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EFFECT OF PRE-HEATING ON THE THERMAL DEHYDRATION OF LANTHANIDE MONTMORILLONITES

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ABSTRACT

Simultaneous DTA–TG, TPD–GC, BET specific surface area and FT-IR measurements have been carried out on Ln–montmorillonites (Ln ≡ La, Nd, Gd, Ho or Yb) in order to study the effect of air-heating at 300 °C on Ln^{III} fixation and subsequent thermal dehydration. In the unheated samples, the hydration shell of the exchangeable 4f ions contains an average number of H_2O molecules which ranges from 20 (La) to 12 (Yb). This decrease can be ascribed to partial hydrolysis of interlamellar cations, which increases for all the samples on heating at 300 °C. Deprotonation of the montmorillonites by reaction of their structural OH groups with the interlamellar 4f hydroxides is suggested.

INTRODUCTION

The chemical interaction of lanthanides with clay minerals at temperatures around 300 °C is of importance in connection with the storage of high-level nuclear wastes in continental or marine repositories [1]. If waste materials escape from their canisters, they can be expected to be contained by surrounding geological formations. The major barrier for preventing movement of waste and reducing environmental impact will be interactions between radionuclides and the clays surrounding the canisters [2]. Trivalent 4f ions are used to simulate the interaction of radionuclides with clay minerals. Miller et al. [1,3] have studied the sorption of Eu^{III}, Ho^{III} and Yb^{III} on a montmorillonite from Upton, Wyoming.

In a previous work, it has been observed in our laboratory that the mechanism for retention of exchangeable 4f ions by montmorillonite on heating at about 300 °C is mainly hydrolysis of the hydrated exchangeable cations to produce interlamellar 4f hydroxides [4]. The interlamellar lanthanide hydroxides could also react with the structural OH groups of montmorillonite. Using IR spectroscopy Russell [5] has observed the latter

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reaction between ferruginous montmorillonites and alkali metal hydroxides under air-dry conditions, the specific interaction depending on the cation size. Hydrolysis of the exchangeable hydrated cations and reaction between the interlamellar lanthanide hydroxides and the montmorillonite OH groups could affect the thermal dehydration pattern of the lanthanide montmorillonite. It is the aim of the present paper to study the effect of air-heating at 300 °C on the thermal dehydration of a montmorillonite saturated with La^{III}, Nd^{III}, Gd^{III} Ho^{III} or Yb^{III} ions. The study of the same montmorillonite saturated with lithium or sodium has also been included for comparative purposes. The structural interaction of the exchangeable ions with the montmorillonite has been examined using Fourier-transform IR (FT-IR) spectroscopy. The thermal dehydration of the unheated lanthanide montmorillonites has already been studied [6].

EXPERIMENTAL

Methods

Differential thermal analysis (DTA) and thermogravimetry (TG) were carried out using a Rigaku system, model PTC-10A. A temperature-programmed decomposition gas chromatograph (TPD-GC) was used in this work, which operates with a He flow of 30 ml min^{-1} at normal pressures. The evolved water was analysed using a Hewlett–Packard 5834A chromatograph. Quantitative TPD calibrations of H_2O were performed by decomposing variable amounts of $CuSO_4 \cdot 5H_2O$. All the thermal decomposition experiments were carried out at a linear heating rate of 8 °C min^{-1}.

BET (Brunauer–Emmett–Teller) specific surface areas [7] were determined using a Micrometrics system, model 2200A, using N_2 as the adsorbate at 77.35 K.

IR spectra were recorded in a Fourier-transform Nicolet 5 DXE spectrometer. Samples were suspended in water, 1 kg m^{-3}, and allowed to sediment onto plastic slides. The suspensions were evaporated to dryness overnight and the resulting oriented aggregate films were peeled from the foil. The spectra at reduced pressures, less than 10^{-4} Torr, were obtained by placing the films in a heatable and evacuable cell, with no metallic parts, which has been designed and built in our laboratory. When recording the FT-IR spectra a satisfactory signal-to-noise ratio was obtained by co-adding 100 interferograms.

