

## EFFECTS OF TEMPERATURE ON THE SORPTION OF LANTHANIDES BY MONTMORILLONITE

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**Abstract**—The diffusion of exchanged Yb, Ho, and Eu from interlayer positions in montmorillonite was studied using infrared spectroscopy (IR), X-ray powder diffraction, and cation-exchange measurements. Dehydration of exchanged montmorillonite between 100° and 280°C caused the ions to diffuse into the hexagonal rings of surface oxygens. Subsequent migration into vacant octahedral sites was small regardless of the radius of the cation. Considerable ion fixation in excess of the cation-exchange capacity of the clay was observed at 20°C in both water and a 1:1 water:95% ethanol mixture. Evidence for hydrolysis as a possible mechanism for cation fixation was obtained by observing frequency shifts for deuterated hydroxyl groups using IR spectroscopy. A major IR band centered at 2680 cm<sup>-1</sup> was observed for all three lanthanide-exchanged montmorillonites studied and assigned to the OH-stretching frequency of a lanthanide hydroxide. This band intensified on heating at 300°C for 1 hr. An IR band between 690 and 710 cm<sup>-1</sup> also was observed for all three lanthanide-exchanged montmorillonites and was assigned to a lanthanide-hydroxyl deformation mode. No hydrolysis was observed for Na-montmorillonite, as expected from the very low hydration energy of Na<sup>+</sup>.

**Key Words**—Adsorption, Cation exchange, Hydrolysis, Infrared spectroscopy, Lanthanides, Montmorillonite, X-ray powder diffraction.

### INTRODUCTION

The disposal of high-level fission waste products requires the exclusion of radionuclides from the environment for as long as they are a source of substantial radioactivity. The U.S. Department of Energy is pursuing this problem on several fronts, one of which is the Sub-seabed Disposal Project. This project is performing initial studies on a proposal to implant corrosion-resistant canisters containing the high-level radioactive wastes into suitable sites in the marine sediments of the seafloor. One of the tasks of the Subseabed Disposal Project is to measure the rates at which radionuclides buried in the seabed diffuse through the sediment. If these rates are such that hazardous radioactivity would decay long before any element can reach the sea floor, sub-seabed disposal is environmentally acceptable.

Three main barriers exist to the emergence of the radioactive nuclides in the marine ecosystem: (1) the nature of the waste form itself (currently glassy borosilicate); (2) the canister; and (3) the surrounding marine sediments. It is expected that the first two barriers will retain wastes for as long as several thousand years; they fail because of devitrification of the glassy matrix at the relatively high temperatures generated by the radioactive wastes and the action of the corrosive marine environment on the canister materials. The major barrier for preventing waste movement will be the interaction between radionuclides and the deep-sea clays surrounding the canister (Russo, 1979). For waste elements that have minimal or no interaction with the

clays, the mean time required for material to diffuse from the canister to the seafloor is proportional to the diffusion coefficient for that element in the particular sediment (Heath, 1977). For materials buried at a depth of about 100 m below the seafloor, the mean time for waste ions to transit to the ocean is about 10<sup>5</sup>–10<sup>6</sup> years, based on a diffusion coefficient of 3 × 10<sup>-10</sup> m<sup>2</sup>/sec. For elements which interact with (i.e., are sorbed by) clays, mean diffusion times could be considerably greater than 10<sup>6</sup> years, thus making seabed implantation environmentally acceptable. To date, no studies have furnished data on the specifics of the clay-waste interaction, whether it is physical or chemical in nature or reversible or irreversible, or on the sites of irreversibly bound species.

Geochemical data from sediment cores, including giant piston cores at deep-sea study sites (Heath *et al.*, 1978), indicate that smectites, specifically montmorillonites, and iron and manganese oxyhydroxides likely will be the major components responsible for ion sorption. The deep-sea clay sediments are saturated with seawater and have high porosities but generally display very low permeabilities. Implantation will take place at depths of 4000–6000 m where pressures exceed 400 atm. Although such "in situ" conditions have been considered, this report deals only with studies performed at atmospheric pressure; the effect of pressure is addressed elsewhere.

The nature of this clay-waste interaction was studied by examining the temperature dependence of the inter-

action between lanthanide ions, specifically  $\text{Eu}^{+3}$ ,  $\text{Ho}^{+3}$  and  $\text{Yb}^{+3}$ , and an Upton, Wyoming, montmorillonite. Lanthanide ions were substituted for chemically similar actinide ions due to the greater ease with which the lanthanides can be handled. The ionic radii of members of both series are, of course, similar.

Montmorillonite can be viewed as a layered oxygen structure, 9.6 Å thick (Clementz *et al.*, 1973) with localized sites of negative charge. The charge imbalance, though localized, is partially distributed throughout the structure, specifically, to the ten interlayer surface oxygen atoms of the four oxygen tetrahedra whose apices are linked to the octahedral site where the charge imbalance originates. These surface oxygens are, therefore, weak electron donors (Farmer and Russell, 1971). Clay chemistry, in its simplest form, is directed towards establishing a minimum energy state by the distribution or neutralization of the existing charge imbalance. Farmer and Russell (1971) proposed a neutralization arrangement applicable to a range of hydration states. Dissolved cations have primary and secondary spheres of coordinated water which can act as dielectric links between the two point charges (cation and surface oxygen) by hydrogen bonding. A stable state of low electrostatic energy in the interlayer position results from minimum hydrogen bonding between cation and both adjacent layers. For 001 spacings  $>20$  Å, Shainberg and Kemper (1966a) concluded that a hydrated ion sees an equipotential surface, and cations interact with the clay through hydrogen bonding (complete hydration sphere) or direct residence on the interlayer surface (partial dehydration). This is the anticipated state for clay suspensions or pastes. Air-dried thin films of clay generally have 001 spacings below 20 Å. For such materials, Shainberg and Kemper (1966b) concluded that a hydrated ion encounters a variable potential in its motion parallel to the layer and, therefore, becomes more localized. Thus, the hydration status of a specific cation is determined by its competing electrostatic interaction with coordinated water and the clay lattice surface.

Because the clay structure of the charge imbalance is the motive force in cation adsorption in a specific thermodynamic state, the hydration state established in minimizing the energy will also be the state of minimum charge imbalance. Cations with low hydration energies ( $<100$  kcal/mole) reside directly on the surface oxygens. Cations with higher hydration energies ( $>100$  kcal/mole) hydrogen bond to the surface oxygens at room temperature and require heating to establish direct surface residence through endothermic dehydration. When direct cation-surface oxygen contact occurs, the charge imbalance shows a marked decrease. Thermogravimetric analyses by Berkheiser and Mortland (1975) show a direct parallel between cation hydration energy and the number of water molecules coordinated to the cation. Initial water loss from a fully expanded hydrated clay always affects hydrogen bond-

ing between interlayer waters and not direct linkages to surface oxygens.

Residence in the hexagonal holes is commonly accepted as the site of direct cation-surface oxygen interaction (Calvet and Prost, 1971). Such residence allows a cation to approach the octahedrally localized negative potential of one layer while maintaining water hydrogen bonded to the adjacent layer (Farmer and Russell, 1971). "Depth" of hexagonal hole residence relative to the plane of the surface oxygens is dependent on a cation's ease of dehydration and its size. Increased residence depth provides a closer approach to the octahedral negative potential and a decrease in the charge imbalance (Calvet, 1973).

