

## THE EFFECT OF HEAT TREATMENTS ON THE TOTAL CHARGE AND EXCHANGEABLE CATIONS OF Ca-, Na-, AND Li-SATURATED KAOLINITE

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**Abstract**—The effect of heat treatments on the total charge and water adsorption by Ca-, Na- and Li-saturated kaolinite was studied using extraction techniques and thermal gravimetric analysis, respectively. Measurements of cation exchange capacity indicated that the total charge of Li-kaolinite was reduced by approximately 50% after heating to 110 or 130°C. In contrast, the total charge of Ca-kaolinite remained essentially constant while that of Na-kaolinite decreased slightly. Water adsorption and desorption on Ca- and Li-kaolinite following heat treatments at 150°C were consistent with the total charge of the respective kaolinites. Ion extraction of Li-kaolinite using NH<sub>4</sub>Cl revealed that only 6% of the Li remained exchangeable after heating, while Al and H were released. Thus, non-exchangeable Li ions not only reduced the total charge of the kaolinite but also displaced Al and H from the kaolinite structure. Infrared spectroscopy also indicated that Li migrated into the kaolinite structure and replaced a portion of the Al from the octahedral sheet. The results presented here indicate that Li-kaolinite represents a surface of reduced charge rather than a surface free of cation-hydration effects. Therefore, Li-kaolinite is not recommended as a reference for the study of vapor-phase adsorption, and conclusions based on such a reference material should be reevaluated.

**Key Words**—Kaolinite, Cation exchange capacity, Water adsorption, Lithium retention.

### INTRODUCTION

The effect of exchangeable ions on the adsorption and desorption of water vapor by kaolinite has been studied in great detail (Jurinak, 1961, 1963; Jurinak and Volman, 1961a, 1961b; Keenan *et al.*, 1951; Martin, 1959). Of particular interest is the Li ion, which has been shown to have no apparent effect on water adsorption. Martin (1959) reported that Li-saturated kaolinite did not exhibit hysteresis due to cation-hydration effects at relative humidities below 80%, whereas Ca-, Mg-, and Na-saturated kaolinites each yielded hysteretic adsorption-desorption isotherms. In addition, kaolinite saturated with Li has been found to adsorb less water than kaolinite saturated with Na, despite the fact that Li has a slightly greater hydration energy than Na (Keenan *et al.*, 1951). Based on these data, Li-saturated kaolinite is generally considered to represent a mineral surface independent of cation-hydration effects and has frequently been utilized as a reference surface in the study of water and organic vapor sorption on kaolinite (Jurinak, 1963; Jurinak and Volman, 1961b; Rhue *et al.*, 1989).

Although published data present strong evidence for the absence of Li hydration, the mechanisms responsible for such behavior have not been clearly identified. Keenan *et al.* (1951) hypothesized that Li ions fit into the tetrahedral layer of kaolinite such that hydration is sterically hindered by the outer oxygen atoms. In contrast, Martin (1959) postulated that the hydration energy of Li is not sufficient to overcome the specific

adsorption energy of the ion for the clay surface, and thus true ionic hydration does not occur. In both of these studies the kaolinite was dried at 70°C in a vacuum prior to the adsorption experiments. This has been shown to be equivalent to air-drying at 115°C (Keenan *et al.*, 1951).

The effect of heating on the cation exchange capacity (CEC) of kaolinite saturated with Ca, Mg, Na, and Li was studied by Greene-Kelly (1955). Interestingly, the CEC of Li-kaolinite, as determined from NH<sub>4</sub> exchange, was only 50% of the original level after heating to 100°C. The heat treatment had no apparent effect on the CEC of Ca-, Mg-, and Na-kaolinites. A reduction in NH<sub>4</sub> exchange by Li-kaolinite after heating to 300°C was also reported by Cashen (1959). These data suggest that the reason water adsorption on Li-saturated kaolinite was less than that of Na-saturated kaolinite was actually due to a reduction in CEC. Keenan *et al.* (1951), Martin (1959), and Jurinak (1961) failed to report the CEC of kaolinite following cation saturation and heat treatments, and were apparently unaware of possible charge reductions upon heating.

Greene-Kelly (1955) also reported that heating substantially decreased the amount of Li that could be extracted from Li-kaolinite using 1 N NH<sub>4</sub>AOC. These data suggest that a portion of the Li ions was fixed within the kaolinite structure. A similar phenomenon, the migration of Li ions into the structure, has been observed for montmorillonite (Brindley and Ertem, 1971; Calvet and Prost, 1971; Greene-Kelly, 1953;

Hofmann and Klemen, 1950; Jaynes and Bigham, 1987; Lim and Jackson, 1986; Luca and Cardile, 1989; Luca *et al.*, 1989; Sposito *et al.*, 1983). It has been referred to as the Hofmann-Klemen effect (Glaeser and Mering, 1971). Two positions have been proposed for the location of non-exchangeable Li ions in montmorillonite: (1) the bottom of the pseudohexagonal cavities of the basal surface; and (2) vacant octahedral sites. Calvet and Prost (1971), using infrared (IR) spectroscopy, found that only a fraction of the non-exchangeable Li resides within the octahedral layer, the remainder being located in the hexagonal cavities. These data were supported by Luca and Cardile (1989), who based their work on electron spin resonance measurements and reported that  $\text{Fe}^{3+}$  migrates into the pseudohexagonal cavities, but not into the vacant octahedral sites of dehydrated montmorillonite. Although there remains some controversy over the exact location of non-exchangeable Li ions, it is clear that upon heating Li migrates into the montmorillonite structure.

The purpose of this study was to determine the effect of heating on the total charge and exchangeable cations of Ca-, Na-, and Li-saturated kaolinites. It was hypothesized that Li migrates into kaolinite upon heating, in a manner similar to that reported for montmorillonite (i.e., the Hofmann-Klemen effect). Infrared spectroscopy was utilized to infer the location of Li ions in heat-treated kaolinite. The effect of heat and vacuum treatments on the adsorption and desorption of water vapor by kaolinite was also studied.

