

PREPARATION AND CHARACTERIZATION OF REDUCED-CHARGE HECTORITES

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Abstract—A series of reduced-charge (RC) hectorites were prepared by multiple heat (250°C) treatments of Mg-saturated hectorites (SHCa-1). Cation exchange capacity (CEC) measurements and alkylammonium exchange indicated that a decrease in layer charge occurred with each Mg-250 treatment. Chemical analyses showed that decreases in structural Li and increases in structural Mg contents coincided with charge reduction. Fluorescence measurements of adsorbed quinoline indicated that the hectorite surface was acidified during charge reduction; hydroxyl group deprotonation is a possible source for the acidity. Fourier transform infrared spectra (FTIR) indicated that the Mg-250 treatment induced the loss of structural Li and shifted the SiO stretch band to a position similar to that in talc. The relative intensities of the OH and SiO stretch bands in FTIR spectra suggest that some of the hydroxyl groups in hectorite were lost, possibly by deprotonation. However, thermogravimetric data (TG) reveal no significant difference in the hydroxyl contents of the hectorites.

The FTIR spectra, CEC, layer charge, chemical, and TG data all supported the view that Mg substitution for octahedral Li occurred which resulted in a more "talc-like" structure. Charge reduction in smectites is evidently a general phenomenon and can be induced by heat treatment with the proper exchangeable cation. The ability to reduce the charge of hectorites makes it possible to prepare a series of clays which vary in charge but lack structural Fe. Such RC smectites should be suitable for expandable clay mineral studies which utilize spectroscopic techniques that are sensitive to Fe content.

Key Words—Alkylammonium exchange, Cation exchange capacity, Dehydroxylation, Deprotonation, Fluorescence, Infrared spectroscopy, Quinoline, Surface acidity, Thermogravimetry.

INTRODUCTION

Reduced-charge (RC) montmorillonites produced by the heating of Li-saturated samples (Hofmann and Klemen, 1950) have been used to relate layer charge to other clay mineral properties. For example, Calvet and Prost (1971) and Sposito *et al.* (1983) employed a series of RC montmorillonites and infrared (IR) spectroscopy to examine relationships between layer charge and solvation properties. Brindley and Ertem (1971) investigated the effect of layer charge on the expansibility of RC montmorillonites solvated in H₂O and in selected organic solvents.

Unfortunately, the octahedral Fe²⁺ and Fe³⁺ in montmorillonites renders them unsuitable for many studies employing optical spectroscopies sensitive to electronic transitions (Traina, 1990). Chen *et al.* (1979) found that structural Fe³⁺ in montmorillonites strongly absorbs ultraviolet (UV) light. Hectorite, on the other hand, contains little or no Fe and has been utilized in a number of fluorescence and UV/VIS absorption/transmission studies. The production of RC hectorites would facilitate studies of the effects of layer charge on electronic transitions in molecules adsorbed onto hectorite, but Li-induced charge reduction cannot be used because all of the octahedral sites in hectorite are oc-

cupied. Furthermore, the layer charge in hectorite is attributed to the natural substitution of Li⁺ for Mg²⁺ in the octahedral sheet. The incorporation of any additional Li⁺ into this region could only occur at the expense of Mg²⁺ and cause an increase in cation exchange capacity (CEC).

Jaynes and Bigham (1987) found that charge reduction could be induced in hectorite by heat treatment (250°C) of a Mg-saturated sample. Loss of structural Li⁺ and acidification coincided with a decrease in layer charge. Jaynes and Bigham (1987) attributed the charge reduction in hectorite to the migration of Mg²⁺ ions into octahedral sites formerly occupied by Li⁺ ions, and the acidification to deprotonation of structural hydroxyl groups. Manipulation of this technique could provide a series of RC hectorites with a range in CEC which would facilitate studies on the effects of layer charge on the electronic transitions in adsorbed molecules.