Charge neutralization due to cation migration through the base of the hexagonal holes into the vacant octahedral sites has been observed for a variety of ions, but at low temperatures it appears to be restricted to those ions having radii  $<0.85$  Å (McBride, 1976). Where octahedral migration is possible, it occurs at a temperature that is dependent on the ionic hydration energy. Calculations by Calvet and Prost (1971) indicate that migration to octahedral sites is energetically favored only if neighboring hydroxyl groups are oriented perpendicular to the layer. Because most hydroxyl groups are aligned at about  $16^\circ$  to the clay layers, octahedral migration and hydroxyl pivoting (to  $90^\circ$ ) must occur simultaneously. Calvet and Prost (1971) observed this spectroscopically. Occupation of an octahedral site by a metal cation is the most effective method of charge neutralization but requires the largest energy input. Cation migration into the vacant octahedral holes is also limited to those ions which have the correct radii.

A third mechanism by which charge neutralization can be achieved is hydrolysis. This possibility has been described by McBride *et al.* (1975b). Di- and trivalent ions, not capable of being satisfied electrically by a single potential site, attempt to interact with both available sites. Using infrared spectroscopy, Farmer and Russell (1971) showed that multivalent trihydrated ions preferentially reside in one of two superimposed hexagonal holes. As lower hydrates form, the remaining water ligands become highly polarized from increased ion-dipole interactions. This process continues until proton dissociation via hydrolysis occurs. Hydrolysis increases with the hydration energy of the cation involved and occurs even in fully expanded clays with large hydration energies ( $>500$  kcal/mole; Mortland and Raman, 1968). Mortland and Raman (1968) suggested that upon hydrolysis, the proton migrates into the localized octahedral charge site, while the hydroxylated cation occupies the adjacent hexagonal hole.

To obtain a better understanding of the interaction between radioactive waste materials and the surrounding clay sediments, we have studied the sorption of a series of lanthanide ions on an Upton, Wyoming, mont-

morillonite with temperature as a variable. Because the position of the sorbed ions is important in determining the nature and strength of the waste-clay interaction, we have used X-ray powder diffraction, sorption techniques, and infrared spectroscopy to determine the position of the sorbed ions within the montmorillonite structure. Finally, realizing the importance of ionic radii in the sorption process, we have chosen three lanthanide ions of different ionic radii; namely, Yb<sup>3+</sup> (0.848 Å), Ho<sup>3+</sup> (0.894 Å), and Eu<sup>3+</sup> (0.950 Å).

## EXPERIMENTAL

### Clay preparation

An Upton, Wyoming, montmorillonite having the approximate unit-cell formula  $M^{+3}_{0.21}(Al_{3.06}Fe_{0.32}Mg_{0.66})(Al_{0.10}Si_{7.90})O_{20}(OH)_4$  (Ross and Mortland, 1966) was used. The sample was dried at low temperatures and pulverized, and the <325-mesh fraction (<44 μm) was collected. Samples weighing 0.1 g were weighed into 40-ml centrifuge tubes and exchanged with Na as follows: 25 ml of 0.68 M NaCl solution was added to each centrifuge tube, and the suspension was shaken vigorously. The suspension was placed in an ultrasonic bath for 5 min and then centrifuged at 8000 rpm for 10 min. The supernatant liquid was discarded, and the procedure was repeated three times. The samples were then washed with deionized water until no Cl<sup>-</sup> was detected in the supernatant liquid with AgNO<sub>3</sub>. The Na-saturated samples were then saturated with Eu, Ho, or Yb by triplicate washes with 5-ml portions of 0.1 M LnCl<sub>3</sub>·6H<sub>2</sub>O (Ln = Eu, Ho, or Yb), using the wash method described above. The samples were freeze dried and lightly ground in a mortar and pestle to a uniform texture.

### pH determinations

The pH of the suspensions was measured twice during the clay preparation using a Corning Model 610A pH meter and combination reference/pH glass electrode. After Na saturation and removal of excess salts, a suspension of the clay in deionized water gave a pH of 9.1. After Yb saturation and resuspension of the sample in the presence of excess salts, a pH value of 5.7 was obtained. In both cases, the samples were allowed to settle to minimize interference from clay particles.

### Polarographic analysis

Two 0.015-g samples of each of the lanthanide-exchanged clays were heated at each of the following temperatures for 24 hr: 20°, 100°, 160°, 200°, 280°C. The samples were cooled and placed in 40-ml centrifuge tubes. Ten milliliters of deionized water was added to one tube of each pair, and a mixture of 5 ml of deionized water and 5 ml of 95% ethanol was added to the other. These suspensions were capped, shaken vigorously, treated in an ultrasonic bath for 5 min, and, after a 10-

min exposure to the solvent, centrifuged at 15,000 rpm for 10 min to maximize clay-supernatant separation. The supernatant was separated for analysis. This process was repeated twice more, and all three supernatants were combined. The combined supernatant contained all lanthanide ions not sorbed by the clay.

A 3.0-ml portion of the combined supernatant was placed in a glass polarographic sample cup and analyzed for lanthanide ion concentrations using the method described by Florence and Smythe (1960). The experiments were run on a Princeton Applied Research 374 Polarograph.

### X-ray powder diffraction (XRD) analysis

Samples of each lanthanide-exchanged clay (Ln-clay) (0.1 g) were added to 7.5 ml of deionized water in a 40-ml centrifuge tube. The tube was capped, shaken vigorously, and placed in an ultrasonic bath for 5 min to suspend the clay. Aliquots (0.35 ml) of the uniform suspension were placed in each of ten glass slides for each Ln-clay and allowed to dry. For each Ln-clay, a pair of samples was heated at the following temperatures for 25 hr: 20°, 100°, 160°, 200°, 280°C. Samples were scanned from 4° to 11°2θ on a Philips diffractometer using monochromatized CuKα radiation.

### Infrared (IR) spectroscopic analysis

A 0.4-g sample of each Ln-clay was added to 30 ml of deionized water in a 40-ml centrifuge tube. The tube was capped, shaken vigorously, and placed in an ultrasonic bath for 5 min to resuspend the clay. A 0.25-ml portion of the uniform suspension of each Ln-clay was placed onto a 2.0-cm diameter Irtran II disk (1 mm thick) and allowed to dry to a thin film. Drying of clay suspensions resulted in the orientation of a majority of the clay layers parallel to one another and to the supporting surface. The Irtran disk was then placed in a stainless steel sample holder of an IR vacuum cell and the cell closed and placed in position for analysis. The IR sample cell (Figure 1) was fitted with Irtran II windows. Because Irtran II is highly transparent from 4000 to 600 cm<sup>-1</sup>, all IR absorption in this region could be observed. IR analysis was performed by lowering the sample into the IR beam by means of a ground glass crank attached to the sample holder via a wire. A reference cell, identical to the sample cell, with a blank Irtran II sample disk was placed in the reference beam. By operating the Perkin Elmer Model 281 IR spectrometer in the double beam mode, the spectra recorded by the instrument represents the absorption difference between the sample and reference beam and is essentially that due to only the clay thin film.

