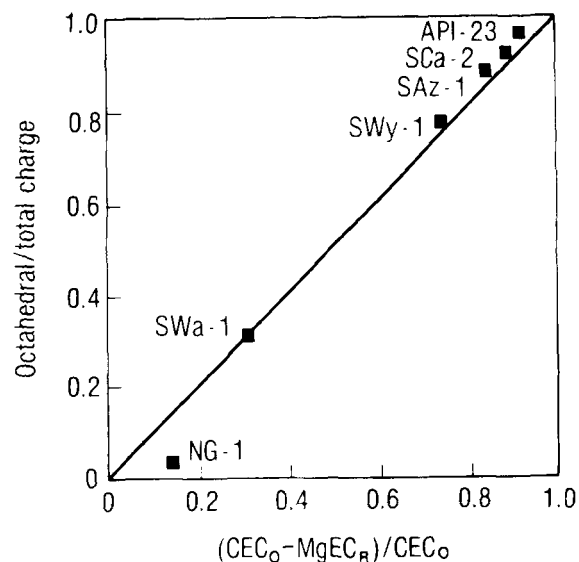


Figure 4. Reduction of cation-exchange capacity ( $CEC_0 - MgEC_R$ ) vs. octahedral layer charge.

present approach, only two values, consisting of the initial and the reduced CEC, are required for calculation of the octahedral charge, and corrections for variable charge contributions from crystal edge sites are not necessary.

#### *Li expulsion and charge reduction in hectorite*

Lithium substitution for Mg in the octahedral sheet of hectorite imparts a negative structural charge, whereas Li apparently neutralizes the octahedral charge in heated, Li-montmorillonite. If the driving force of the Hofmann-Klemen effect is neutralization of octahedral charge, then heating a Mg-saturated hectorite might induce exchange of Mg for Li in the octahedral sheet with a consequent reduction in charge.

To evaluate this possibility, both Mg- and Li-saturated hectorites were heated for 12 hr at 250°C in silica crucibles. The heat-treatment caused the Mg-hectorite to change color from white to black, whereas no color change was noted in the heated Li-hectorite. Chemical data (Table 5) indicate that charge reduction occurred in the Mg-hectorite and that Li was lost from the structure, presumably by partial replacement of octahedral Li by Mg. The Mg-250 hectorite was also acidified as were the Li-250 montmorillonites (Figure 2). In contrast, the Li-250 hectorite remained alkaline and exhibited no charge reduction or change in total Li content.

Charge reduction and loss of octahedral Li in heated, Mg-saturated hectorite suggests that cation movement by the Hofmann-Klemen effect is favored whenever octahedral charge is neutralized. It also demonstrates the mobility of octahedral Li during mild heat treatment and provides further support for the original con-

Table 5. Li expulsion and charge reduction in hectorite (SHCa-1).

Sample <sup>1</sup>	Exchange-able Li (meq/100 g)	MgEC <sub>R</sub> <sup>2</sup> (meq/100 g)	Titrateable acidity (meq/100 g)	CEC reduction (meq/100 g)	Total <sup>3</sup> Li (meq/100 g)
Li-250	—	87.1	0	2.1	83.5
Mg-250	15.0	80.2	0.9	9.0	67.0

<sup>1</sup> Li-250 and Mg-250 samples prepared by heating Li-saturated and Mg-saturated (< 2 μm) specimens, respectively, at 250°C for 12 hr.

<sup>2</sup> MgEC<sub>R</sub> = Reduced CEC obtained by saturating heated (250°C) clays with Mg and measuring Mg displaced with 1 N CaCl<sub>2</sub>.

<sup>3</sup> Total Li content of untreated clay = 82.8 meq/100 g.

clusion of Hofmann and Klemen that charge reduction in heated, Li-saturated dioctahedral clays occurs by the migration of these small ions into vacant octahedral sites.

## SUMMARY AND CONCLUSIONS

Studies of the Hofmann-Klemen effect were complicated by the existence of collapsed interlayers (with entrapped Li) so that direct measurements of readily exchangeable Li after heat treatment led to overestimates of charge reduction. In contrast, expansion of collapsed interlayers with Mg and subsequent determinations of exchangeable Mg provided accurate measurements of reduced charge. In the dioctahedral smectites, excess Li was retained as a consequence of the deprotonation of structural hydroxyl groups coordinated to octahedral Fe. Mild acid treatment of the heated, Li-saturated smectites reprotonated these hydroxyls and released excess Li without alteration of layer charge. Residual total Li contents were comparable to measured charge reductions.

Layer-charge determinations by the alkylammonium method varied systematically with total charge estimates based on CEC and confirmed that uniform charge reduction had occurred in samples with octahedral charge. By comparison, CEC determination appeared to be a more accurate and less time-consuming approach to measure average charge and charge reduction. Because CEC reduction was found to be equivalent to octahedral charge, measurement of the reduction in CEC following Li saturation and heat treatment might be used as a direct index of montmorillonite content in clays. It might also be used to study changes in the proportion of tetrahedral to octahedral charge during weathering.

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