

## EFFECT OF PRESSURE ON THE SORPTION OF Yb BY MONTMORILLONITE

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**Abstract**—X-ray diffraction, infrared, and cation-exchange capacity measurements of the reaction products of montmorillonites with  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  show that at 1 atm irreversible sorption of  $\text{Yb}^{3+}$  increases with increasing temperature in the range 20° to 280°C, whereas at 110 atm it decreases with increasing temperature. Above 100°C, less irreversible sorption occurs at 110 atm than at 1 atm. The decreased sorption at high pressure is attributed to reduced cation hydrolytic fixation and to rapid expulsion of interlayer  $\text{Yb}^{3+}$  by interlayer water at higher temperatures, with a concomitant decrease in  $\text{Yb}^{3+}$  migration to octahedral sites. At 110 atm, 160° and 200°C treatments cause changes in infrared absorption bands ( $884\text{ cm}^{-1}$ ,  $848\text{ cm}^{-1}$ ) suggesting that sorbed  $\text{Yb}^{3+}$  is charge compensated by the deprotonation of  $\text{Fe}^{3+}$ - and  $\text{Mg}^{2+}$ -hydroxyl groups. At 290°C deprotonation is restricted to  $\text{Fe}^{3+}$ -hydroxyl groups.

**Key Words**—Cation fixation, Deprotonation, Infrared spectroscopy, Lanthanides, Ytterbium.

### INTRODUCTION

As part of the Seabed Disposal Program, which is assessing the feasibility of permanently disposing high-level nuclear wastes by burial beneath the seafloor, Miller *et al.* (1982) examined the effect of temperature on the irreversible fixation of lanthanide ions on an Upton, Wyoming, montmorillonite. The high levels of irreversible sorption, which can even exceed the cation-exchange capacity of the clay, appear to result from the hydrolysis of lanthanide ions. Inasmuch as the seabed implantation of canisters containing radioactive waste materials would take place at oceanic depths of 4000–6000 m, where pressures exceed 400 atm and the initial temperatures at canister surfaces are expected to exceed 200°C, it is appropriate also to study the effect of pressure on the fixation of lanthanide ions as a function of temperature.

This study considers the effects of both temperature and pressure on the irreversible fixation of lanthanide ions on the same Upton, Wyoming, montmorillonite studied by Miller *et al.* (1982). The Yb-exchanged montmorillonite is representative of the lanthanide-exchanged clays considered previously because: (1) octahedral migration, although small, is greater for Yb than for Ho and Eu; and (2) Yb-exchanged montmorillonites hydrolyze more extensively at a given temperature than their Eu or Ho counterparts. These differences are related to differences in ionic radii; specifically,  $\text{Yb}^{3+}$  (0.858 Å),  $\text{Ho}^{3+}$  (0.894 Å), and  $\text{Eu}^{3+}$  (0.950 Å) (Weast, 1975).

### EXPERIMENTAL

#### Clay preparation

An Upton, Wyoming, montmorillonite having the approximate unit-cell chemical formula  $\text{M}^{+3}_{0.21}$

$(\text{Al}_{3.06}\text{Fe}_{0.32}\text{Mg}_{0.66})(\text{Al}_{0.10}\text{Si}_{7.90})\text{O}_{20}(\text{OH})_4$  (Ross and Mortland, 1966) was dried at low temperatures and pulverized, and the <325-mesh fraction (<44 μm) was collected. The sample was subjected to three Na-exchange washes and saturated with  $\text{Yb}^{3+}$  as described by Miller *et al.* (1982). Following the second lanthanide wash, several 0.1-g Yb-exchanged samples were resuspended for a third time in 5.0-ml portions of 0.1 N  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$ . The samples were added to the 22-ml, stainless steel cup of a Parr Instruments bomb calorimeter. The lid was tightened and the bomb was pressurized and flushed several times with He gas to remove most of the oxygen, before the vessel was pressurized to 110 atm. After pressurization, the bomb was heated to one of the following temperatures: 20°, 100°, 160°, 200°, 290°C. It was then cooled and depressurized, and the clay suspension was placed in a 40-ml centrifuge tube and centrifuged at 15,000 rpm for 10 min. The supernatant liquid was discarded, the interior walls of the tube were dried to remove excess wash solution, and the sample was placed in a refrigerator-freezer as soon as possible following depressurization. The frozen samples, now saturated with  $\text{Yb}^{3+}$  ions, were placed in a freeze drier for about 30 hr. The freeze-dried samples were removed and lightly ground in a mortar and pestle to create a uniform clay sample.