Heat treatment of the three Ln-clays was performed in air as follows: after placing the supported thin film in the sample holder, the cell was closed and all stopcocks were closed. A room temperature spectrum was obtained by centering the sample cell and reference cell

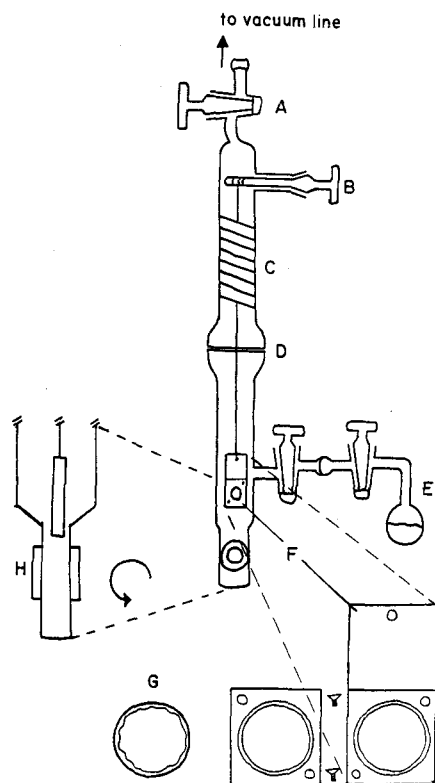


Figure 1. Infrared spectrometer high-vacuum cell. A. High-vacuum stopcock. B. Ground glass crank. C. Furnace. D. O-ring vacuum fixture. E.  $D_2O$  reservoir. F. Thin-film sample holder. G. Thin film mounted on Irtran II disk. H. Irtran II windows.

sample holders in their respective IR beams and allowing the instrument to make a 24-min scan. The sample was then raised into an internal furnace (Figure 1) where it was heated at  $100^\circ\text{C}$  for 24 hr. The sample, after cooling, was then repositioned in the IR beam for analysis. The process was repeated at  $160^\circ$ ,  $200^\circ$ , and  $280^\circ\text{C}$ . To resuspend the samples, the supported thin film was removed and immersed in 0.25 ml of the desired solvent. The sample was allowed to dry, and the analysis was repeated at room temperature.

Deuteration of samples was performed as follows: an Irtran II-supported thin film was placed into the sample holder, and the IR cell was closed. The IR cell was then attached to a vacuum line equipped with a vacuum pump and backed by a liquid nitrogen trap. The IR cell was evacuated to about 1.0 torr, and the stopcock to the vacuum line was closed.  $D_2O$  (17 torr) was introduced by exposing the sample to a liquid  $D_2O$  reservoir for a 12-hr period. An IR spectrum of the sample was then obtained. The cell was evacuated to 1.0 torr and another spectral scan was taken. The sample was then raised into an internal furnace and heated for 1 hr at  $300^\circ\text{C}$ . Some samples (as indicated on the spectra) were

subjected to more extensive heat treatment. At all times, the reference cell was treated identically to the sample cell.

## RESULTS AND DISCUSSION

### *X-ray powder diffraction*

The distinct  $15.2\text{-}\text{\AA}$  001 spacing common to all three Ln-clays is comparable to the  $15.0\text{-}\text{\AA}$  and  $15.2\text{-}\text{\AA}$  spacings recorded for Mg- and Ca-montmorillonite, respectively (Berkheiser and Mortland, 1975; McBride *et al.*, 1975b). Both alkaline earth metals have a hydration sphere in an octahedral configuration. In the presence of a negative potential arising from octahedral substitution, these complexes orient themselves in the interlayer with two opposite vertices on a perpendicular line to the clay layers (Berkheiser and Mortland, 1975). This orientation, while not providing a maximum number of water ligand-surface oxygen interactions, places the axial waters close to octahedral charge sites in the silicate framework (hexagonal hole). Studies of hydrated lanthanide chlorides show that upon dissolution, the chloride ion is displaced from the cation's first hydration sphere by water molecules (Florence and Smythe, 1960). Because of its larger ionic radius, solvated Eu is expected to have nine water ligands in its primary hydration sphere, whereas Ho and Yb have eight (Habenschuss and Spedding, 1979). Though the configuration and orientation of these ions in an interlayer region is not known, the arrangement should allow the closest approach of the water ligands to the octahedral charge sites.

Heat treatment yielded a variety of 001 spacings due to interlayer dehydration (Table 1). The  $15.2\text{-}\text{\AA}$  spacing decreased to  $14.73\text{ \AA}$  on heating probably due to the loss of one or several water molecules not involved in dielectric linkages to the silicate surface. The broad, nondistinct band which developed in the  $12.6\text{-}\text{\AA}$  region (Figure 2) indicates the lack of a specifically preferred, stable configuration at this dehydration level. This result contrasts with the distinct  $12.4\text{-}\text{\AA}$  spacing observed at  $25^\circ\text{C}$  for Cu(II)-montmorillonite, representing a  $\text{Cu}(\text{H}_2\text{O})_4^{+2}$  complex (Clementz *et al.*, 1973). Here, all four water molecules are in a plane parallel to the clay layers. Our results show that lanthanide clays do not establish a distinct aqueous monolayer configuration, but instead pass through a series of closely related states ( $13\text{--}11.8\text{ \AA}$ ) until the distinct  $10.0\text{-}\text{\AA}$  state is formed. The  $c$  dimension of a montmorillonite is  $9.6\text{ \AA}$ , indicating that the  $10.0\text{-}\text{\AA}$  state is not fully collapsed, though significant loss of interlayer water has occurred. Similar collapsed 001 spacings were observed in Cu(II)-montmorillonite ( $9.7\text{ \AA}$ ) and Mg-hectorite ( $10.3\text{ \AA}$ ) where the ion exists as a mono- or dihydrate (Farmer and Russell, 1971; McBride, 1976). The  $10\text{-}\text{\AA}$  spacing decreased to  $9.7\text{ \AA}$  at  $280^\circ\text{C}$ . Thus, a structure similar to a di- or monohydrate must have been formed with

Table 1. 001 spacings (Å) for lanthanide-exchanged montmorillonites as a function of temperature.

	20°C	100°C	160°C	200°C	280°C
Yb <sup>+3</sup>	15.237 s	14.979 s 10.048 w	14.979 m 13.192 m 10.048 m 9.612 m	14.730 m 12.627 m 10.048 m 9.612 m	9.612 s
Ho <sup>+3</sup>	15.237 s	14.979 s 10.048 w	14.979 m 13.192 m 10.048 m	14.730 m 12.627 m 9.937 m	9.612 s
Eu <sup>+3</sup>	15.237 s	14.979 s 10.048 w	14.979 10.048	14.730 13.393 10.048	14.979 m 9.825 s
<i>Resuspended samples (water)</i>					
Yb <sup>+3</sup>	14.979 s	14.979 s	14.979 s	14.979 s	14.730 m 12.998 m 10.048 w
Ho <sup>+3</sup>	14.979 s	14.979 s	14.979 s	14.979 s	14.979 m 10.048 w
Eu <sup>+3</sup>	14.979 s	14.979 s	14.979 s	14.979 s	14.979 s 10.048 w
<i>1:1 solvent (water:95% ethanol)</i>					
Yb <sup>+3</sup>	14.979 s	14.979 s	14.979 s	14.979 s	14.730 s 10.048 w
Ho <sup>+3</sup>	14.979 s	14.979 s	14.979 s	14.979 s	14.979 s 10.048 w
Eu <sup>+3</sup>	14.979 s	14.979 s	14.979 s	14.979 s	14.979 s 10.048 w

w—weak, m—medium, s—strong.

these 001 spacings, with the ion residing in a hexagonal hole and the remaining ligands hydrogen-bonded to surface oxygens on the adjacent layer. A 001 spacing corresponding to 9.6 Å first appeared as a small peak or shoulder at 160°C and grew as the temperature increased. By 280°C, a large percentage of the layers showed this 9.6-Å spacing, especially in the Ho and Yb samples.