## MATERIALS AND METHODS

### *Kaolinite samples*

The kaolinite samples studied were colloidal kaolinite (K-6, Lot #731063), obtained from Fisher Scientific Products, and KGa-1 kaolinite from Washington County, Georgia, obtained from the Source Clay Minerals Repository of The Clay Minerals Society. The reported CEC values for KGa-1 kaolinite range from 1.7 to 2.4 meq/100 g (van Olphen and Fripiat, 1979). The KGa-1 kaolinite was considered to be well-crystallized, with an  $\text{N}_2$  surface area of  $10.05 \pm 0.02 \text{ m}^2/\text{g}$ . The Fisher kaolinite had a slightly larger CEC (4.2 meq/100 g at pH 5.5) and an  $\text{N}_2$  surface area of  $13.6 \text{ m}^2/\text{g}$ .

### *X-ray diffraction studies*

Mineralogical data for the Fisher kaolinite are lacking. Therefore, X-ray diffraction (XRD) studies were undertaken to provide a preliminary mineralogical characterization and to determine the relative degree of order in the mineral structure. Oriented mounts of Fisher kaolinite were prepared for XRD analysis by depositing  $\sim 300 \text{ mg}$  of kaolinite from suspension onto a ceramic tile under suction. The kaolinite mounts were treated with 1 M  $\text{MgCl}_2$  and KCl, and washed free of

salts with deionized water. A 30% glycerol solution was applied to the Mg-saturated samples. Semirandom powder mounts were also prepared in order to evaluate crystallinity. All mounts were scanned with a computer-controlled XRD system operated at  $2.0^\circ 2\theta$  per minute using  $\text{CuK}\alpha$  radiation. The XRD analyses were performed at room temperature ( $\sim 24^\circ\text{C}$ ) and after overnight heating at 110, 300, and  $550^\circ\text{C}$ .

### *Cation exchange capacity experiments*

Prior to cation saturation, Fisher kaolinite was treated with 1 M NaAOC buffered to pH 4.11 with acetic acid to remove carbonates. Homoionic samples of Ca-, Na-, and Li-saturated Fisher kaolinite were prepared by washing the kaolinite with the appropriate 1 M chloride salt until no other cations were detected in the supernatant using atomic absorption spectroscopy (AAS). Following cation saturation, the kaolinite was repeatedly washed with 95% ethanol until a negative chloride test was achieved using  $\text{AgNO}_3$ . The kaolinite was then air-dried at room temperature and ground with an agate mortar and pestle. With the exception of the NaAOC treatment, the same procedure was followed to saturate the KGa-1 kaolinite with Ca, Na, and Li.

A preliminary experiment was conducted to determine the effect of heating ( $130^\circ\text{C}$ ) on the CEC of Fisher kaolinite saturated with Ca, Na, and Li. The amount of saturating cation which remained exchangeable after 0, 2, 7, and 15 days of exposure to heat was measured using an  $\text{Mg}(\text{NO}_3)_2$  extraction procedure. Approximately 0.5 g of kaolinite was placed in a 50 ml polyethylene centrifuge tube. Ten ml of 0.5 M  $\text{Mg}(\text{NO}_3)_2$  was added to each tube and was mixed until the kaolinite was completely dispersed. The clay was then separated by centrifugation at 2500 rpm for 5 minutes. The supernatant from five  $\text{Mg}(\text{NO}_3)_2$  washes was collected in a 100 ml volumetric flask that was brought to volume with deionized water. The concentration of the appropriate cation (i.e., Ca, Na, Li) in the  $\text{Mg}(\text{NO}_3)_2$  extract was measured by AAS and expressed as meq/100 g. Aluminum was also measured in the  $\text{Mg}(\text{NO}_3)_2$  extracts of Na- and Li-saturated kaolinite on day 15.

After seven days of heating, the total charge of the Ca-, Na-, and Li-saturated Fisher kaolinite was determined by Ca-exchange. An additional 0.5 g sample of kaolinite was placed in a 50 ml polyethylene centrifuge tube. The kaolinite was washed five times with 20 ml of 1 M  $\text{CaCl}_2$ , and excess salt was removed by repeatedly washing the kaolinite with 95% ethanol until a negative chloride test was achieved using  $\text{AgNO}_3$ . Calcium was extracted with 0.5 M  $\text{Mg}(\text{NO}_3)_2$ , following the same procedure as described previously.

A second, more extensive study was initiated to determine the effect of heating at  $110^\circ\text{C}$  on the total charge and exchangeable cations of Ca-, Na-, and Li-saturated Fisher and KGa-1 kaolinite. Approximately 0.5 g of

kaolinite was placed in individual 50 ml polyethylene centrifuge tubes. The samples were washed with 20 ml of 1 M  $\text{NH}_4\text{Cl}$  to extract exchangeable Ca, Na, Li, Mg, and Al. The total charge of the kaolinite was then determined by Ca-exchange, as described previously. During Ca-exchange of the saturating cation, the pH of the Fisher and KGa-1 kaolinite supernatant was approximately 5.3 and 6.0, respectively. The Na- and Li-saturated kaolinite samples were also treated with 0.1 M HCl for 30 minutes to extract additional Na, Li, and Al. All extractions described herein were replicated four times.

#### Hysteresis experiments

Thermal-gravimetric analyses (TGA) of Ca- and Li-saturated Fisher and KGa-1 kaolinite were conducted to determine the effect of heating on water vapor adsorption and desorption. Approximately 15 mg of kaolinite was placed in the sample pan of a computer-controlled thermal-gravimetric analyzer. The samples were equilibrated with a high relative humidity (RH) (~90–95%) air flow stream for 2 hours at 24°C, heated at 150°C (at a rate of 20°C per minute) for 48 hours, and then allowed to reequilibrate with the high RH flow stream at 24°C for ~20 hours. A second treatment sequence consisted of exposure to the high RH flow stream with the temperature alternating between 24°C and 150°C every 2 hours.

A Cahn® electrobalance was used to study the effect of exposure to a vacuum on the adsorption and desorption of water vapor by Ca- and Li-saturated Fisher kaolinite. Approximately 25 mg of kaolinite was placed on a hanging sample pan which was counterbalanced by an empty hanging pan. A glass tube containing water was placed over the sample pan in order to expose the kaolinite to water vapor. The kaolinite was allowed to equilibrate until the sample weight was constant, ~2 hours. The glass tube was then replaced by one containing no water and a vacuum of ~0.18 torr was applied to the system. The kaolinite was allowed to equilibrate for about 8 hours, after which time the system was returned to atmospheric pressure and the empty glass tube was replaced with one containing water. The weight of kaolinite was recorded by an IBM-AT compatible computer connected to the Cahn® microprocessor via an RS-232 cable.