The surface acidity of clays can be measured from the extent to which adsorbed organic bases are protonated by the clay (Rupert *et al.*, 1987). Karickhoff and Bailey (1976) found that clays protonate many organic bases to a greater extent than would be predicted by suspension pH and organic base pK_a. Ainsworth *et al.* (1987) determined that the cationic form

of quinoline, an organic base, was preferentially sorbed by clays even at $\text{pHs} \gg \text{pK}_a$, and Traina (1990) found that only the protonated form of quinoline fluoresces. Hence, the fluorescence of adsorbed quinoline can be used as an indirect measure of surface acidity.

In this paper, the effects of sequential Mg-saturation and heating on the chemical properties of hectorite will be investigated. The objectives of this study are to prepare a series of RC hectorites, further evaluate the nature of the charge reduction, and demonstrate the utility of the RC hectorites in spectroscopic studies by assessing their surface acidity from the fluorescence of adsorbed quinoline.

MATERIALS AND METHODS

Charge reduction

Hectorite (SHCa-1) was obtained from the Source Clay Repository of The Clay Minerals Society. A 200-g sample of SHCa-1 was treated with $\text{pH} = 5$, Na-acetate/acetic acid buffer ($\text{pH} = 5$, M NaOAc/HOAc) to remove carbonates, and then washed free of salts with H_2O . This sample was dispersed in H_2O and wet-sedimented to separate the $<2\text{-}\mu\text{m}$ fraction. The resulting SHCa-1 clay was Mg-saturated with 0.5 M MgCl_2 , washed free of salts, frozen, and freeze-dried. A 20-g subsample of the freeze-dried, Mg-saturated, $<2\text{-}\mu\text{m}$ size fraction was washed three times with 50 ml of 0.5 M MgCl_2 followed by three H_2O washings to remove excess salts. This sample was subsequently oven-dried (60°C), placed in a quartz crucible, and heated at 250°C for 8–12 hr. A quartz crucible was used rather than glass in order to avoid possible ion-exchange reactions with glass that could affect the charge reduction process (Byström-Brusewitz, 1976; Lim and Jackson, 1986). The heated sample was then removed from the crucible and ground in an agate mortar. A 2-g subsample, designated Mg-250I, was placed in a glass vial and saved for later analysis. The remaining material was washed with 50 ml of $\text{pH} = 5$, M NaOAc-HOAc buffer, Mg-saturated with three washes of 0.5 M MgCl_2 , washed free of excess salt, and heated (250°C) for 8–12 hr. The NaOAc-HOAc wash served to re-expand the clays and remove exchangeable Li. The material was then ground in an agate mortar and a 2-g subsample (Mg-250II) was removed for later analysis. The above process was repeated until a total of nine RC samples (Mg-250I, Mg-250II, . . . Mg-250IX) were obtained.

Chemical analysis

Subsamples of (150 mg) of SHCa-1 and Mg-250I to Mg-250IX were washed three times with 5-ml aliquots of $\text{pH} = 5$, M NaOAc-HOAc buffer to promote expansion of collapsed layers and assure complete removal of exchangeable Mg and Li. The clays were then washed three times with 5 ml of 0.5 M CaCl_2 , followed by three

washes with H_2O . The clays were subsequently dried at 110°C .

Acid digests were obtained from each clay by weighing 25–50 mg into a Teflon-lined decomposition bomb that contained 4 ml of concentrated HF and 3 drops of aqua regia; complete dissolution was achieved by heating the sealed bombs for 1 hr at 110°C (Bernas, 1968). Following acid dissolution, the digests were diluted to 100 ml and analyzed for Li by flame emission spectroscopy, and for Mg by atomic absorption spectroscopy.

Separate, Ca-saturated subsamples (50 mg) were fused with NaOH in Ni crucibles and subsequently dissolved in 1 liter of H_2O that was acidified with HCl. The resulting solutions were analyzed for total SiO_2 by the molybdenum blue colorimetric method of Shapiro and Brannock (1962).