Distinctions were noted for Eu, Ho, and Yb samples heated at 160°, 200°, and 280°C. The Eu samples, though displaying the same 001 spacings, dehydrated less at a given temperature and even maintained a broad peak in the 15.2-Å region after being treated at 280°C. Because hydration energies for lanthanide ions increase in the series Eu < Ho < Yb (Cotton and Wilkinson, 1972), dehydration alone cannot account for this observation.

Ionic migration to vacant octahedral sites can only occur in heat-treated clays. For ions such as the lanthanides with large hydration energies (>1000 kcal/mole), octahedral migration occurs only at relatively high temperatures. Octahedral migration is very effective in charge neutralization so that ions in a high energy state will prefer this route when it is available.

MacKenzie (1963) observed that octahedral migra-

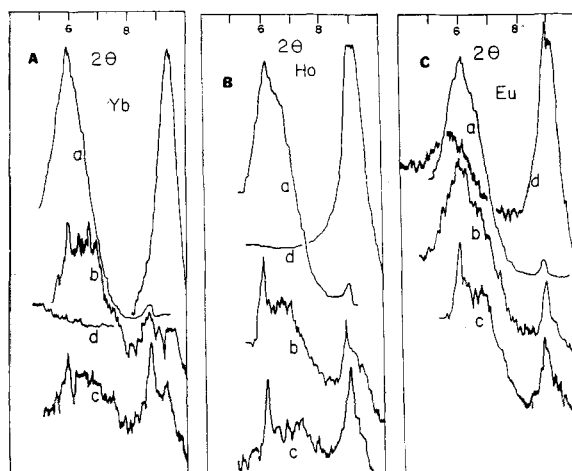


Figure 2. A. X-ray powder diffraction pattern of heat-treated Yb-montmorillonite. 24-hr treatment in air at (a) 100°C, (b) 160°C, (c) 200°C, (d) 280°C. B. X-ray powder diffraction pattern of heat-treated Ho-montmorillonite. 24-hr treatment in air at (a) 100°C, (b) 160°C, (c) 200°C, (d) 280°C. C. X-ray powder diffraction pattern of heat-treated Eu-montmorillonite. 24-hr treatment in air at (a) 100°C, (b) 160°C, (c) 200°C, (d) 280°C.

tion occurs preferentially for ions having an ionic radius of about 0.85 Å or less. McBride (1976) found the optimum ionic radii for octahedral migration to be between 0.74 Å and 0.97 Å. Octahedral migration is, therefore, preferred according to the series Yb (0.858 Å) > Ho (0.894 Å) > Eu (0.950 Å). Even though this sequence is in accord with the observed results, XRD measurements by themselves should not be taken as definitive proof of octahedral migration. It is also possible that anion intercalation might be partly responsible for the persistence of the 15.2-Å peak following heat treatment at 280°C.

Unique mechanisms were probably involved in the swelling of collapsed, heat-treated clay layers by the addition of deionized water. The 1:1 water:95% ethanol mixture was capable of separating fully collapsed layers regardless of the amount of layer-charge reduction that occurred, and water, with its high dielectric constant, was able to swell the clays to large 001 spacings. Reexpansion by water alone (Figure 3) was determined by the extent of charge neutralization that occurred and the hydration energy of the interlayer ions. For clays having interlayer cations with large hydration energies, reexpansion can occur even when extensive charge neutralization has taken place (Brindley and Ertem, 1971). The present results show the 1:1 solvent to be effective in expanding all clay samples to a 001 spacing of 15.0 to 15.2 Å. Only in the samples heated at 290°C did a small 10-Å peak persist. Reexpansion by water also gave the predominant 15.0–15.2-Å peak in all cases.

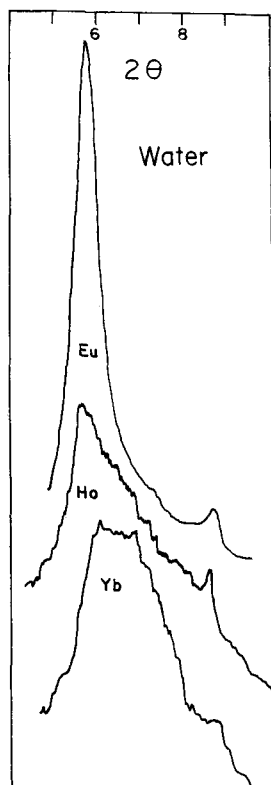


Figure 3. X-ray powder diffraction pattern of water-resuspended Ln-montmorillonites treated at 280°C for 24 hr.

The 280°C-heated samples (Figure 3) showed the largest distinction between the solvent used and the lanthanide ion involved. For water, a small 10-Å peak persisted for all three elements. However, the degree of complete (15.2 Å) reexpansion decreased in the series Eu > Ho > Yb. The 15.0–15.2-Å peaks were all larger in the 1:1 solvent, however, the Eu-clay again had a larger, more symmetric peak than the others.

Several authors have observed differential fixation between ions residing in the hexagonal holes and those that migrate into vacant octahedral sites due to heat treatment (Brindley and Ertem, 1971; Calvet and Prost, 1971; MacKenzie, 1963; McBride *et al.*, 1975b). Octahedral migration generally results in more effective charge neutralization and preferential collapse of the interlayer. McBride (1975c) observed octahedral fixation in ethanol-reexpanded layers of Li, an ion with less steric hindrance to migration out of octahedral sites than would be expected for lanthanide ions. In general, octahedral migration reduces the amount of complete reexpansion (15.2 Å) that occurs in clay layers. Recalling that octahedral migration is preferred in the series Yb > Ho > Eu, this proposal is consistent with the inhibited reexpansion observed in the samples heated at 280°C.

Table 2. Polarographic desorption data.

Samples and heating temp. (°C)	Lanthanide in mobile state (meq/100 g clay)		Relative amount of lanthanide irreversibly adsorbed (meq/100 g clay)	
	Water	1:1 water-95% ethanol	Water	1:1 water-95% ethanol
<i>Yb-montmorillonite</i>				
20	104.7	100.7	61.8	65.8
100	61.3	64.0	105.2	102.5
160	31.3	40.0	135.2	126.5
200	15.3	5.3	151.2	161.2
280	3.3	—	163.2	—
<i>Ho-montmorillonite</i>				
20	116.0	115.3	50.5	51.2
100	73.3	74.0	93.2	92.5
160	44.0	43.3	122.5	123.2
200	20.7	11.3	145.8	155.2
280	5.3	5.3	161.2	161.2
<i>Eu-montmorillonite</i>				
20	133.3	130.0	33.2	36.5
100	91.3	82.0	75.2	34.5
160	64.0	64.7	102.5	101.8
200	28.7	18.0	137.8	148.5
280	11.3	8.7	155.2	157.8
<i>Yb-montmorillonite (110 atm)</i>				
290	150	166.5	16.5	0

#### Adsorption measurements

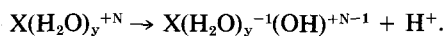
The experimental techniques used in this study ensured lanthanide ion concentrations in excess of the cation-exchange capacities (CEC) of the prepared clays. After heat treatment, the triplicate deionized water or 1:1 water:95% ethanol washes analyzed polarographically, yielded the amount of the ions which remain in the mobile state. The clay phase was not digested and analyzed to determine the actual amount of irreversibly bound lanthanide ion on each sample. A relative value for the amount of irreversibly bound lanthanide ion can be obtained by comparing the amount of lanthanide ion in the mobile state for each clay sample. An upper limit to the concentration of lanthanide ions in the mobile phase was obtained by considering the sample (290°C/110 atm/24 hr, Yb-clay) which yielded the highest concentration of ions in solution (166.5 meq/100 g). Although the effect of pressure is considered elsewhere, it is noteworthy that very little irreversible adsorption occurred when the temperature was increased to 290°C at a pressure of 110 atm. It follows that all 0.1-g samples, having been saturated with lanthanide ions in an identical manner, should have at least this amount (166.5 meq/100 g) initially available to the clay phase. A relative value of the amount irreversibly bound after heat treatment and triplicate resuspension can be obtained by subtracting the mobile phase (measured polarographically, Table 2) from 166.5

meq/100 g. This value is also shown in Table 2. The reported CEC of the starting montmorillonite is 89.3 meq/100 g (McBride, 1976). Taking 166.5 meq/100 g as the amount initially available to the clay, at least 77.2 meq/100 g of the lanthanide ion associated with each 0.1 g clay sample was excess salt content.