#### Infrared spectroscopy experiments

Suspensions of Fisher kaolinite were made by placing ~1.5 g of kaolinite in 10 ml of deionized water. A sample from the suspension was air-dried onto a small piece of a 25 mm × 2 mm ZnSe disk. The ZnSe was positioned on a standard KBr mount in a sample compartment evacuated to 0.05 torr in order to eliminate interferences from atmospheric  $\text{CO}_2$  and water vapor. Infrared spectra were collected using a Bomem DA3.10

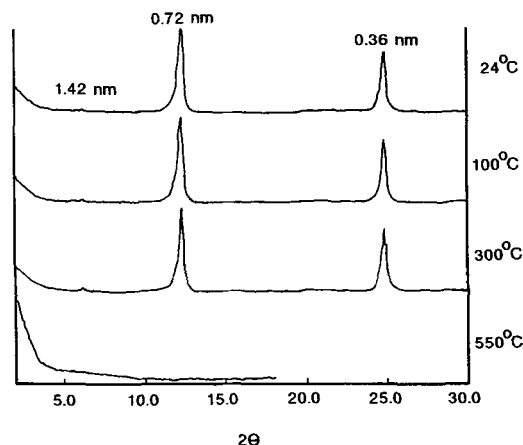


Figure 1. XRD patterns of K-saturated Fisher kaolinite after overnight exposure to the specified temperatures.

Fourier-transform IR spectrometer. The DA3.10 spectrometer was equipped with a Michelson interferometer containing a KBr beamsplitter positioned at a 30° angle to the optical axis. A mercury-cadmium-telluride (MCT) detector with a  $D^*$  value of  $3.13 \times 10^9 \text{ cm}^2\text{Hz}^{0.5}$  and a low-frequency cutoff of  $400 \text{ cm}^{-1}$  ( $25 \mu\text{m}$ ) was used in this study. The Bomem DA3.10 spectrometer was controlled by a DEC Vaxstation-II computer via an IEEE-488 interface. An optical resolution of 2.0 wavenumbers was used for collection of the reported IR spectra.

## RESULTS AND DISCUSSION

#### X-ray diffraction studies

The K-saturated Fisher kaolinite sample exhibited strong peaks at 0.72 and 0.36 nm, which are characteristic of 001 and 002 reflections for kaolinite (Figure 1). A very small peak, located at 1.42 nm, was investigated in more detail to determine if the kaolinite was contaminated with smectite. Heating the sample to 110 and 300°C had no discernable effect on the 1.42 nm peak. All peaks were eliminated at 550°C. Saturation with Mg and glycerol treatment did not result in a shift of the 1.42 nm peak. These data indicate that the 1.42 nm peak was not due to smectite contamination, but was probably attributable to a chlorite of relatively low thermal stability. The K-saturated silt fraction (50–2  $\mu\text{m}$ ) was identical to that of the whole clay, indicating that the 1.42 nm peak existed in both fractions. However, the small peak at 0.99 nm was attributed to mica (Figure 2). A faint peak was also observed in the whole-clay sample near 0.99 nm. The contamination noted here was likely to have little effect on the CEC and surface area of the kaolinite because it appeared to be attributable to non-expanding phyllosilicates of low surface charge.

A comparison of the XRD diffraction patterns for

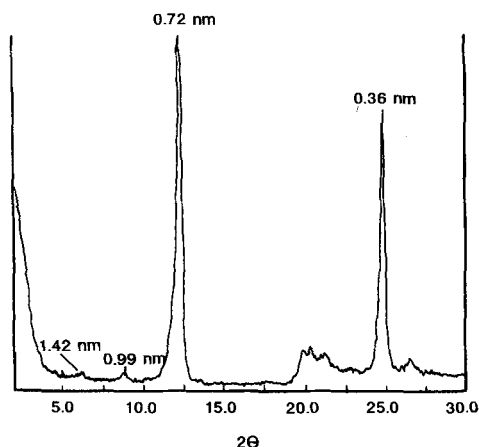


Figure 2. XRD pattern of K-saturated silt fraction of Fisher kaolinite.

the semirandom powder mounts of Fisher kaolinite, well-crystallized Georgia kaolinite, and poorly-crystallized Georgia kaolinite are shown in Figure 3. The 020,  $1\bar{1}0$ ,  $1\bar{1}1$ ,  $1\bar{1}\bar{1}$ ,  $02\bar{1}$ , and 021 reflections were clearly identifiable in the Fisher kaolinite and well-crystallized Georgia kaolinite, but were not readily discernable in the poorly-crystallized Georgia kaolinite. These data suggest that the Fisher kaolinite approached the order of the well-crystallized kaolinite, and thus was considered to be medium- to well-crystallized.

#### Cation exchange capacity

The results of the preliminary CEC experiment are presented in Table 1. After seven days of heating at 130°C the amount of Ca extracted from Ca-saturated Fisher kaolinite remained essentially unchanged, whereas extractable Na and Li were 81 and 10%, respectively, of their original levels. The total charge of Ca- and Na-kaolinite, as determined by Ca exchange, was not affected by the heat treatment, but decreased by about 50% for Li-kaolinite. The disparity between the charge attributable to the saturating cation and that determined by Ca exchange for Na- and Li-kaolinite

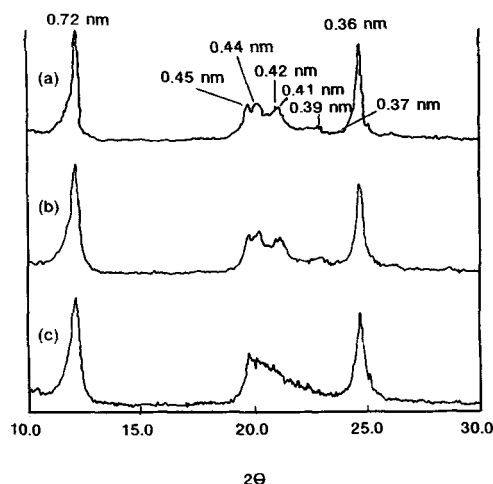


Figure 3. XRD patterns from powder mounts of (a) well-crystallized Georgia kaolinite, (b) Fisher kaolinite, and (c) poorly-crystallized Georgia kaolinite. The d-spacing of the 001, 020,  $1\bar{1}0$ ,  $1\bar{1}1$ ,  $1\bar{1}\bar{1}$ ,  $02\bar{1}$ , 021, and 002 reflections are shown for well-crystallized kaolinite.

suggests that other ions were involved in the exchange process. To test this hypothesis, the  $Mg(NO_3)_2$  extracts of Na- and Li-kaolinite were analyzed for Al on day 15. Aluminum was not detected in the Na-kaolinite extract, but was present in the Li-kaolinite extract. This suggests that Li displaced Al from the kaolinite structure. It should also be noted that the color of the Li-kaolinite changed from white to gray upon heating. The color of Ca-kaolinite was not affected by the heat treatment, while that of Na-kaolinite became darker. A similar color change has been reported for Li-saturated montmorillonite subjected to heat treatment (Jaynes and Bigham, 1987).