Cation-exchange capacity

Using both Na and Ca as index cations, CEC values were obtained for the natural and RC hectorites by employing a mechanical extractor as described by Jaynes and Bigham (1986). Briefly, clay samples were weighed (0.3–0.4 g), mixed with 0.5 g Celite powdered paper pulp, and transferred to extraction tubes. The extraction tubes were placed on a mechanical extractor and Na-saturated by an 8 hr extraction with 50 ml of $\text{pH} = 7$, M NaCl. Excess salts were removed by one extraction with 50 ml of 0.04 M NaCl, followed by two extractions with 50 ml of 95% ethanol. Exchangeable Na was then displaced by an 8-hr extraction with 50 ml of $\text{pH} = 7$, 0.5 M CaCl_2 . Concentrations of Na in the extracts were determined using flame emission spectroscopy and were used to calculate Na-exchange capacity (NaEC) values.

After exchangeable Na^+ was displaced with Ca^{2+} , excess salts in the Ca-saturated clays were removed by one extraction with 50 ml of 0.01 M CaCl_2 , followed by two 50-ml extractions with 95% ethanol. Exchangeable Ca^{2+} was then displaced by an 8-hr extraction with 50 ml of $\text{pH} = 7$, 0.5 M MgCl_2 . Concentrations of Ca in the extracts were determined by atomic absorption spectroscopy and were used to calculate Ca-exchange capacity (CaEC) values. All CEC values were calculated on an oven-dry (110°C) basis and expressed in meq/100 g of clay.

Alkylammonium exchange

Octadecylammonium (C18) complexes of natural and RC hectorite samples were prepared as oriented aggregates on glass slides using a modification of the method of Rühlicke and Kohler (1981). Octadecylammonium chloride (4 ml, 0.05 M) was added to 30-mg clay samples in 15 ml centrifuge tubes. The clay samples were sealed in the tubes and then equilibrated at 60°C for 12 hr. The alkylammonium-clays were subsequently washed three times with 5 ml aliquots of

95% ethanol, ultrasonically dispersed in 2 ml of ethanol, and dried on glass slides. All prepared slides were stored under vacuum until immediately prior to X-ray analysis. Basal X-ray diffraction spacings were 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.

Infrared spectroscopy

A 5-mg sample of Mg-saturated SHCa-1 was mixed with 195 mg of spectroscopic-grade KBr and ground with a sapphire mortar and pestle. The resulting powder was oven-dried under vacuum (110°C) for 48 hr and then stored over P_2O_5 for 1 week. This process was repeated for samples Mg-250I through Mg-250IX and for a sample of talc (<2- μm fraction) obtained from the J. T. Baker Company. Powdered samples were hand-packed into a 3-mm conical sample cup and the upper surface was smoothed with a glass microscope slide. Diffuse reflectance, Fourier transform infrared spectra (DR-FTIR) were then measured on each sample using a Mattson-Polaris FTIR equipped with a broad-band mercury-cadmium-telluride (MCT) detector, a KCl beam-splitter, and a Harrick Praying-Mantis diffuse reflectance cell; the spectrometer was interfaced to an MS-DOS computer. All spectra were recorded as an average of 500 scans made at 1 cm^{-1} resolution. DR-FTIR spectra were analyzed using the computer program, Lab Calc, obtained from Galactic Industries.

Thermal gravimetric analysis

Thermal gravimetric analyses (TG) of talc, Li-saturated SHCa-1, Na-saturated SHCa-1, Mg-saturated SHCa-1, and Na-saturated Mg-250I, Mg-250V, and Mg-250VIII were obtained with a Seiko 200 TG/DTA analyzer. Approximately 30 mg of air-dried clay were placed into a Pt boat and heated at 100°C under flowing N_2 . After 15 min, a constant weight was obtained and the temperature was increased 20°C/min until a final temperature of 1150°C was attained.

Surface acidity measurements

Fluorescence spectra of adsorbed quinoline were collected to assess the effects of charge reduction on the surface acidity of the hectorites. Because fluorescence is restricted to the protonated, quinolinium ion (Traina, 1990), a measurement of the fluorescent intensity of adsorbed quinoline indirectly indicates the quantity of protons present on the clay surface if the quinoline is added in excess of the acidity. In the present study, 10-mg samples of SHCa-1 and each of the RC hectorites were weighed into polypropylene centrifuge tubes and dispersed in 1:1 ethanol/ H_2O with the aid of ultrasonic agitation. The clays were then centrifuged, decanted, and washed once with 2 ml of H_2O . Quinoline was added (2 ml of 250 $\mu\text{mol/liter}$), and the final volume