At 20°C, a significant amount of irreversible adsorption occurred for all three Ln-clays, the amount increasing in the series Yb > Ho > Eu. An elevation in temperature resulted in an increase in irreversible adsorption to the point of exceeding the CEC of the clay. Even though irreversible adsorption again increased in the series Yb > Ho > Eu, the difference was less pronounced at higher temperatures. There is a slight tendency toward lower levels of exchangeable lanthanide in the ethanolic washes.

The adsorption techniques used in this study allowed adequate time for the establishment of equilibrium, and the 24-hr heat treatment provided adequate time for the movement of ions into irreversible adsorption sites. The desorption technique used permitted adequate time for ions in reversible exchange sites to desorb. All other ions were assumed to be irreversibly bound and, therefore, should have remained in that state regardless of the desorption period used.

The high levels of irreversible adsorption were initially surprising. However, other workers (Bower and Truog, 1941; DeMumbrum and Jackson, 1956) also observed cation fixation in excess of anticipated CEC values and attributed it to hydrolysis:



This hydrolysis process involves the dissociation of acidic water coordinated to a central metal ion and fixation of the metal ion to the clay phase. Although the hexagonal hole sites involved in typical cation-exchange reactions may be the preferred sites for hydrolytic fixation because of their immediate association to octahedral charge imbalance, other surface oxygen atoms may also be involved to provide an interaction in excess of that predicted by the CEC.

#### *Infrared (IR) spectroscopy*

The results of the XRD and sorption studies suggested the need for additional experimental evidence to determine: (1) the position of lanthanide ions in the clay structure, and (2) the positive identification of the hydrolytic products. IR spectra of air-dried thin films provided information on the hydration status of clay interlayers as well as the location of exchangeable cations relative to the clay structure.

#### *4000–2300-cm<sup>-1</sup> region*

Spectra of Ln-montmorillonites in air at room temperature show two dominant absorption peaks at 3620 cm<sup>-1</sup> and 3340 cm<sup>-1</sup> (Figure 4). The symmetric 3620-

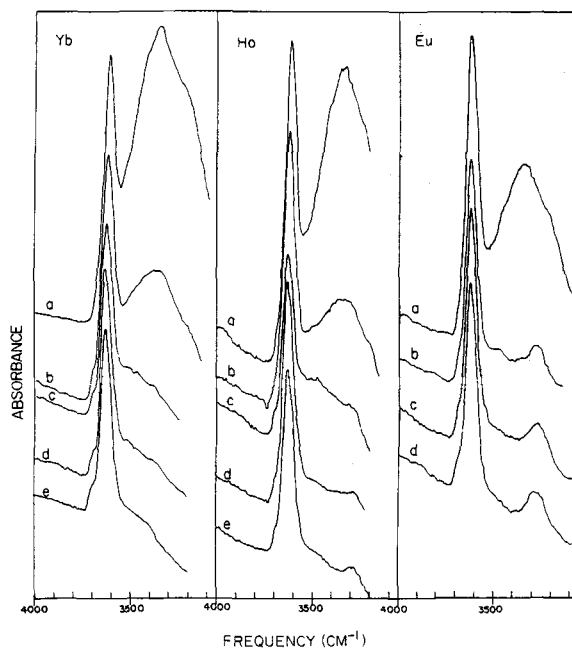


Figure 4. Infrared spectra (4000–3000-cm<sup>-1</sup>) in air of Yb-, Ho-, and Eu-montmorillonites at (a) 20°C, (b) 100°C, (c) 160°C, (d) 200°C, (e) 240°C.

cm<sup>-1</sup> band has been assigned to the stretch of lattice-hydroxyl groups in the octahedral region (Calvet and Prost, 1971). The peak is known to be a combination of several absorption bands, each individual absorption being due to a lattice-OH group situated between a unique pair of octahedral metal ions. The dominant absorption is due to an octahedral-OH group located between two Al ions (AlAlOH), other absorptions being due to AlMgOH and MgMgOH. Since octahedral substitution of Mg for Al is the major source of charge imbalance in the clay structure, cation exchange will preferentially occur where Mg substitution is maximized, specifically near MgMgOH or AlMgOH.

Heat treatment resulted in a shift in the maximum of the 3620-cm<sup>-1</sup> band to 3631–3633 cm<sup>-1</sup> (240°C/24 hr) and the development of a weak 3700-cm<sup>-1</sup> shoulder. Shoulders centered at 3700 cm<sup>-1</sup> have been observed by other authors (Calvet and Prost, 1971) and were assigned to lattice-OH groups which underwent an orientation change relative to the oriented clay layers. OH groups normally orient themselves at approximately 16° to the clay layers, but on octahedral migration of an exchange ion, will shift to a 90° orientation. The shoulder at 3700 cm<sup>-1</sup> (Figure 4) suggests that octahedral migration occurred only to a limited extent and does not appear to be an important process in charge neutralization for the lanthanide ions studied.

Though the hexagonal holes overlying MgMgOH groups will have the largest negative potential on their surface oxygens making them the preferred sites for

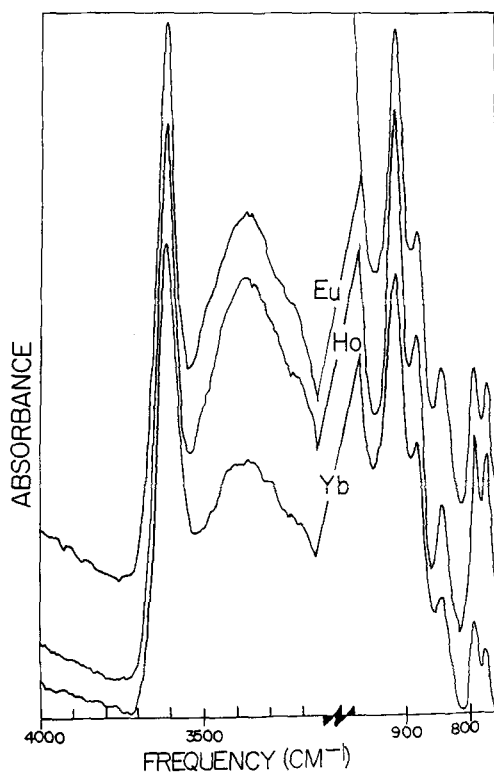


Figure 5. Infrared spectra in air of water-resuspended, heat-treated Ln-montmorillonites.

cation exchange, they are not as numerous as the AlMgOH groups. Heat treatment and cation octahedral migration should then also result in a new stretching peak from reoriented ( $16^\circ$  to  $90^\circ$ ) AlMgOH groups. Calvet and Prost (1971) observed such a peak at  $3670\text{ cm}^{-1}$  using Li and a clay of slightly higher Mg content. Only under more extreme conditions ( $1.0\text{ torr}/290^\circ\text{C}/18\text{ hr}$ ), did we also observe the anticipated shoulder at  $3655\text{ cm}^{-1}$ , indicating a small amount of octahedral migration near AlMgOH configurations.