#### Polarographic analysis

Five, 0.015-g samples of the pressure-treated Yb-montmorillonite samples were weighed into labeled, 40-ml centrifuge tubes, shaken vigorously with 10 ml of deionized water, placed in an ultrasonic bath for 5 min, and, after 10-min exposure to the solvent, centrifuged at 15,000 rpm for 10 min to maximize clay-supernatant separation. The supernatant solution was poured off into

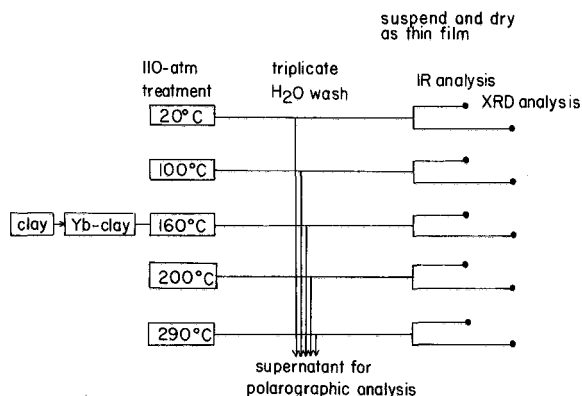


Figure 1. Flow chart outlining procedures used in characterizing the Yb-exchanged montmorillonite.

a container for analysis. This procedure was repeated twice more, and all three supernatant portions were combined. The supernatant solution contained all  $\text{Yb}^{3+}$  ions not fixed to the clay phase. A 3.0-ml portion of the combined supernatant solution was placed in a glass sample cup and analyzed by the polarographic technique of Florence and Smythe (1960).

#### Infrared spectroscopic analysis

Samples of the pressure-treated clay (0.4 g) were added to 30-ml of deionized water in 40-ml centrifuge tubes. The tubes were capped, shaken vigorously, and placed in an ultrasonic bath for 5 min to resuspend the clay phase. A 0.25-ml portion of each uniform suspension was placed on a 1 mm thick  $\times$  2.0-cm diameter Irtran disk and allowed to dry to a thin film. Drying of the 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 infrared vacuum cell which was positioned in the infrared beam. The specifics regarding the design of the infrared cell are described in detail by Miller *et al.* (1982).

#### X-ray powder diffraction analysis

Samples of the pressure-treated Yb-exchanged montmorillonite, each weighing 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 ensure complete suspension of the clay. Aliquots (0.35 ml) of the uniform suspension were placed onto glass slides and allowed to dry. Samples were scanned for  $4^\circ$  to  $11^\circ 2\theta$  on a Philips XRD diffractometer using monochromatized  $\text{CuK}\alpha$  radiation.

#### Determination of $\text{Fe(II)}$

The disappearance of the hydroxyl-bending vibration assigned to  $(\text{Fe(III)AlOH})$  in the  $800\text{--}900\text{ cm}^{-1}$  region of the infrared spectra suggested that  $\text{Fe}^{+3}$  had been re-