was brought to 10 mL with H_2O . This amount of quinoline is equivalent to 5 mmol per 100 g of clay; surface acidity greater than 5 meq/100 g of clay would not be measured. The initial pH values for each sample were measured in a 2:1 water/clay slurry and ranged from 7.2 for SHCa-1 to 6.2 for Mg-250IX. After a reaction time of 8–12 hr, we collected fluorescence emission spectra for each sample using a Perkin-Elmer, LS-5 spectrofluorimeter interfaced to an MS-DOS computer. Fluorescence emission spectra were obtained from 350 to 600 nm using an excitation wavelength of 320 nm, a scanning speed of 60 nm/min, and 5-nm excitation and emission slits. All measurements were made in 1-cm, quartz cuvettes at ambient temperature.

RESULTS AND DISCUSSION

Thermal treatment of Mg-saturated hectorite caused the naturally light-colored mineral to become gray-black. The darkened hectorites remained gel-like and easily dispersible in water up to five heat treatments. After five heat treatments, the hectorites became progressively more aggregated and difficult to disperse. All the heated clays required an initial ultrasonic treatment with a sonic probe placed into an ethanol/ H_2O suspension to ultimately achieve satisfactory dispersion in water.

Chemical analysis

Partial chemical analyses (Table 1) of natural hectorite and reduced-charge samples were expressed as the respective metal oxides. Total Li content decreased with each successive Mg-250 heat treatment, whereas total Mg and Si increased (based on dry weight). The progressive decrease in Li_2O content with heat treatment reflects loss of Li from the octahedral sheet. The increases in MgO content with heat treatment are consistent with the migration of Mg^{2+} ions into vacancies in the octahedral sheet created by the ejection of octahedral Li^+ . However, some Mg may be exchangeable Mg^{2+} trapped within the interlayers of collapsed layers. The apparent increase in SiO_2 content subsequent to the heat treatments (Table 1) was a consequence of H_2O loss. Reductions in sample mass due to H_2O loss may also account for part of the increase in Mg content. Partial unit cell contents were calculated from the chemical analyses in order to make changes in the composition of hectorite more evident. For this calculation, the measured SiO_2 was assumed to represent eight Si atoms in the unit cell.

Charge measurement

Concomitant with decreases in solid-phase Li content, sequential Mg-250 heat treatments caused a reduction in NaEC and CaEC values (Figure 1a). Whereas the two CEC's both indicated a reduction in layer charge with successive Mg-250 heat treatments, the CaEC values were greater than the NaEC values. It is

Table 1. Partial chemical analysis and calculated unit cell composition of natural and reduced-charge hectorites.¹

Sample	SiO ₂ %	MgO %	Li ₂ O %	Unit cell ²		
				#Si	#Mg	#Li
SHCa-1	54.4	21.9	1.02	8.00	4.79	0.60
Mg-250I	55.6	21.6	0.82	8.00	4.63	0.48
Mg-250II	55.4	24.2	0.68	8.00	5.19	0.39
Mg-250III	57.3	22.3	0.57	8.00	4.63	0.32
Mg-250IV	57.3	25.9	0.52	8.00	5.38	0.29
Mg-250V	59.1	26.1	0.42	8.00	5.26	0.23
Mg-250VI	58.7	26.9	0.37	8.00	5.46	0.21
Mg-250VII	59.1	26.7	0.34	8.00	5.38	0.18
Mg-250VIII	59.5	27.0	0.33	8.00	5.41	0.18
Mg-250IX	59.6	27.5	0.32	8.00	5.51	0.17

¹ Samples were Ca-saturated prior to dissolution and analysis.

² Calculated assuming that the % SiO₂ of each sample represents 8 Si atoms in the unit cell.

possible that some exchange sites inaccessible to Na exchange were opened to Ca exchange. The effect of Mg-250 heat treatments on Li content and CEC was greatest over the range of one to five treatments. Successive treatments (Mg-250VI through Mg-250IX) produced smaller changes in these properties (Figure 1a).