To substantiate the findings of the preliminary experiment, a second study was conducted to determine the effect of heating on the CEC and extractable cations of kaolinite. The total charge determined by Ca exchange of Fisher and KGa-1 kaolinite air-dried at 110°C is presented in Table 2. After seven days of heating,

Table 1. Results of preliminary experiments to determine the effect of heating at 130°C on the CEC of Ca-, Na-, and Li-saturated Fisher kaolinite.

Elapsed days of heating	Extraction method	Ca-kaolinite, meq/100 g	Na-kaolinite, meq/100 g	Li-kaolinite, meq/100 g
0	$Mg(NO_3)_2$ <sup>1</sup>	4.107 ± 0.005	3.547 ± 0.056	3.809 ± 0.039
2	$Mg(NO_3)_2$	3.951 ± 0.018	3.034 ± 0.057	0.598 ± 0.014
7	$Mg(NO_3)_2$	3.981 ± 0.031	2.862 ± 0.066	0.391 ± 0.027
	$CaCl_2$ <sup>2</sup>	3.709 ± 0.032	3.523 ± 0.022	1.985 ± 0.009
15	$Mg(NO_3)_2$	—	2.283 ± 0.022	0.209 ± 0.007
	$Mg(NO_3)_2/Al$ <sup>3</sup>	—	0.000 ± 0.000	0.819 ± 0.015

<sup>1</sup>  $Mg(NO_3)_2$  extraction of the saturating cations.

<sup>2</sup>  $CaCl_2$  wash, 95% ethanol rinse, and  $Mg(NO_3)_2$  extraction of Ca.

<sup>3</sup>  $Mg(NO_3)_2$  extraction of Al.



Table 2. Total charge of Ca-, Na-, and Li-saturated Fisher and KGa-1 kaolinites as determined by Ca exchange, after oven-drying at 110°C.

Elapsed days of heating	Cation exchange capacity		
	Ca-kaolinite, meq/100 g	Na-kaolinite, meq/100 g	Li-kaolinite, meq/100 g
Fisher kaolinite			
0	3.938 ± 0.050	4.272 ± 0.041	3.789 ± 0.005
2	3.597 ± 0.016	3.667 ± 0.022	2.450 ± 0.058
7	3.445 ± 0.054	3.485 ± 0.025	1.947 ± 0.019
KGa-1 kaolinite			
0	2.443 ± 0.011	2.453 ± 0.032	2.149 ± 0.025
2	2.434 ± 0.009	2.306 ± 0.025	1.766 ± 0.072
8	2.075 ± 0.027	1.803 ± 0.019	1.291 ± 0.020
18	2.301 ± 0.003	1.951 ± 0.005	1.450 ± 0.029

the total charge of Ca-, Na-, and Li-saturated Fisher kaolinite was 87, 82, and 51%, respectively, of the charge prior to heating. The KGa-1 kaolinites exhibited a similar trend after 18 days of heating, although the decrease in charge of Ca- and Li-kaolinite was less than that of the corresponding Fisher kaolinite. The reduction in total CEC of Li-kaolinite was consistent with the findings of Greene-Kelly (1955) and Cashen (1959). In addition, no chloride was detected in the Mg(NO<sub>3</sub>)<sub>2</sub> extracts, indicating that positive charges did not develop as a result of heating.

The effect of heating on the amount of Ca, Na, Li, Mg, and Al extracted from Fisher and KGa-1 kaolinites

is presented in Tables 3 and 4, respectively. A slight decrease in extractable Ca was observed for Ca-kaolinite, along with trace amounts of Na, Mg, and occasionally Al. In contrast, Li-kaolinite exhibited a dramatic decrease in exchangeable Li upon heating, with a corresponding increase in Al. The retention of Li ions after heating has also been reported for Li-saturated Peerless No. 2, English Clays, and Merck kaolinite (Greene-Kelly, 1955). A similar trend was observed for Na-kaolinite, but to a much lesser degree than for Li-kaolinite. It should be noted that the Fisher and KGa-1 kaolinite exhibited an almost identical decrease in the percentage of Li ions extracted with 1 M NH<sub>4</sub>Cl. However, the initial reduction (day 2) in extractable Li was less than that measured at 130°C, which suggests that temperature influenced the rate of Li retention. The data presented here clearly demonstrate that heating Li-saturated kaolinite results in Li retention and a decrease in total CEC.

The sum of charge attributable to Ca, Na, Mg, and Al extracted from Ca-saturated Fisher and KGa-1 kaolinite remained essentially constant over the treatment periods (Figures 4 and 5). These data are in agreement with the total charge measured by Ca-exchange. In contrast, the sum of cation charges for Na-kaolinite decreased slightly, while that of Li-kaolinite decreased substantially as a result of heating. Figures 4c and 5c indicate that Al was the dominant exchange cation present on the surface of Li-kaolinite after heating, and

Table 3. Charge attributable to Ca, Na, Li, Mg, and Al extracted from Ca-, Na-, and Li-saturated Fisher kaolinite using 1 M NH<sub>4</sub>Cl, after oven-drying at 110°C.