The  $3340\text{-cm}^{-1}$  band is asymmetric and has been assigned to hydroxyl stretching of interlayer water molecules in a variety of environments. This region has received much attention (Farmer and Russell, 1971), but is utilized here only to indicate the extent of dehydration (loss of interlayer water) that has occurred. The  $20^\circ$  and  $100^\circ\text{C}$  heat-treatment spectra show a decrease in the size of the  $3340\text{-cm}^{-1}$  band at a given heat treatment in the series  $\text{Yb} > \text{Ho} > \text{Eu}$ , stressing the identical trend in decreasing hydration energy (Figure 4).

Aqueous resuspension of the clay thin films caused the redevelopment of the  $3340\text{-cm}^{-1}$  band, down field shift to  $3621\text{ cm}^{-1}$ – $3623\text{ cm}^{-1}$  of the lattice-OH groups and the loss of the  $3700\text{-cm}^{-1}$  shoulder (Figure 5). The large hydration energies apparently promote the rehydration of most interlayers; the small levels of irre-

versible octahedral migration observed by XRD data were not observed by infrared.

Upon the loss of the  $3340\text{-cm}^{-1}$  band, several samples showed a small band centered at  $3280\text{ cm}^{-1}$ . Subsequent work using  $\text{D}_2\text{O}$ , have enabled us to assign this band to  $\text{NH}_4^+$  contamination which occurred during the handling of the clay films.

To account for the levels of cation adsorption which were in excess of the CEC, the possibility of hydrolysis was further investigated by deuterating the clay samples and observing the shifts in infrared frequencies of the resulting OD groups. Others (Calvet and Prost, 1971; Farmer and Russell, 1971) have achieved deuteration of all interlayer water without altering octahedral-OH groups by introducing  $\text{D}_2\text{O}$  vapor at room temperature. Russell and Fraser (1971) exchanged interlayer water without altering octahedral-OH groups by  $\text{D}_2\text{O}$  vapor introduction at room temperature. Repeated heat treatment (1–16 hr,  $350^\circ\text{C}$ ) in fresh  $\text{D}_2\text{O}$  vapor was required for deuteration of octahedral OH. They observed that 25% of the octahedral OH could be deuterated by three 1-hr/ $100^\circ\text{C}$  heat treatments in 17 torr of  $\text{D}_2\text{O}$ .

Spectra recorded in the presence of  $\text{D}_2\text{O}$  vapor (17 mm Hg/24 hr) at room temperature showed a  $3620\text{-cm}^{-1}$  band and a  $2500\text{-cm}^{-1}$  band with a high-frequency shoulder centered at  $2680\text{ cm}^{-1}$  (Figure 6). Evacuation caused a decrease in the intensity of both bands, but more so for the  $2500\text{-cm}^{-1}$  band. Farmer and Russell (1971) observed similar peak maxima at  $2690\text{ cm}^{-1}$  and  $2500\text{ cm}^{-1}$  in deuterated Mg-montmorillonite. They assigned the  $2690\text{-cm}^{-1}$  band to OD groups involved in weaker hydrogen bonding to surface oxygens and indicated that the  $2500\text{-cm}^{-1}$  band resulted from stronger hydrogen bonding between interlayer-OD groups. The larger decrease in the intensity of the  $2500\text{-cm}^{-1}$  band relative to the  $2680\text{-cm}^{-1}$  band is due to the more rapid removal of outersphere and uncoordinated  $\text{D}_2\text{O}$ , because the loss of all  $\text{D}_2\text{O}$ , with the exception of that directly coordinated to exchange cations, would have increased the percentage of OD groups involved in hydrogen bonding to surface oxygens. Heat treatment ( $300^\circ\text{C}$ , 1 hr) caused a large increase in the intensity of the  $2680\text{-cm}^{-1}$  band, simultaneous with a complete loss of the  $2500\text{-cm}^{-1}$  band. Further heating in vacuum ( $300^\circ\text{C}$ , 18 hr) caused no significant change in the intensity of the  $2680\text{-cm}^{-1}$  band. This result suggests that the OD groups responsible for the IR absorption at  $2680\text{ cm}^{-1}$  corresponds to a highly dehydrated cation configuration; most likely one in which the cations reside in the hexagonal holes with the remaining ligands hydrogen bonded to the adjacent oxygen surface atoms. Because the intensity of the  $2680\text{-cm}^{-1}$  band does not decrease with time of heating, it is reasonable to assume that the migration of these cations into the vacant octahedral holes is not significant for the lanthanides studied regardless of ionic radii. Penetration of these cations



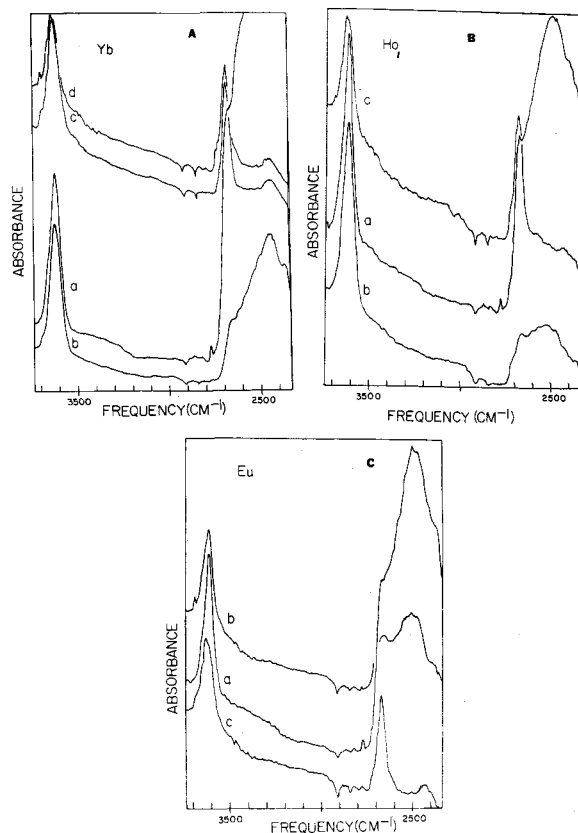


Figure 6. A. Infrared spectra ( $4000\text{--}2400\text{-cm}^{-1}$ ) of the effect of deuteration on Yb-montmorillonite: (a)  $\text{D}_2\text{O}$  vapor at  $20^\circ\text{C}$ , (b) Evacuated, (c)  $300^\circ\text{C}$ , 1 hr, (d)  $300^\circ\text{C}$ , 18 hr. B. Infrared spectra ( $4000\text{--}2400\text{-cm}^{-1}$ ) of the effect of deuteration on Ho-montmorillonite: (a)  $\text{D}_2\text{O}$  vapor at  $20^\circ\text{C}$ , (b) Evacuated, (c)  $300^\circ\text{C}$ , 1 hr. C. Infrared spectra ( $4000\text{--}2400\text{-cm}^{-1}$ ) of the effect of deuteration on Eu-montmorillonite: (a)  $\text{D}_2\text{O}$  vapor at  $20^\circ\text{C}$ , (b) Evacuated, (c)  $300^\circ\text{C}$ , 1 hr.

through the base of the hexagonal holes would require complete dehydration with a consequent loss in intensity of the IR band at  $2680\text{ cm}^{-1}$ .