Octadecylammonium expansion of the natural and RC hectorites indicated that progressive decreases in mean layer charge occurred with each successive Mg-250 heat treatment (Figure 1b). Basal spacings of the alkylammonium-clays decreased from a bilayer (17.7 Å) in SHCa-1 to a monolayer (13.2–13.6 Å) in samples subjected to four or more MG-250 heat treatments. Although the charge of the hectorites was reduced by the Mg-250 treatments, the persistence of a monolayer octadecylammonium-complex indicates that the hectorites still retained a non-zero layer charge.

IR spectroscopy

Successive MG-250 heat treatments caused significant changes in the DR-FTIR spectra of hectorite (Fig-

ures 2a and 2b, Table 2). Most prominent of these changes were shifts in the octahedral OH stretch and Si-O stretch regions. Calvet and Prost (1971) attributed the appearance of an IR band at 3700 cm⁻¹ in Li-saturated, RC montmorillonites to the stretching mode of hydroxyl groups associated with octahedral Li. A band at 3700 cm⁻¹ is evident in SHCa-1 (Figure 2a). The intensity of this band decreases with successive Mg-250 heat treatments, which is consistent with the loss of octahedral Li. The main Si-O stretch band changed from 988 cm⁻¹ in SHCa-1 to 1034 cm⁻¹ in Mg-250IX (Table 2 and Figure 2b). The Si-O stretch band for SHCa-1 was found at 988 cm⁻¹ in this study, although this band was identified at 1012–1016 cm⁻¹ by Farmer (1979). The 1084 cm⁻¹ Si-O stretch band in SHCa-1 may be present, but it is not resolved from the 1034 cm⁻¹ Si-O stretch in the Mg-250 samples. The Mg-250 heat treatments evidently caused Mg²⁺ to displace octahedral Li⁺ which, in turn, caused a loss of the Li-OH band and a shift in the Si-O band; the resulting clay structure should be more similar to talc.

The DR-FTIR spectrum of talc is compared to those

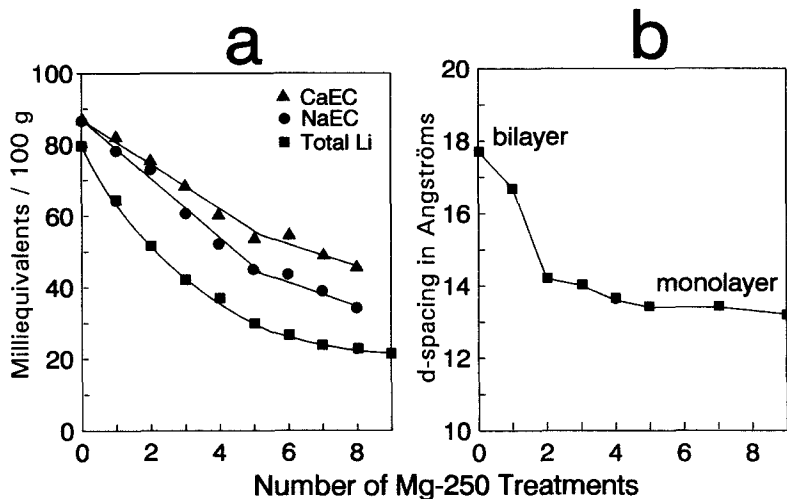


Figure 1. The effects of Mg-250 heat treatments on the charge of hectorites. (a) Total Li content and the cation-exchange capacity. (b) Octadecylammonium expansion.