Elapsed days of heating	Cation extracted	Ca-kaolinite, meq/100 g	Na-kaolinite, meq/100 g	Li-kaolinite, meq/100 g
0	Ca	3.845 ± 0.038	0.075 ± 0.002	0.010 ± 0.002
	Na	0.052 ± 0.010	3.671 ± 0.039	0.062 ± 0.004
	Li	—	—	3.597 ± 0.023
	Al	0.000 ± —	0.000 ± —	0.000 ± —
	Mg	0.025 ± 0.001	0.031 ± 0.001	0.024 ± 0.001
2	Ca	3.684 ± 0.023	0.048 ± 0.000	0.000 ± —
	Na	0.110 ± 0.002	3.013 ± 0.037	0.114 ± 0.006
	Li	—	—	1.163 ± 0.076
	Al	0.097 ± 0.034	0.164 ± 0.039	0.601 ± 0.024
	Mg	0.027 ± 0.002	0.029 ± 0.002	0.020 ± 0.001
7	Ca	3.623 ± 0.018	0.053 ± 0.005	0.000 ± —
	Na	0.157 ± 0.006	2.828 ± 0.031	0.153 ± 0.002
	Li	—	—	0.315 ± 0.004
	Al	0.102 ± 0.007	0.142 ± 0.010	0.977 ± 0.085
	Mg	0.025 ± 0.001	0.027 ± 0.000	0.011 ± 0.001
15	Ca	3.512 ± 0.018	0.044 ± 0.009	0.000 ± —
	Na	0.173 ± 0.002	2.737 ± 0.022	0.195 ± 0.015
	Li	—	—	0.245 ± 0.007
	Al	0.000 ± —	0.157 ± 0.056	1.198 ± 0.066
	Mg	0.030 ± 0.001	0.020 ± 0.000	0.004 ± 0.002
40	Ca	3.554 ± 0.015	0.039 ± 0.003	0.000 ± —
	Na	0.191 ± 0.003	2.624 ± 0.058	0.183 ± 0.006
	Li	—	—	0.205 ± 0.005
	Al	0.000 ± —	0.187 ± 0.032	0.905 ± 0.019
	Mg	0.026 ± 0.003	0.022 ± 0.001	0.007 ± 0.004

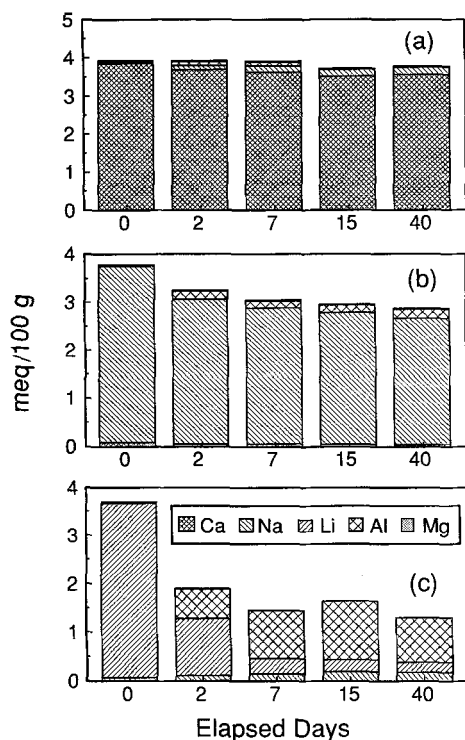


Figure 4. The sum of Ca, Na, Li, Mg, and Al extracted from (a) Ca-, (b) Na-, and (c) Li-saturated Fisher kaolinite using 1 M  $\text{NH}_4\text{Cl}$ .

suggest that a portion of the Li retained by the kaolinite displaced Al from the clay structure. These data are contrary to those reported by Greene-Kelly (1955), who extracted only trace amounts of Al from Li-kaolinite before and after heating, using a 0.001 M HCl and 1 M  $\text{NH}_4\text{Cl}$  extraction procedure. However, Greene-Kelly (1955) apparently washed the kaolinite with 1 M  $\text{NH}_4\text{OAc}$  (pH 7) prior to extracting Li ions. This treatment may have precipitated exchangeable Al, which would not be extractable with the weak acid and  $\text{NH}_4\text{Cl}$ .

Even though Al was the dominant exchange cation on the surface of Na- and Li-kaolinite, a considerable difference remained between the total charge as determined by Ca exchange and that determined from the sum of extractable Ca, Na, Li, Mg, and Al. This discrepancy suggests that other cations contributed to the total charge of the kaolinite. Interestingly, Cashen (1959) reported that heated samples of Na- and Li-saturated Peerless No. 2 kaolinite were far more acid than untreated samples. Thus, the heating of Li-kaolinite and subsequent retention of Li ions also may have caused the displacement of H ions from the clay structure. This hypothesis is supported by Farmer and Russell (1967), who proposed that a portion of the Li ions that migrate into montmorillonite react with interlayer water or structural hydroxyls to liberate protons. Although the inclusion of H ions may bring the charge

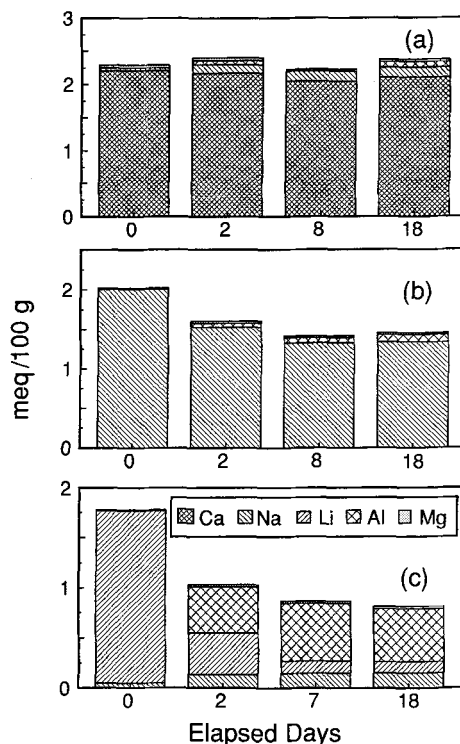


Figure 5. The sum of Ca, Na, Li, Mg, and Al extracted from (a) Ca-, (b) Na-, and (c) Li-saturated Fisher kaolinite using 1 M  $\text{NH}_4\text{Cl}$ .

determined from the sum of extractable cations into agreement with the value obtained by Ca-exchange, the fact remains that the heat treatment reduced the total charge of both Na- and Li-kaolinite.