McBride *et al.* (1975a) emphasized that lower hydrates of di- and trivalent ions may undergo hydrolysis in order to neutralize the charge imbalance in two adjacent hexagonal holes. Lanthanide hydroxide molecules similar to those anticipated from hydrolysis were studied spectroscopically by Swanson *et al.* (1978). The OH-stretching frequencies reported were  $3599\text{ cm}^{-1}$  for  $\text{Yb}(\text{OH})_3$  and  $3596\text{ cm}^{-1}$  for  $\text{Eu}(\text{OH})_3$ . These values, which were obtained for lanthanide hydroxide crystals, are somewhat lower than those expected for lanthanide complexes. The expected frequency shift resulting from deuteration of interlayer OH groups is 1.351. Back-calculating from the  $2680\text{-cm}^{-1}$  band, a value of  $3621\text{ cm}^{-1}$  is obtained. Absorption at this wave number is obscured by the very strong absorption at  $3620\text{ cm}^{-1}$  of  $\text{AlAlOH}$  and can be observed only on deu-

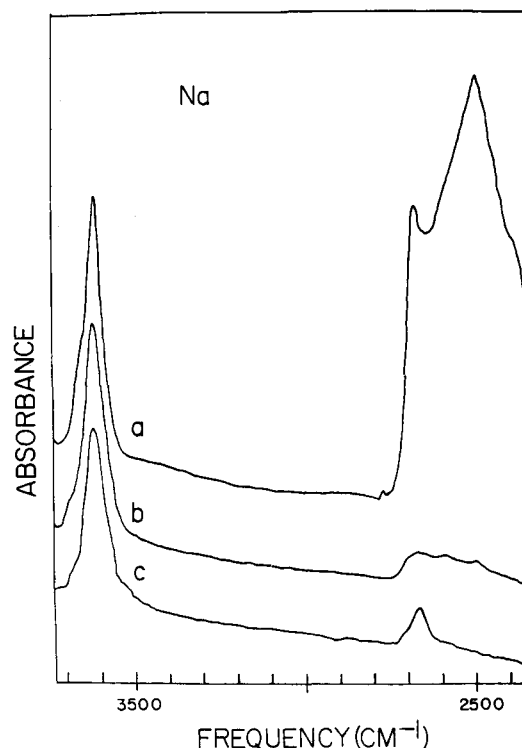


Figure 7. Infrared spectra ( $4000\text{--}2400\text{-cm}^{-1}$ ) of the effect of deuteration on Na-montmorillonite: (a)  $\text{D}_2\text{O}$  vapor at  $20^\circ\text{C}$ ; (b) Evacuated; (c)  $300^\circ\text{C}$ , 1 hr.

teration. The strong band centered at  $2680\text{ cm}^{-1}$ , which is produced by heating the sample, can then be assigned to a lanthanide hydroxide group produced by hydrolysis. The unexpectedly large amount of irreversible cation fixation observed at room temperature can now be accounted for if a percentage of the  $2680\text{-cm}^{-1}$  absorption band in the  $\text{D}_2\text{O}$ -expanded thin film is assigned to the hydrolytic product. Figure 6b shows that even following extensive evacuation at  $20^\circ\text{C}$ , a well-defined shoulder attributable to the hydrolytic product remained.

The possibility that the infrared absorption band centered at  $2680\text{ cm}^{-1}$  is due to deuterated octahedral OH groups, specifically  $\text{AlMgOD}$  and  $\text{AlAlOD}$  must be considered. Na-montmorillonite, due to the low hydration energies associated with the interlayer Na ions would not be expected to undergo hydrolysis. The spectra which resulted when a Na-montmorillonite sample was treated with  $\text{D}_2\text{O}$  in the same way as the lanthanide clays is shown in Figure 7. The Na-clay displayed the familiar bands at  $2680\text{ cm}^{-1}$  and  $2500\text{ cm}^{-1}$ . Evacuation of the sample greatly decreased both the  $2680\text{-cm}^{-1}$  and  $2500\text{-cm}^{-1}$  bands and heat treatment ( $300^\circ\text{C}/1\text{ hr}$ ) gave a single small symmetric band at  $2670\text{ cm}^{-1}$ . Unheated Na-montmorillonite behaves similarly to Ln-montmorillonite. The  $2680\text{-cm}^{-1}$  and  $2500\text{-cm}^{-1}$  bands can be as-

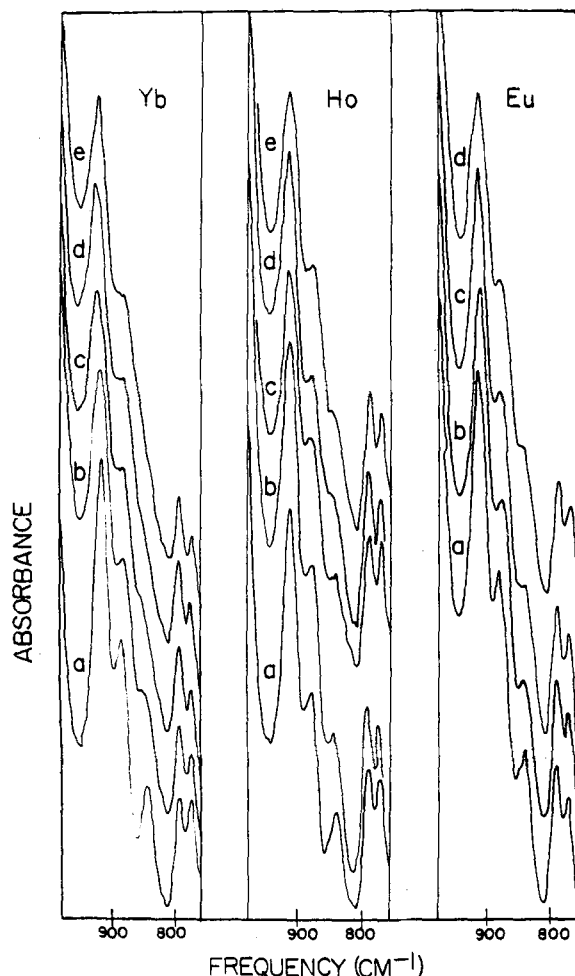


Figure 8. Infrared spectra (950–700-cm<sup>-1</sup>) in air of Yb-, Ho-, and Eu-montmorillonites at: (a) 20°C, (b) 100°C, (c) 160°C, (d) 200°C, (e) 240°C.

signed to various hydrogen-bonded interlayer OD groups. The 2670-cm<sup>-1</sup> band which developed as a result of the heat treatment at 300°C is undoubtedly due to the deuteration of a small number of octahedral hydroxyl groups.

#### 950–600-cm<sup>-1</sup> region

All room temperature spectra (Figure 8) showed three infrared bands due to OH-bending modes at 918 cm<sup>-1</sup> (AlAlOH), 884 cm<sup>-1</sup> (Fe(III)AlOH), and 847 cm<sup>-1</sup> (MgAlOH). These band assignments have been confirmed by others (Calvet and Prost, 1971; Farmer and Russell, 1971). A fourth room temperature absorption band in the 690–710-cm<sup>-1</sup> region was observed for all three Ln-montmorillonites. The 803-cm<sup>-1</sup> band (MgMgOH) which is expected to be small was obscured by the quartz doublet centered at 797 cm<sup>-1</sup> and 775 cm<sup>-1</sup>.