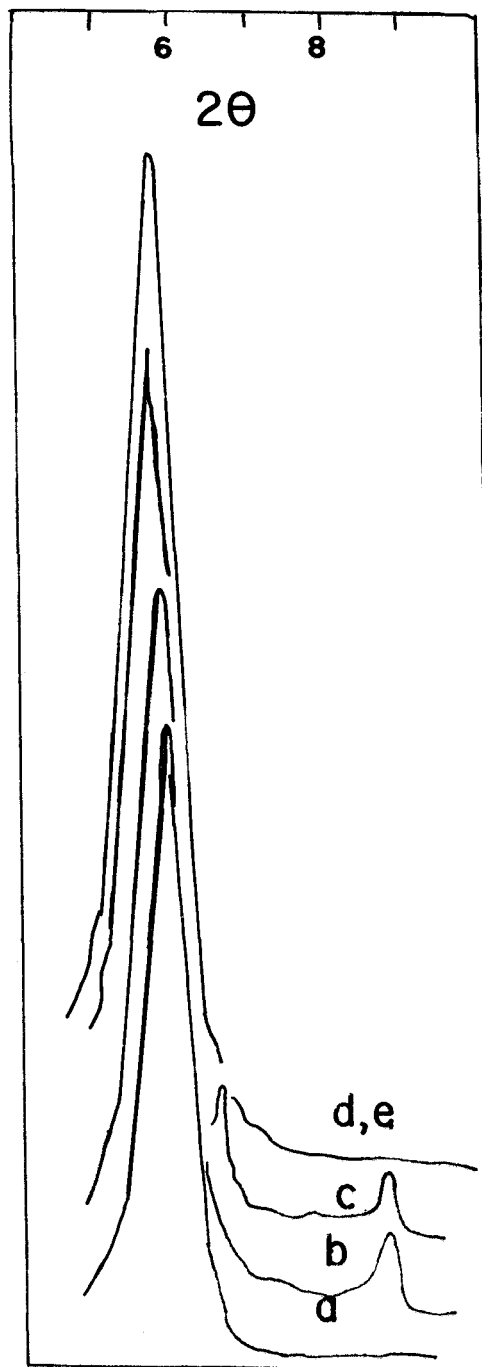


Figure 2. X-ray powder diffraction patterns of Yb-montmorillonite heated at 110 atm. (a) 20°C, (b) 100°C, (c) 160°C, (d) 200°C, (e) 290°C.

duced to  $\text{Fe}^{+2}$  during high pressure treatment. To confirm this possibility, several samples were analyzed for  $\text{Fe}^{+2}$  by the titration technique of Wilson (1955).

A flow chart outlining the various procedures used to characterize the Yb-exchanged montmorillonite is shown in Figure 1.

## RESULTS AND DISCUSSION

*X-ray powder diffraction (XRD) and polarography*

Following high pressure (110 atm) treatment, all Yb-montmorillonites had a predominate spacing of 15  $\nu\text{\AA}$  regardless of the heat treatment (20°–290°C) involved (Figure 2). Samples heat treated at 100° and 160°C show, in addition, a weak 10- $\text{\AA}$  reflection. The polarographic data (Table 1) indicate that at 110 atm the amount of Yb<sup>3+</sup> sorbed by the clay phase decreased as the temperature increased in marked contrast to the 1-atm experiments of Miller *et al.* (1982).

The swelling behavior and sorbed ion content of the samples treated at 110 atm and 20°C are nearly identical with the samples examined at 1 atm by Miller *et al.* (1982). For 100° and 160°C, less irreversible Yb-sorption took place at 110 atm than at 1 atm, and more 10.0- $\text{\AA}$  interlayers persisted. Such persistent 10.0- $\text{\AA}$  interlayers were observed for aqueous resuspensions of samples treated at 1 atm only after extensive dehydration due to heating. This 10.0- $\text{\AA}$  spacing was attributed to a hydrolyzed di- or monohydrate of the lanthanide ion resident in hexagonal holes which would develop only during interlayer dehydration. Apparently, similar interlayer dehydration took place at 110 atm during the 100° and 160°C runs.