In an attempt to extract non-exchangeable Na and Li from the heat-treated Fisher kaolinite, the kaolinite was washed with 0.1 M HCl for successive 15-minute intervals. However, only a small amount of Li and trace levels of Na were recovered (Table 5). A total elemental analysis of the heat-treated kaolinite would likely recover all of the retained Li. However, the exact quantity of Li involved in charge reduction would still be difficult to ascertain. Following the original heat treatment, Greene-Kelly (1955) reported that Peerless kaolinite was capable of fixing an additional 11 meq/100 g of Li after nine LiCl washes and heat treatments, with a further reduction in total charge of only 0.5 meq/100 g. These data, although somewhat puzzling at first, suggest that only a portion of the retained Li was actually involved in charge reduction, while the remainder displaced Al and H ions which were then exchangeable.

#### Adsorption and desorption of water vapor

The adsorption and desorption of water following heating of Ca- and Li-saturated Fisher kaolinite, as measured by TGA, are presented in Figures 6, 7, and

Table 4. Charge attributable to Ca, Na, Li, Mg, and Al extracted from Ca-, Na-, and Li-saturated KGa-1 kaolinite using 1 M NH<sub>4</sub>Cl, after oven-drying at 110°C.

Elapsed days of heating	Cation extracted	Ca-kaolinite, meq/100 g	Na-kaolinite, meq/100 g	Li-kaolinite, meq/100 g
0	Ca	2.199 ± 0.012	0.000 ± —	0.000 ± —
	Na	0.044 ± 0.007	2.000 ± 0.022	0.047 ± 0.004
	Li	—	—	1.719 ± 0.014
	Al	0.000 ± —	0.000 ± —	0.000 ± —
	Mg	0.043 ± 0.001	0.019 ± 0.002	0.011 ± 0.002
2	Ca	2.164 ± 0.012	0.000 ± —	0.000 ± —
	Na	0.124 ± 0.007	1.522 ± 0.035	0.131 ± 0.006
	Li	—	—	0.417 ± 0.012
	Al	0.064 ± 0.038	0.144 ± 0.013	0.460 ± 0.044
	Mg	0.045 ± 0.001	0.028 ± 0.001	0.025 ± 0.003
8	Ca	2.038 ± 0.021	0.000 ± —	0.000 ± —
	Na	0.151 ± 0.003	1.324 ± 0.023	0.147 ± 0.003
	Li	—	—	0.125 ± 0.001
	Al	0.000 ± —	0.067 ± 0.067	0.569 ± 0.019
	Mg	0.031 ± 0.001	0.023 ± 0.008	0.013 ± 0.001
18	Ca	2.101 ± 0.014	0.000 ± —	0.000 ± —
	Na	0.149 ± 0.004	1.334 ± 0.017	0.152 ± 0.007
	Li	—	—	0.113 ± 0.005
	Al	0.085 ± 0.056	0.092 ± 0.031	0.524 ± 0.049
	Mg	0.038 ± 0.002	0.024 ± 0.001	0.023 ± 0.003

8. Figures 6 and 7 are representative of the weight change recorded for Fisher and KGa-1 kaolinite samples exposed to an air flow stream at ~90–95% RH, subject to the following sequence of heat treatments: (1) room temperature for two hours, (2) 150°C for 48 hours, and (3) room temperature for approximately 24 hours. The Ca- and Li-kaolinites regained an average of  $98.9 \pm 1.8\%$  and  $46.3 \pm 1.3\%$ , respectively, of their original weight loss due to the 150°C heat treatment. The degree of hysteresis exhibited by Li-kaolinite was consistent with the 50% reduction in the total charge measured for Li-kaolinite after seven days at 110 and 130°C. The absence of hysteresis observed for Ca-kaolinite was in agreement with the stability of the total charge of Ca-kaolinite upon heating. The KGa-1 kaolinite also exhibited hysteresis. Ca- and Li-saturated KGa-1 kaolinite regained  $84.8 \pm 5.2\%$  and  $57 \pm 5.0\%$ ,

respectively, of their original weight loss after heating. The total charge reduction of Ca- and Li-kaolinite was 94 and 67%, respectively, of the level prior to heating. This discrepancy may have been due to particle coalescence of the well-crystallized KGa-1 kaolinite during heat treatments. However, the overall similarity between the magnitudes of hysteresis and reduction in total charge of kaolinite upon heating suggests that the reduced water adsorption observed for Li-kaolinite was simply due to a reduction in the total CEC of Li-kaolinite.

The percentage of weight regained by Li- ( $55.5 \pm 3.5\%$ ) and Ca-saturated ( $97 \pm 2.5\%$ ) Fisher kaolinite subjected to temperatures of 24 and 150°C for alternating two hour intervals was essentially the same as that measured after 48 hours at 150°C (Figure 8). These data indicate that a 2-hour treatment at 150°C was

Table 5. Amount of Li, Na, and Al extracted from Na- and Li-saturated Fisher kaolinite using 0.1 M HCl, after oven-drying at 110°C.

Elapsed days of heating	HCl Trt., min	Na-kaolinite, meq/100 g		Li-kaolinite, meq/100 g	
		Na	Al	Li	Al
0	15	—	—	0.000 ± —	1.040 ± 0.009
	30	—	—	0.000 ± —	0.295 ± 0.011
2	15	0.011 ± 0.001	1.577 ± 0.022	0.007 ± 0.000	0.995 ± 0.051
	30	0.005 ± 0.000	0.443 ± 0.014	0.000 ± —	0.478 ± 0.045
7	15	0.014 ± 0.001	1.519 ± 0.013	0.025 ± 0.002	1.169 ± 0.020
	30	0.002 ± 0.000	0.699 ± 0.021	0.008 ± 0.001	0.721 ± 0.062
15	15	0.014 ± 0.013	1.531 ± 0.443	0.019 ± 0.001	1.046 ± 0.026
	30	0.001 ± 0.001	0.395 ± 0.021	0.006 ± 0.002	0.356 ± 0.012
40	15	0.000 ± —	1.758 ± 0.049	0.042 ± 0.062	1.344 ± 0.042
	30	0.000 ± —	0.356 ± 0.016	0.010 ± 0.001	0.345 ± 0.024