Materials

A Trancos smectite mineral from Gador, Almeria (Spain), was used [8]. The < 2 μm fraction was collected after suspension in water. It was then saturated with sodium using a 1 N solution of NaCl.

Chemical analysis of the Na–Mt sample (Mt, montmorillonite) by X-ray fluorescence was carried out, yielding the formula

$(\mathrm{Si}^{4+}_{7.64}\mathrm{Al}^{3+}_{0.36})(\mathrm{Al}^{3+}_{3.09}\mathrm{Fe}^{3+}_{0.28}\mathrm{Mg}^{2+}_{0.69})\mathrm{O}_{20}(\mathrm{OH})_4$

with a calculated charge deficit per unit cell of 0.87 (0.36 + 0.51). The experimental value of the cation exchange capacity (CEC) amounts to 100 meq/100 g.

The Green-Kelly test [9] was applied, and the inability of the Na–Mt sample to re-expand with glycerol after Li saturation and air-heat treatment at 300 °C for 24 h was observed. This behaviour also indicates that the charge of the mineral is predominantly octahedral since the migrating Li^+ neutralizes the octahedral charge.

The Na–Mt was used for the preparation of Ln–Mt (Ln ≡ La, Nd, Gd, Ho or Yb), according to the method described by Miller et al. [1], except that the samples were washed with water until excess $\mathrm{Ln}^{\mathrm{III}}$ was eliminated.

RESULTS AND DISCUSSION

Thermal analysis of previously unheated samples

The thermograms of smectite minerals show effects which are generally interpreted as being caused by the loss of molecular water at temperatures below about 500 °C and by dehydroxylation at higher temperatures. The experimental DTA and TG curves of all our samples show a principal thermal effect from room temperature to 200 °C, followed by an almost linear trace up to about 450 °C. Figure 1 shows the DTA curves for the prepared lanthanide montmorillonites in the range from room temperature to 250 °C. The samples saturated with Li or Na are also shown for comparative purposes. Before each experiment the sample was conditioned at 55% relative humidity. The loss of molecular water is influenced by the nature of the exchangeable cations; in the cases of Li and $\mathrm{Ln}^{\mathrm{III}}$ two overall steps are observed. The first step corresponds to the loss of molecular water on the external free surface, condensed in mesopores and weakly bonded between the structural sheets of the montmorillonite. The second is seen as a shoulder in the interval 150–200 °C. This effect, which depends on the nature of the exchangeable ion, can be ascribed to molecular water in its hydration shell.

Deconvolution of the thermal curves in order to separate both classes of molecular water is not an easy task. In a recent study on the effects of pressure on the dehydration of M–Mt (M ≡ Na, K, Mg or Ca) it was found that this reaction occurs in two separate steps [10]. A physical model was elaborated to explain the persistence of some of the interlayer water molecules in Mg- and in Ca-montmorillonite. The average number of H_2O