As anticipated, these results suggest that hydrolysis is the mechanism of Yb fixation at 110 atm. Increased temperatures should accelerate both interlayer dehydration and hydrolysis. While aiding hydrolytic fixation of Yb<sup>3+</sup>, dehydration could also remove interlayer cations during the expulsion of interlayer water. In the 100° and 160°C runs, hydrolytic fixation appears to have occurred at significant levels, judging from the polarographic and XRD data. At 200° and 290°C however, no 10- $\text{\AA}$  XRD reflections were observed, implying that interlayer water was expelled fast enough to drive out exchangeable ions before they could establish residence in hexagonal holes. This is supported by polarographic data (Table 1) which show a significant decrease in Yb-fixation at these temperatures.

*Infrared spectroscopy (IR)*

Room temperature IR spectra in air (Figure 3) show variations with temperature for the 24-hr, 110-atm runs. The 20°, 100°, 160° and 200°C treatments all display ab-

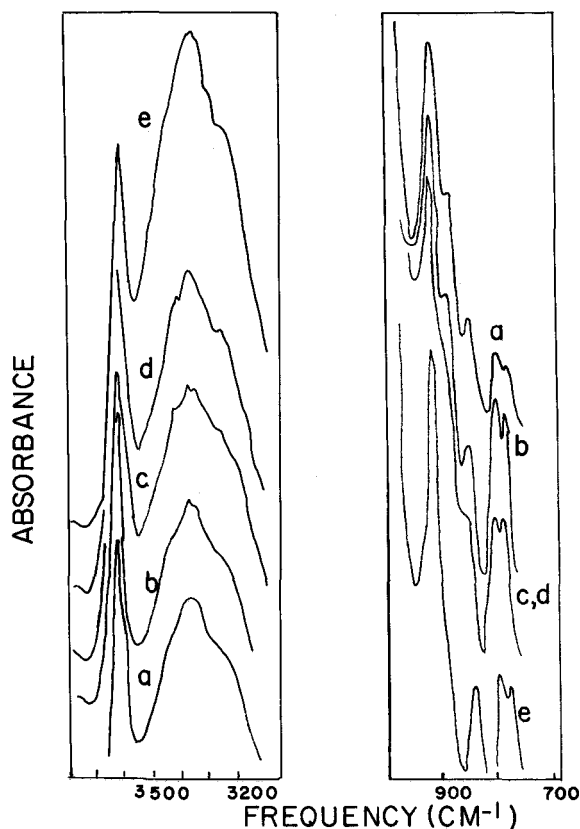


Figure 3. Infrared spectra of Yb-montmorillonites heated at 110 atm. (a) 20°C, (b) 100°C, (c) 160°C, (d) 200°C, (e) 290°C.

sorption bands common to the Upton, Wyoming, montmorillonite, with no indication of perturbations arising from the movement of Yb<sup>3+</sup> ions into vacant octahedral sites. The observed frequencies for these bands are consistent with observations of other authors (Calvet and Prost, 1971; Farmer and Russell, 1971). The weakening of the 884-cm<sup>-1</sup> and 848-cm<sup>-1</sup> bands observed at 160° and 200°C are discussed below. The absorption band centered at 884 cm<sup>-1</sup> is missing from the sample treated at 290°C. Likewise, there is a slight shift to 910 cm<sup>-1</sup> and 841 cm<sup>-1</sup> for the (AlAlOH) and (AlMgOH) band, respectively.

The disappearance of the 884-cm<sup>-1</sup> band has previously been attributed to loss or reduction of octahedral Fe<sup>3+</sup> (Farmer and Russell, 1964). Chemical analysis of our samples indicated that no Fe<sup>2+</sup> was present, negating the possibility of Fe<sup>3+</sup> reduction. Heller-Kallai (1975a, 1975b) reversed the high temperature protonation of structural hydroxyl groups in clay by the addition of alkali halides. This deprotonation, which is promoted by an excess (greater than the cation-exchange capacity) of exchangeable cations in the presence of proton acceptors (halide ions), seems to be controlled by two mechanisms: (1) proton delocalization by

Table 1. Polarographic desorption data.