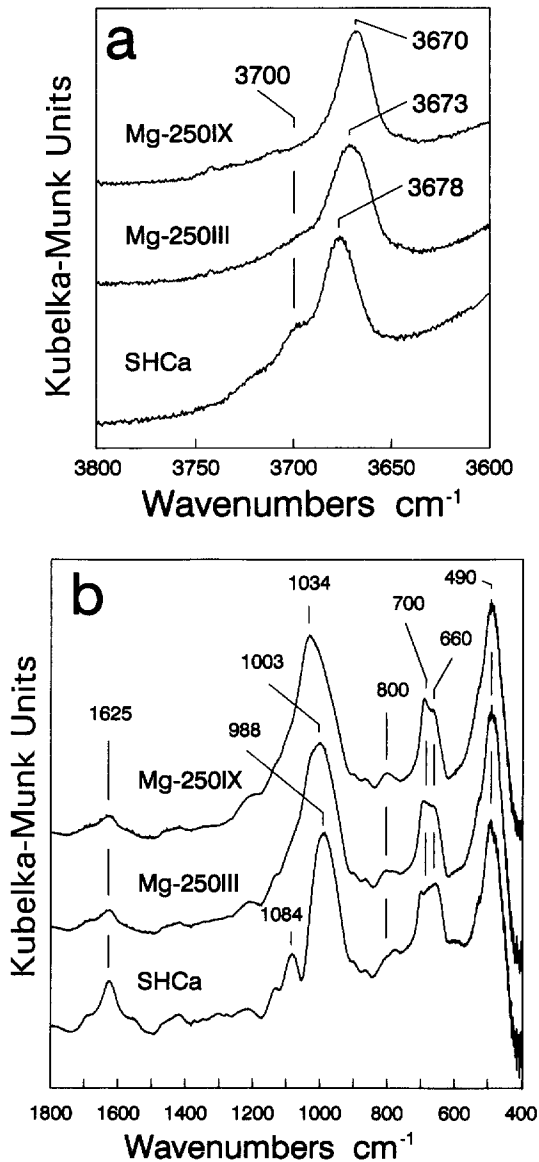


Figure 2. DR-FTIR spectra of SHCa-1, Mg-250III, Mg-250IX (a) 3800 to 3500 cm^{-1} spectrum, (b) 1800 to 400 cm^{-1} spectrum.

of SHCa-1 and Mg-250IX in Figure 3. The asymmetry of the Si-O stretching band of Mg-250IX suggests that it is composed of two or more individual bands. This band was deconvoluted with the spectral analysis program, Lab Calc. It was assumed that two separate bands were present in the experimental data, and no additional constraints were imposed on the deconvolution process. The results suggest that the Si-O stretching band of Mg-250IX is composed of two separate bands at 1008 and 1039 cm^{-1} . These are similar to the two bands present in the talc spectra (1008 and 1043 cm^{-1}) and to the talc Si-O bands reported by Farmer (1974).

Table 2. Peak assignments for DR-FTIR spectra of natural hectorite.

Peak maxima (cm^{-1})	Assignments ¹
SHCa-1 <2 μm	
3700	OH stretching, Li
3678	OH stretching
3400	hydration, OH stretching
1625	hydration, HOH deformation
1084	SiO stretching out-of-plane
988	SiO stretching in-the-plane
700	SiO deformation out-of-plane
660	OH deformation
490	SiO deformation in-the-plane

¹ Peak assignments were based on those of Farmer (1979) for the CMS hectorite SHCa-1 and the OECD laponite.

The 3700 cm^{-1} OH stretch peak assignment was based on that made by Calvet and Prost (1971) for reduced-charge montmorillonite.

Van der Marel and Beutelspacher (1976) found that tilting self-supporting clay films with respect to the IR source produced new absorption bands at 1046 and 1080 cm^{-1} in talc and hectorite, respectively, in addition to those at 1012 cm^{-1} . Similarly, Farmer (1979) assigned a 1045 cm^{-1} band in talc to an Si-O out-of-plane stretch and a 1018 cm^{-1} band as an Si-O in-the-plane stretch. Evidently, the Mg heat treatments have shifted the Si-O out-of-plane stretch band in hectorite from about 1080 cm^{-1} to 1040 cm^{-1} , as in talc.

Integrated peak area ratios of the hectorite octahedral OH stretch region to the Si-O stretch region for each spectrum suggest that a fraction of the structural hydroxyl groups were lost with each Mg-250 heat treatment (Table 3). The water content was significantly higher in the natural hectorite than in the heated samples, as evidenced by the relative peak intensities in the hydration OH stretch (3600–2800 cm^{-1}) and hydration HOH deformation regions (1600–1700 cm^{-1}).