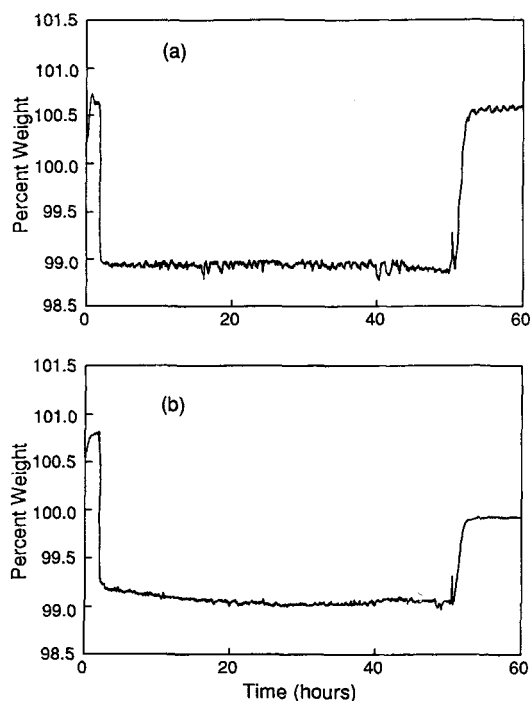


Figure 6. Adsorption and desorption of water by (a) Ca-saturated and (b) Li-saturated Fisher kaolinite exposed to a high RH air flow stream for 2 hours at 24°C, heated to 150°C for 48 hours, and then allowed to reequilibrate with the high RH air flow stream at 24°C.

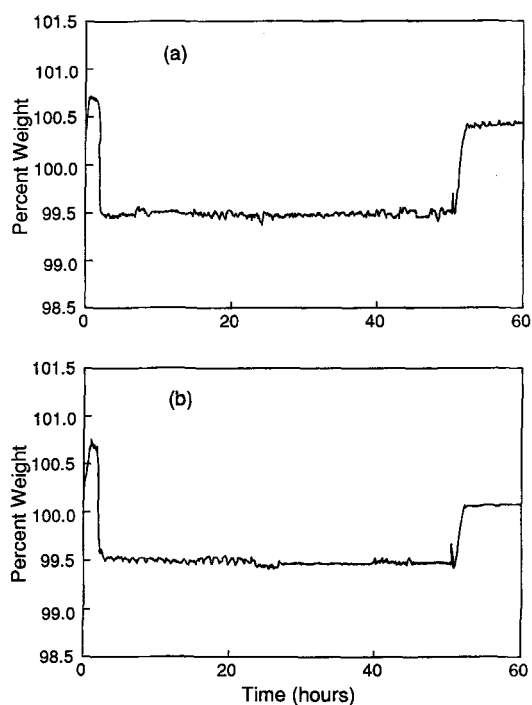


Figure 7. Adsorption and desorption of water by (a) Ca-saturated and (b) Li-saturated KGa-1 kaolinite exposed to a high RH air flow stream for 2 hours at 24°C, heated to 150°C for 48 hours, and then allowed to reequilibrate with the high RH air flow stream at 24°C.

sufficient to reduce water adsorption to a level corresponding to the charge reduction observed after 7 days at 110 and 130°C. This finding is consistent with the increased rate of Li retention observed at 130°C versus 110°C, and indicates that temperature influences the rate of Li retention and CEC reduction.

Similar experiments were conducted to determine if exposure to a vacuum would induce hysteresis by Li-saturated Fisher kaolinite. After equilibration in a high RH atmosphere, Ca- and Li-kaolinite regained  $67 \pm 6.0\%$  and  $54 \pm 1.0\%$  of the weight lost following exposure to the vacuum (Figure 9). The considerable hysteresis observed for Ca-kaolinite suggests that the actual effect of the vacuum on water adsorption by Li-kaolinite was minimal. It is possible that the vacuum resulted in considerable particle coalescence. Thus, even though the results of these experiments suggest that the vacuum treatment induced a slight reduction in the water-adsorption capacity of Li-kaolinite, the utility of such a technique is limited by coincidental hysteresis effects.

#### Location of non-exchangeable Li

The location of exchangeable cations on kaolinite is considered to be limited to the basal plane of the tetrahedral layer, in response to permanent charge arising

from the substitution of  $\text{Al}^{3+}$  for  $\text{Si}^{4+}$  in the outer tetrahedral sheet (Bolland *et al.*, 1976; Follet, 1965; Weiss and Russow, 1963). However, a portion of the negative charge may still be the result of pH-dependent charges. Reduced water adsorption on Li-kaolinite led Keenan *et al.* (1951) to propose that Li occupied a position in the tetrahedral layer from which hydration was sterically hindered by outer oxygen atoms. However, other cations, although small enough to fit between oxygen atoms of the tetrahedral layer, were readily hydrated. Greene-Kelly (1955) was aware of the fact that Li retention and CEC reductions occurred after heating Li-kaolinite. He proposed that Li ions migrate into vacant octahedral coordination sites, as has been suggested to explain a similar phenomenon in montmorillonite. The inner hydroxyls of kaolinite, which are oriented toward the octahedral cavity, yield an IR spectra band at  $3620 \text{ cm}^{-1}$ . It was hypothesized that the migration of Li into vacant octahedral sites would alter the orientation of inner hydroxyls, resulting in a shift in the  $3620 \text{ cm}^{-1}$  band or the creation of several unresolved bands.

Infrared spectra obtained from air-dried Na- and Li-saturated Fisher kaolinite, and heat-treated Li-saturated Fisher kaolinite are shown in Figure 10. The  $3575\text{--}3725 \text{ cm}^{-1}$  region was deconvoluted using a non-linear, least-squares fitting program to quantitatively



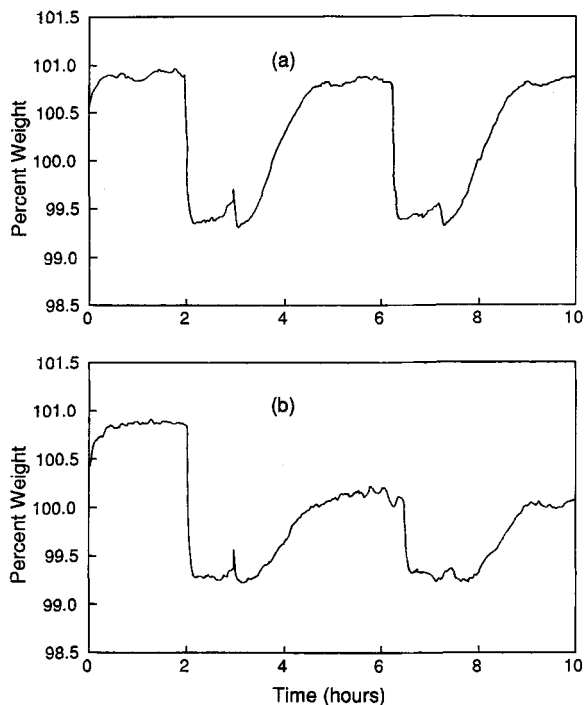


Figure 8. Adsorption and desorption of water by (a) Ca-saturated and (b) Li-saturated Fisher kaolinite exposed to a high RH air flow stream and repeated 150°C heat treatments.