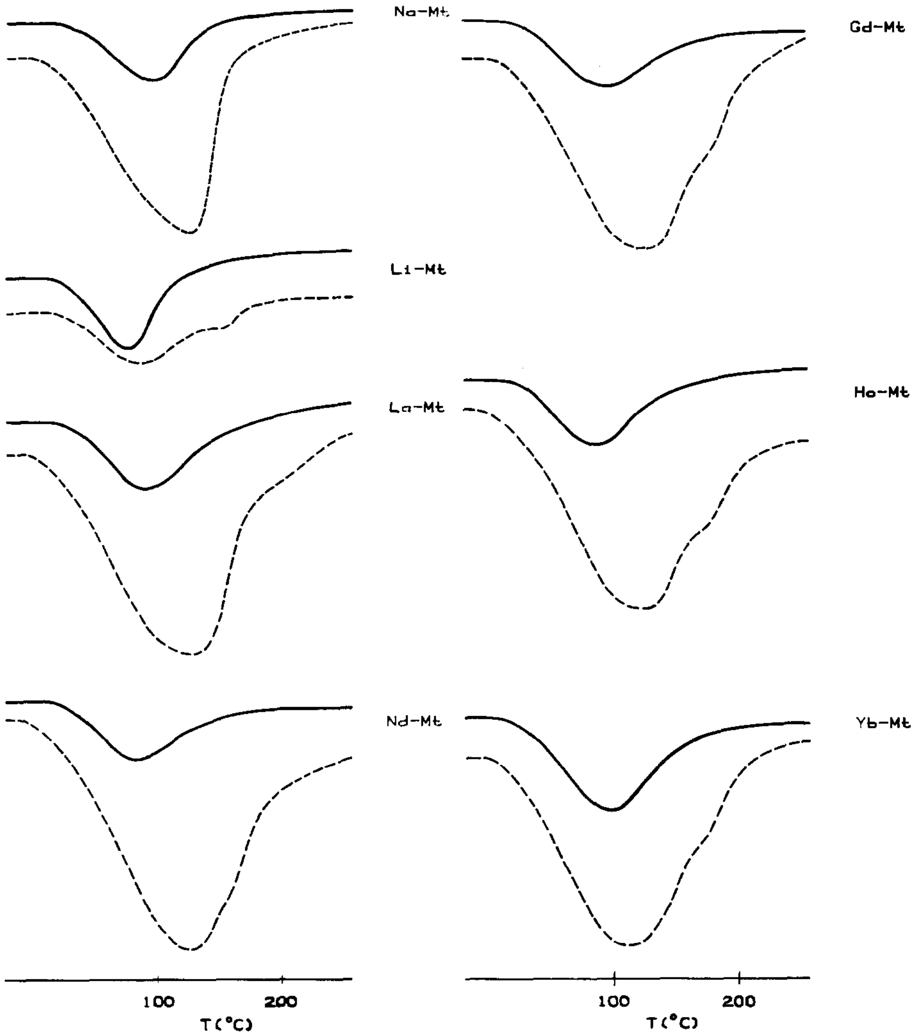

Fig. 1. DTA curves for M-montmorillonites (M ≡ Na^{I}, Li^{I}, La^{III}, Nd^{III}, Gd^{III}, Ho^{III} or Yb^{III}): ———, air-heated samples (300 °C, 24 h); – – –, unheated samples.

molecules per exchangeable cation was estimated: Mg and Ca each had a total of 13–14 molecules in their hydration shell. The hydration shells of Na and K contained 4–5 molecules and 3–4 molecules, respectively. However, as these conclusions were drawn from high-pressure thermal analysis, the possibility of rearrangement of the water molecules in the smectite under the drastic operating conditions (1 kbar) exists. In the present work the thermal dehydration of a few representative samples was studied under flowing nitrogen at 1 atm pressure with the evolved water being analysed by gas chromatography (TPD-GC). Prior to heating, the samples were dried overnight under flowing nitrogen at room temperature in order to reduce molecular water on the external surface (condensed in mesopores and