Thermal analysis

Thermogravimetric weight loss data for natural hectorites, Na-saturated RC hectorites, and talc are pre-

Table 3. Integrated peak areas from DR-FTIR spectra of natural and reduced-charge hectorites.

Sample	Integrated peak areas ¹		
	OH peak	SiO peak	OH/SiO area ratio
SHCa-1	3678	988	0.075
Mg-250III	3673	1003	0.063
Mg-250V	3671	1031	0.054
Mg-250VII	3671	1028	0.047
Mg-250IX	3670	1034	0.046

¹ Position of peak maxima in wavenumbers (cm^{-1}). The area of the OH stretch was integrated from 3646 to 3717 cm^{-1} and the area of the SiO stretch was integrated from 844 to 1176 cm^{-1} .

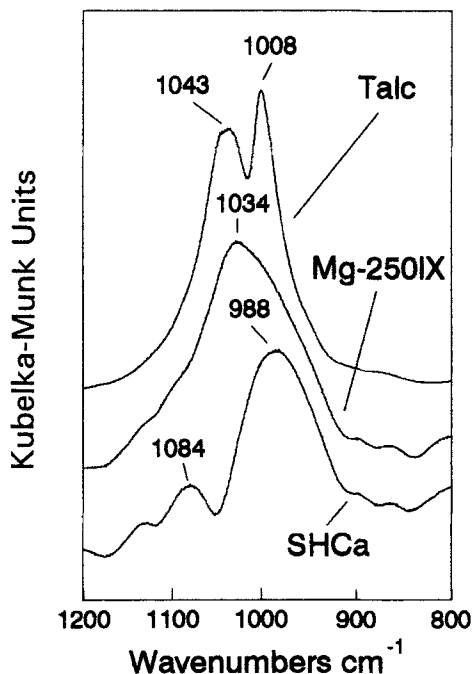


Figure 3. DR-FTIR spectra of SHCa-1, Mg-250IX, and talc from 1200 to 800 cm^{-1} .

sented in Table 4. The TG data on the Li-, Mg-, and Na-saturated natural hectorites clearly indicate that the exchangeable cation affects weight loss in the 100°–400°C and in the 400°–1150°C temperature ranges. Mackenzie and Caillère (1979) found that there was considerable overlap between the weight losses in smectites due to the loss of adsorbed water and hydroxyls. Theoretically, phyllosilicates such as smectites, talc, and pyrophyllite should undergo a weight loss of about 5% due to dehydroxylation. The talc sample (Table 4) has a weight loss of 5.08% in the 400°–1150°C range; hence, the present study used weight losses in the 400°–1150°C range as an indication of hydroxyl content. Using this criterion, the Li-hectorite lost 6.28%, the Mg-hectorite lost 3.79%, and the Na-hectorite lost 3.26%. Clearly, the weight losses from

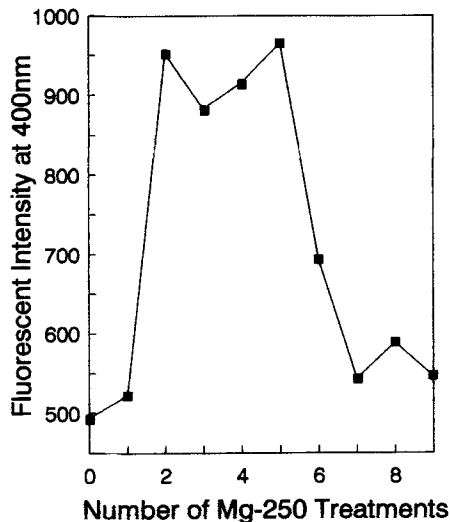


Figure 4. Fluorescent intensity of quinoline adsorbed to hectorites as a measure of surface acidity.

the Na-clays in the 400°–1150°C range conservatively estimate the hydroxyl contents. Weight losses in the 400°–1150°C range indicated that the hydroxyl contents of the natural and RC hectorites were similar; however, the Mg-250 heat treatments have shifted the temperature range of maximum dehydroxylation from 400°–800°C to 800°–1150°C. Maximum dehydroxylation in talc occurred in the 800°–1000°C range, but, unlike talc, the hectorites lost significant weight in the 1000°–1150°C range.