determine the position, width, and intensity of each band. Air-dried Na-kaolinite yielded a single band at  $3620\text{ cm}^{-1}$ , whereas heat-treated Li-kaolinite exhibited bands at  $3620\text{ cm}^{-1}$  and  $3615\text{ cm}^{-1}$ . Two plausible explanations exist to account for the alteration of the inner hydroxyl stretching band: (1) Li migration into vacant octahedral sites or (2) Li replacement of Al within the kaolinite structure. Previous studies using montmorillonite demonstrated that Li migration into vacant octahedral sites results in the formation of bands of greater wave number (Calvet and Prost, 1971). Therefore, it was postulated that a portion of the Al in the octahedral sheet was replaced by Li ions. This hypothesis is consistent with the observed displacement of Al from kaolinite, and suggests that Li migration into the kaolinite structure was directly responsible for the reduction in charge of Li-kaolinite upon heating.

### CONCLUSIONS

In a number of vapor phase adsorption studies Li-saturated kaolinite has been utilized as a reference mineral surface, considered to be independent of cation-hydration effects. However, the data presented here indicate that the heating of Li-kaolinite, and to a lesser extent Na-kaolinite, results in a decrease in the total CEC of the kaolinite. This effect was manifested in measurements of water adsorption following heating, which were directly related to the magnitude of CEC

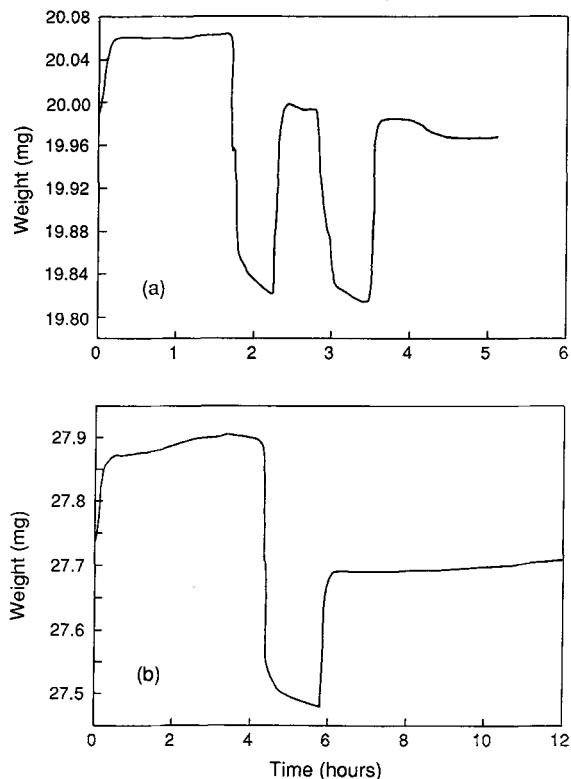


Figure 9. Adsorption and desorption of water by (a) Ca-saturated and (b) Li-saturated Fisher kaolinite equilibrated with water vapor, subjected to a vacuum of  $\sim 0.18$  torr, and reequilibrated with water vapor.

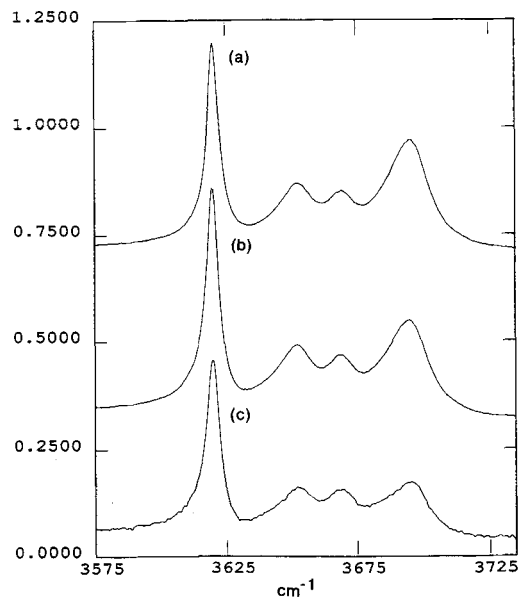


Figure 10. IR spectra of (a) air-dried Na-saturated, (b) oven-dried Li-saturated, and (c) air-dried, Li-saturated Fisher kaolinite in the inner hydroxyl stretching region.

reduction determined by Ca-exchange. These findings suggest that the reduced water adsorption observed for Li-kaolinite in previous studies was actually the result of a decrease in the CEC of heated Li-kaolinite samples. Therefore, heat-treated Li-kaolinite represents a surface of reduced charge, rather than a surface free of cation-hydration effects.

Extraction of Li-kaolinite with  $\text{NH}_4\text{Cl}$  revealed that only 6% of the Li ions remained exchangeable after heat treatment. A considerable amount of Al was extracted from the Li-kaolinite, and yet the sum of Al, Li, Mg, Na, and Ca accounted for only 75% of the reduced CEC. Based on previous reports of increased acidity following heating, it appears likely that H contributed to the residual charge. Thus, the remaining exchange capacity of the heated Li-kaolinite was satisfied by Li, Al, and possibly H.

The Li ions rendered non-exchangeable by heating apparently acted to (1) reduce the total charge, and (2) displace Al and H from the structure. The fact that an additional 11 meq/100 g of Li reportedly has been introduced to kaolinite with only a corresponding 0.5 meq/100 g reduction in total charge suggests that the magnitude of total charge reduction is fixed or limited, whereas a considerable quantity of Al and H can be displaced from the structure. Infrared spectroscopy suggests that Li migrated into the kaolinite structure and replaced a portion of the Al from the octahedral sheet. Regardless of the specific location of Li ions in the kaolinite structure, these data demonstrate that heated Li-kaolinite cannot be treated as a reference surface, and conclusions drawn from such an assumption should be reevaluated. In particular, the assumption that Li-kaolinite is free of cation-hydration effects may lead to erroneous estimates of the number of water molecules associated with each exchangeable cation (e.g., Keenan *et al.*, 1951).

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