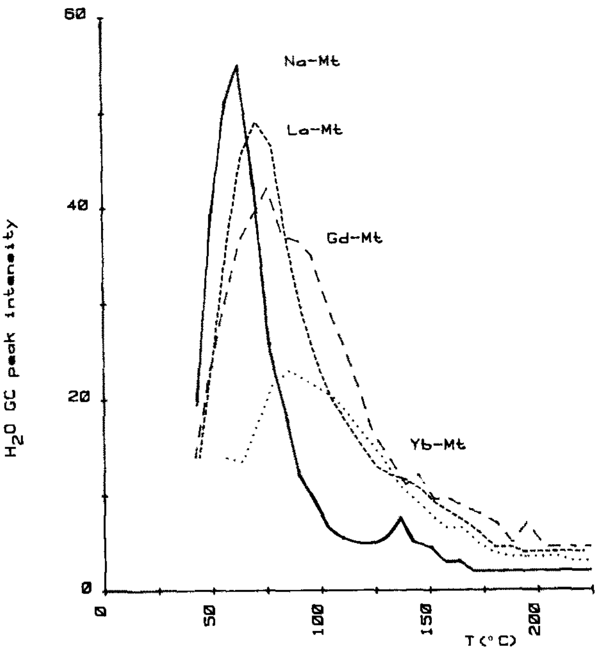

Fig. 2. TPD-GC curves for M–montmorillonites (M ≡ Na^I, La^{III}, Gd^{III} or Yb^{III}).

weakly bonded between the montmorillonite sheets). Figure 2 shows the TPD-GC diagrams for the previously unheated samples. The water content calculated from Fig. 2 is given in Table 1. La^{III}, Gd^{III} and Yb^{III} have been selected, on account of their positions in the lanthanide series.

The data in Table 1 agree with those of Koster van Groos and Guggenheim [10] for unheated Na–Mt. The lanthanide montmorillonites can be classified according to the nature of the exchangeable cation. Those montmorillonites saturated with 4f cations from the first part of the lanthanide series have a total of about 20 molecules per ion in their hydration shell. This agrees with the high ionic potential shown by the lanthanide cations. As the atomic number of the lanthanide increases, a

TABLE 1

Molecular water content, from TPD-GC, of M–Mt (M ≡ Na, La, Gd or Yb) in molecules per exchangeable ion

Samples	Unheated	Air-heated (300 ° C, 24 h)
Na–Mt	4	–
La–Mt	19	12
Gd–Mt	20	10
Yb–Mt	12	6

decrease is observed, down to 12 molecules per ion in the case of Yb^{III}. This effect may result from partial hydrolysis of the hydrated exchangeable 4f ions during the preparation of the samples, which has been demonstrated previously through the adsorption of NH_3 using IR spectroscopy [4]. The extent of hydrolysis increases with the ionic potential of the cation, as expected.

The above-mentioned values, 20 to 12 molecules per ion, respectively correspond to 12% to 7% weight loss of the sample. The total loss of molecular water observed in the previously unheated Ln–Mt was about 25%. The specific surface area of the montmorillonite saturated with lithium, sodium or lanthanides has been measured, rendering values which are in the range of 100 ± 10 m^2 g^{-1}. This implies that the contribution to the molecular water content of water adsorbed as multilayers on the external free surface and that condensed in the mesopores must be almost the same for each sample. This is to be expected since all of the samples were obtained from that saturated with sodium. The total weight losses corresponding to molecular water therefore lead to the conclusion that in the lanthanide montmorillonites there is a large contribution from the so-called weakly bonded water between the structural sheets of montmorillonite.

Thermal analysis of pre-heated samples

The effect of air-heating at 300 °C for 24 h on montmorillonites saturated with Ln ions was studied. After heating, the samples were rehydrated at room temperature and 0.55 relative humidity and their DTA (Fig. 1) and TG curves were obtained. The weight loss data in Table 2 were calculated from the TG curves using a reference weight at 500 °C by extrapolation of the linear TG trace, because structural dehydroxylation begins around 450 °C.

TABLE 2

Weight loss, from TG, of air-heated (300 °C, 24 h) M–Mt (M ≡ Li, Na, La, Nd, Gd, Ho or Yb)

Sample	Weight loss (%)	
	20–500 °C	500–900 °C
Li–Mt	4.7	5.6
Na–Mt	3.7	4.8
La–Mt	6.0	4.5
Nd–Mt	4.8	4.5
Gd–Mt	6.0	4.6
Ho–Mt	5.1	4.6
Yb–Mt	7.9	4.6