Surface acidity

The fluorescence emission intensity of adsorbed quinoline was enhanced by Mg-250 heat treatments (Figure 4). The greatest intensity was observed in those samples which received two to five heat treatments, after which the fluorescent intensity diminished. The suspension pH values of these samples were all in excess of the pK_a for quinoline (4.96). Because the quinolinium cation is the only species which fluoresces under ambient conditions, quinoline was most likely

Table 4. Thermogravimetric weight loss data for natural hectorites, reduced-charge hectorites, and talc.¹

Sample	Temperature range °C				Total 400–1150
	100–400	400–800	800–1000	1000–1150	
	% Weight loss				
Li SHCa-1	4.93	4.56	0.79	0.93	6.28
Mg SHCa-1	3.62	1.49	1.11	1.19	3.79
Na SHCa-1	1.08	1.88	0.83	0.55	3.26
Na Mg-250I	0.94	1.84	1.14	0.60	3.58
Na Mg-250V	1.07	1.27	1.51	0.60	3.38
Na Mg-250VIII	1.08	0.91	1.45	1.04	3.40
talc	0.66	0.71	4.22	0.15	5.08

¹ Mg-250 clays were Na-saturated prior to thermal analysis.

protonated on the clay surfaces to form the quinolinium cation. Farmer and Russell (1967) noted that Li-montmorillonites became acidified after heating, and suggested that the acidity was generated by deprotonation of structural hydroxyl groups. Similarly, Brindley and LeMaitre (1987) reviewed the literature and found evidence that proton delocalization occurs in hydrous silicates below the dehydroxylation temperature. In the present study, thermal- and Mg-induced deprotonation of structural hydroxyls may have caused the acidity in the RC hectorites. This view is supported by changes in the DR-FTIR spectra in the 3670–3680 cm^{-1} and 640–660 cm^{-1} regions. In contrast, no effect of Mg-250 heat treatments on hydroxyl content was discerned by TG (Table 4); however, the fraction of hydroxyls deprotonated may not be large enough for detection by this method. Jaynes and Bigham (1987) measured a titratable acidity of 0.9 meq/100 g in a Mg-saturated SHCa-1 sample heated once at 250°C: deprotonation of only 2% of the hydroxyl groups in hectorite would generate 10 meq/100 g of acidity.

Decreased quinolinium fluorescence was observed from samples Mg-250VI to Mg-250IX, although the fluorescent intensity was still in excess of that observed for SHCa-1. This was the net effect of surface acidification and charge reduction caused by the Mg-250 treatments. Thus, while acidity of the clay increased, the adsorption capacity decreased. This latter effect likely resulted in lower surface concentrations of quinolinium and diminished emission intensity. Because the samples were washed with Na-acetate buffer and MgCl_2 prior to each Mg-250 heat treatment, the measured acidity should largely reflect that produced during the last heating.

SUMMARY AND CONCLUSIONS

A series of reduced-charge hectorites were prepared by multiple heat treatments of Mg-saturated samples at 250°C. Cation-exchange capacity values and alkylammonium expansion indicated a progressive decrease in the layer charge with each heating. Total Li and Mg values indicated that incremental loss of structural Li and uptake of Mg coincided with the charge reduction. DR-FTIR spectroscopy supported the view that substitution of Mg for octahedral Li occurred and resulted in a more "talc-like" structure.

The exact cause of the enhancements in surface acidity is not known. Whereas the DR-FTIR spectra suggested that some decrease in structural hydroxyl content occurred, TG detected no changes in hydroxyl content. It is not certain whether Mg-250 heat treatments displaced protons from structural OH groups. Additional research is required to determine the cause of the surface acidity.

It is clear that charge reduction in smectites is a general phenomenon and can be induced by heat treatment with the proper exchangeable cation. The syn-

thesis of RC hectorites permits the preparation of a series of smectites which vary in layer charge but lack structural Fe. These surfaces should be useful in future luminescence studies of photochemical and photo-physical processes on alumino-silicate clays.

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