Sample treatment	Relative amount of Yb irreversibly adsorbed (meq/100 g of clay)	
	1 atm	110 atm
20°C	61.8	66.5
100°C	105.2	48.5
160°C	135.2	49.8
200°C	151.2	32.5
290°C	163.2	16.5

heating, and (2) proton liberation in response to localized exchange-cation fixation. Heller-Kallai also noted that the  $\text{Fe}^{3+}$ -hydroxyl groups seemed to initiate deprotonation. Fripiat *et al.* (1965) showed that appreciable temperature-dependent proton delocalization takes place at 200°C in micas.

In the presence of an excess of  $\text{YbCl}_3$ , two mechanisms probably took place as the temperature was increased. The amount of irreversibly absorbed  $\text{Yb}^{3+}$  decreased (Table 1), possibly due to increased dehydration and expulsion of interlayer  $\text{Yb}^{3+}$ . The second mechanism was an increased delocalization of octahedral protons as the temperature increased. Protons delocalized at 160° and 200°C in the presence of appreciable amounts of fixed  $\text{Yb}^{3+}$  were probably liberated from the clay structure, thereby causing a weakening of the 884- $\text{cm}^{-1}$  and 848- $\text{cm}^{-1}$  bands, assuming delocalization commenced with (Fe(III)AlOH) and, fixation commenced with (MgAlOH). At 290°C, proton delocalization was more extensive, but  $\text{Yb}^{3+}$  fixation dropped off, possibly preventing proton liberation and explaining the observed loss of the 884- $\text{cm}^{-1}$  band, while the 848- $\text{cm}^{-1}$  band redeveloped. Heller-Kallai (1975b) reported similar spectral results in the presence of alkali halides after extensive heating (300°C/16 days). The shifted absorption at 910  $\text{cm}^{-1}$  and 841  $\text{cm}^{-1}$  can be attributed to structure adjustment due to proton delocalization. Though the mechanisms are speculative, the results emphasize that under deprotonation conditions, (Fe(III)AlOH) and (MgAlOH) behave differently.

### CONCLUSIONS

High-pressure experiments suggest that interlayer dehydration increases with temperature and occurs at a sufficiently rapid rate at 290°C to prevent significant interlayer hydrolytic fixation of  $\text{Yb}^{3+}$ . The weakened intensity of the 848- $\text{cm}^{-1}$  and 884- $\text{cm}^{-1}$  bands at 160° and 200°C is explained by deprotonation of the (Fe(III)AlOH) and (MgAlOH) groups, presumably in compensation for the excess  $\text{Yb}^{3+}$  present. At 290°C the disappearance of the 884- $\text{cm}^{-1}$  band and redevelopment of the 848- $\text{cm}^{-1}$  band is attributed to specific deprotonation of the (Fe(III)AlOH) only. Chemical analysis verifies that  $\text{Fe}^{3+}$  reduction does not occur.

Sorption of  $\text{Yb}^{3+}$  in amounts greater than the cation-exchange capacity does not occur at 110 atm as it does at 1 atm for the clay under study, apparently because

dehydration carries  $\text{Yb}^{3+}$  ions out of interlayers, inhibiting interlayer hydrolysis. Thus, increased temperature reduces  $\text{Yb}^{3+}$  fixation by montmorillonite at 110 atm, whereas at 1 atm increased temperature enhances fixation by hydrolysis.

Because this study was performed at elevated temperatures and pressure, there may be implications to initial diagenetic processes. The need for further study to characterize the unique deprotonation behavior of (Fe(III)AlOH) and (MgAlOH) is evident.