The second column in Table 2 gives the weight loss from the initial weight to that at 500 °C. It may be observed from Fig. 1 that the molecular water content decreases as a result of preheating and the shoulder at 150–200 °C almost disappears. One effect of heating is the entrapping of exchangeable ions between the structural sheets. In order to delaminate as much as possible the particles aggregated by heat treatment, the rehydration of the air-heated samples was promoted by interaction of the sample with water vapour at a temperature of about 100 °C [11]. In the case of Na–Mt the initial DTA diagram is reproduced after rehydration, but this is not the case

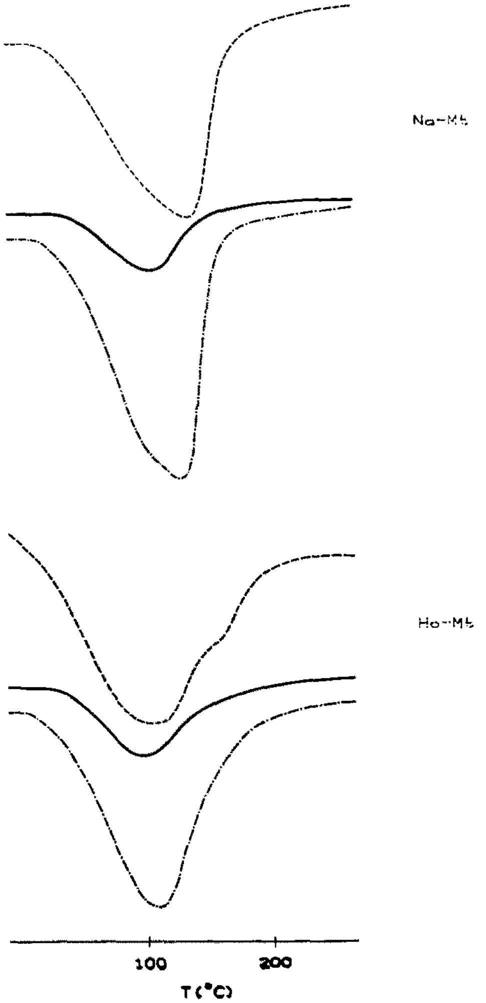

Fig. 3. DTA curves for M–montmorillonites (M ≡ Na^{I} or Ho^{III}): – – –, unheated samples; ———, air-heated samples (300 °C, 24 h) rehydrated at room temperature and 55% relative humidity; –·–·–, air-heated samples (300 °C, 24 h) rehydrated with water vapour at about 100 °C and further dried at 55% relative humidity.

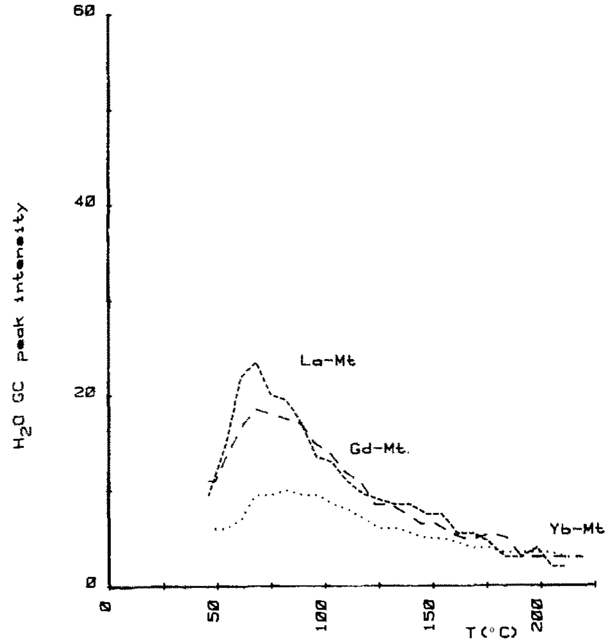

Fig. 4. TPD-GC curves for M-montmorillonites (M ≡ La^{III}, Gd^{III} or Yb^{III}) air-heated (300 °C, 24 h) and rehydrated with water vapour.

for the lanthanide montmorillonites, for which the thermal effect at 150–200 °C apparently remains absent. Figure 3 shows this effect for the montmorillonites saturated with sodium and holmium, by way of an example.