Heat treatment, followed by hydrolysis and cation residence in the hexagonal holes is expected to perturb bending modes of both MgMgOH and AlMgOH, but this will only be observed for AlMgOH. The extent of the perturbation should depend on the depth of penetration into the hexagonal holes and should, therefore, depend on the radius of the cations. Distinctions in this perturbation were observed relative to the lanthanide ion exchanged onto the clay. The 847-cm<sup>-1</sup> peak of Yb-montmorillonite displayed an up-field shift beyond 870 cm<sup>-1</sup> and was, therefore, not observed due to the very strong absorption at 884 cm<sup>-1</sup>. Ho- and Eu-montmorillonites displayed up-field shifts to 865 cm<sup>-1</sup> and 850 cm<sup>-1</sup>, respectively. A comparison of the hexagonal hole radius (1.3 Å) and the ionic radii for Yb<sup>3+</sup> (0.848 Å), Ho<sup>3+</sup> (0.894 Å) and Eu<sup>3+</sup> (0.950 Å) explain the differences observed for the perturbation of the OH-bending mode.

When the Ln-montmorillonite samples were treated with D<sub>2</sub>O in the manner described above, no change in the frequencies of the bending modes of the octahedrally located hydroxyl group was observed. However, the band normally centered in the 690–710-cm<sup>-1</sup> region of the spectrum disappeared from the spectra of all three Ln-montmorillonites. This band was, therefore, assigned to a lanthanide-hydroxyl deformation mode produced by hydrolysis. A Na-montmorillonite treated in a similar way showed no absorption bands in the 690–710-cm<sup>-1</sup> spectral region, suggesting that hydrolysis did not occur.

## CONCLUSIONS

On the basis of this study, hydrolysis of hydrated lanthanide ions, specifically Eu, Ho, and Yb, is a likely mechanism for ion adsorption on montmorillonite. The extent of irreversible adsorption increased with temperature. The sorbed phase was primarily on interlayer oxygen surfaces and within the hexagonal holes. Very little migration into the vacant octahedral holes was observed. Extrapolation of these results to the seawater environment involves considerations not covered in this preliminary study and should proceed with caution. Desorption of lanthanide ions from the clay phase to seawater will result from the presence of other ions in the surrounding solution, a situation not, of course, present in this study. In addition, lanthanides are known to complex with other ions present in seawater to form insoluble products, e.g., basic carbonates. Further studies are required to address these points.

## ACKNOWLEDGMENTS

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**Резюме**—Диффузия обменных  $\text{Yb}$ ,  $\text{Ho}$ , и  $\text{Eu}$  из промежуточных мест в монтмориллоните исследовалась при помощи инфракрасной спектроскопии (ИК), порошковой рентгеновской дифракции и измерений обмена катионов. Результатом дегидратации обменного монтмориллонита в диапазоне температур  $100^\circ$  и  $280^\circ\text{C}$  была диффузия ионов в гексагональные кольца поверхностных атомов кислорода. Последовательная миграция в пустые октаэдрические места была мала несмотря на размер катиона. Значительная фиксация ионов, более величины катионо-обменной способности глины, наблюдалась при  $20^\circ\text{C}$  в воде и в смеси 1:1 вода:95% этаноль. Доказательство, что гидролиз является возможным механизмом фиксации катионов, было получено при наблюдении сдвига частоты колебаний дейтерированных гидроксильных групп при помощи ИК спектроскопии. Главная полоса ИК при  $2680\text{ cm}^{-1}$  наблюдалась для всех трех исследованных монтмориллонитов, обменных лантанидом, и приписывалась к ОН-растягивающей частоте лантанидовой гидроксидной группы. После нагрева при  $300^\circ\text{C}$  в течение 1 часа, эта полоса была более интенсивной. ИК полоса между  $690$  и  $710\text{ cm}^{-1}$  также наблюдалась для всех трех монтмориллонитов, обменных лантанидом, и приписывалась к деформационному колебанию лантанидовой гидроксидной группы. Для Na-монтмориллонита гидролиз не наблюдался, как это можно было предполагать на основе низкой энергии гидратации  $\text{Na}^+$ . [E.C.]

**Resümee**—Es wurde die Diffusion von ausgetauschtem Yb, Ho, und Eu aus Zwischenschichtpositionen in Montmorillonit mit Hilfe von Infrarotspektroskopie (IR), Röntgenpulverdiffraktometrie, und Kationenaustauschmessungen untersucht. Die Dehydratation von ausgetauschtem Montmorillonit zwischen 100° und 280°C bewirkte, daß die Ionen in die hexagonalen Ringe der Oberflächensauerstoffe diffundieren. Eine darauffolgende Wanderung in leere Oktaederstellen war geringfügig, unabhängig vom Radius der Kationen. Eine beachtliche Ionenfixierung wurde zusätzlich zu der Kationenaustauschkapazität des Tones bei 20°C sowohl in Wasser als auch in 1:1 Wasser-95% Äthanol beobachtet. Der Beweis, daß die Hydrolyse ein möglicher Mechanismus für die Kationenfixierung ist, wurde mittels IR-Spektroskopie gefunden. Dabei zeigten sich Frequenzverschiebungen bei deuterierten Hydroxylgruppen. Die stärkste IR-Bande, um 2680  $\text{cm}^{-1}$ , wurde bei allen drei untersuchten Lanthanidenausgetauschten Montmorilloniten gefunden und der OH-Streckschwingung eines Lanthanidenhydroxides zugeschrieben. Diese Bande verstärkte sich beim Erhitzen auf 300°C über 1 Stunde. Eine IR-Bande zwischen 690 und 710  $\text{cm}^{-1}$  wurde ebenfalls bei allen drei Lanthaniden-ausgetauschten Montmorilloniten beobachtet und einer Lanthanidenhydroxyl-Deformationsschwingung zugeschrieben. Bei Na-Montmorillonit wurde keine Hydrolyse beobachtet, wie auf Grund der sehr geringen Hydratationsenergie von  $\text{Na}^+$  erwartet wurde. [U.W.]

**Résumé**—La diffusion de Yb, Ho, et Eu échangés des positions interfolaires de la montmorillonite a été étudiée utilisant la spectroscopie infrarouge (IR), la diffraction poudrée aux rayons-X, et des mesures d'échange de cations. La déshydratation de la montmorillonite échangée entre 100° et 280°C a causé la diffusion des ions dans les cercles hexagonaux des oxygènes de surface. La migration ultérieure dans des sites octaédres vides était petite, quelque'était le rayon du cation. Une fixation considérable d'ions, en excès de la capacité d'échange de cations de l'argile a été observée à 20°C à la fois dans l'eau et dans un mélange 1:1 eau : éthanol 95%. L'évidence pour l'hydrolyse en tant que mécanisme possible pour la fixation de cation a été obtenue en observant les déplacements de fréquence pour les groupes hydroxyles deutérés utilisant la spectroscopie IR. Une bande IR majeure centrée à 2680  $\text{cm}^{-1}$  a été observée pour les trois montmorillonites échangées à la lanthanide étudiées, et a été assignée à la fréquence de l'OH d'élongation d'une hydroxide lanthanide. Cette bande s'est intensifiée à l'échauffement à 300°C pendant une heure. Une bande IR entre 690 et 710  $\text{cm}^{-1}$  a aussi été observée pour les trois montmorillonites échangées à la lanthanide et a été assignée à un mode de déformation d'un hydroxylelanthanide. Aucune hydrolyse n'a été observée pour la montmorillonite-Na, comme on s'y attendrait donné l'énergie d'hydratation très basse de  $\text{Na}^+$ . [D.J.]