### ACKNOWLEDGMENTS

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**Резюме**—Измерения продуктов реакции монтмориллонита с  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  путем рентгеновской порошковой дифракции, инфракрасной спектроскопии и катионо-обменной способности указывают, что при давлении 1 атм необратимая сорбция  $\text{Yb}^{3+}$  увеличивается с ростом температуры в диапазоне от 20° до 280°C, тогда как при 110 атм сорбция уменьшается с ростом температуры. Выше 100°C, при 110 атм сорбция является менее необратимой, чем при 1 атм. Уменьшенная сорбция при большом давлении, вероятно, вызвана уменьшенной гидrolитической фиксацией катионов и быстрым изгнанием межслойных  $\text{Yb}^{3+}$  межслойной водой при повышенной температуре, сопровождаемым уменьшением миграции  $\text{Yb}^{3+}$  в октаэдрические места. При 110 атм обработка при температурах 160° и 200°C приводила к изменению полос инфракрасной спектроскопии (884  $\text{cm}^{-1}$ , 848  $\text{cm}^{-1}$ ), указывая на то что сорбированный  $\text{Yb}^{3+}$  уравнивается по заряду отпротонированием  $\text{Fe}^{3+}$ - и  $\text{Mg}^{2+}$ -гидроксильных групп. При 290°C отпротонирование ограничивается до  $\text{Fe}^{3+}$ -гидроксильных групп. [E.C.E]

**Resümee**—Röntgenpulverdiffraktions-, Infrarot-, und Kationenaustauschkapazitäts-Messungen an den Reaktionsprodukten von Montmorillonit mit  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  zeigen, daß bei 1 atm die irreversible Sorption von  $\text{Yb}^{3+}$  mit zunehmender Temperatur zunimmt. Über 100°C ist bei 110 atm die Sorption weniger reversibel als bei 1 atm. Die verringerte Sorption bei höherem Druck wird einer verringerten hydrolytischen Bindung der Kationen zugeschrieben und einer raschen Verdrängung von eingelagertem  $\text{Yb}^{3+}$  durch Zwischenschichtwasser bei höheren Temperaturen. Dies wird begleitet von einer Verringerung der Besetzung der Oktaederplätze durch  $\text{Yb}^{3+}$ . Bei 110 atm bewirkt ein Erhitzen auf 160° und 200°C eine Veränderung der Infrarotadsorptions-Banden (884  $\text{cm}^{-1}$ , 848  $\text{cm}^{-1}$ ), was darauf hindeutet, daß das sorbierte  $\text{Yb}^{3+}$  ladungsmäßig durch die Deprotonierung von  $\text{Fe}^{3+}$ - und  $\text{Mg}^{2+}$ -Hydroxylgruppen kompensiert wird. Bei 290°C ist die Deprotonierung auf die  $\text{Fe}^{3+}$ -Hydroxylgruppen beschränkt. [U.W.]

**Résumé**—Des mesures de diffraction de rayons-X, infrarouges, et de capacité d'échange de cations des produits de réaction entre la montmorillonite et  $\text{YbCl}_3 \cdot 6\text{H}_2\text{O}$  montrent qu'à 1 atm la sorption irréversible de  $\text{Yb}^{3+}$  augmente proportionnellement à une élévation de la température sur l'étendue de 20° à 280°C, alors qu'à 110 atm, elle diminue proportionnellement à une élévation de température. Au delà de 100°C, une sorption moins irréversible se passe à 110 atm qu'à 1 atm. La sorption moindre sous haute pression est attribuée à une fixation hydrolytique de cations réduite et à l'expulsion rapide de  $\text{Yb}^{3+}$  intercouche par l'eau intercouche à de plus hautes températures entraînant une diminution de la migration de  $\text{Yb}^{3+}$  vers les sites octaédraux. A 110 atm, des traitements à 160° et 200°C causent des changements dans les bandes d'adsorption infrarouges (884  $\text{cm}^{-1}$ , 848  $\text{cm}^{-1}$ ) suggérant que la charge de  $\text{Yb}^{3+}$  sorbé est compensée par la déprotonation des groupes hydroxyles  $\text{Fe}^{3+}$  et  $\text{Mg}^{2+}$ . A 290°C la déprotonation est restreinte aux groupes hydroxyles  $\text{Fe}^{3+}$ . [D.J.]