In order to estimate the change in the so-called hydration shell water content of the lanthanide montmorillonites on heating, the TPD-GC diagrams of Ln–Mt (Ln ≡ La, Gd or Yb) after air-heating and further rehydration with water vapour were obtained (Fig. 4).

The third column in Table 1 gives the calculated number of water molecules per ion. A clear decrease is observed, which can be interpreted as being caused by the increase in the extent of the hydrolysis reaction of the 4f interlamellar hydrated ions on air-heating. Previous data from FT-IR spectroscopy supports this statement [4].

In earlier work on thermal hydrolysis of Ln–montmorillonites already mentioned [6], the loss of residual molecular water at even higher temperatures was shown. TG curves for the unheated, air-dried samples gave an almost linear trace between about 250 °C and about 450 °C. A relationship with the polarizing power of the exchangeable cation was derived from the slopes of the TG curves in that temperature interval for the unheated samples. For the preheated lanthanide montmorillonites such a relationship has not been observed; only a decrease from about 3% to 1% in weight loss occurred over this interval. For Li–Mt, the observed decrease is from 0.8%

to 0.4%, while for the montmorillonite saturated with Na, the heat treatment maintains the weight loss in this middle temperature interval at an almost constant level.

The interpretation of the decrease of the shoulder in the interval between 150 ° C and 200 ° C with the air-heat treatment is different for the lanthanides and for the lithium montmorillonites. In the latter case, migration from the exchange positions to the octahedral sheet has been previously observed from IR spectroscopy measurements [12]. This agrees with the explanation generally accepted for the Hofmann–Klemen effect, recently re-examined from the point of view of over-estimation of charge reduction owing to the existence of collapsed interlayers with entrapped Li [13]. However, this mechanism is not consistent with previous FT-IR data for the lanthanide montmorillonites, from which the hydrolysis of the exchangeable ions seems to be the only mechanism. Hydrolysis of the 4f ions seems to be the only interpretation for the above-mentioned decrease of the DTA band between 150 ° C and 200 ° C, which almost disappears with air-heating in spite of rehydration of the samples. An explanation for the actual state of the partially hydrolyzed ions between the montmorillonite sheets has not yet been found, and this point will be discussed through a study of the dehydroxylation of the samples.

Dehydroxylation of the samples

It has previously been observed that the dehydroxylation of the unheated samples occurs via two overall steps appearing at about 500 ° C and 650 ° C in the DTA curves [6]. In the present work, no shift in these temperatures was observed with the air-heat treatment. The theoretical weight loss for the four OH groups in the structural unit cell of the montmorillonite amounts to 4.9% according to the observed formula. The unheated samples showed values for the dehydroxylation which correspond to the theoretical ones in the montmorillonites saturated with Na, La and Nd. For montmorillonites saturated with cations from Gd to Yb, values around 4.5% were found [6]. The third column of Table 2 shows that for the heated Na montmorillonite the dehydroxylation weight loss remains unchanged, equal to the theoretical value. However, all of the lanthanide montmorillonites yield values in the interval 4.5–4.6%.

In a previous paper by Russell [5] on the interaction of ferruginous montmorillonites with alkali metal hydroxides, deprotonation of structural OH groups was observed using IR spectroscopy to occur as follows

$$\mathrm{MOH} + \mathrm{OH(smectite)} \rightarrow \mathrm{MO(smectite)} + \mathrm{H_2O} \qquad (1)$$

This deprotonation reaction was shown to be specific for octahedral $\mathrm{Fe^{III}}$–OH. The 0.28 Fe atoms per unit cell in the montmorillonite used in this study leads to a calculated potential decrease in the dehydroxylation

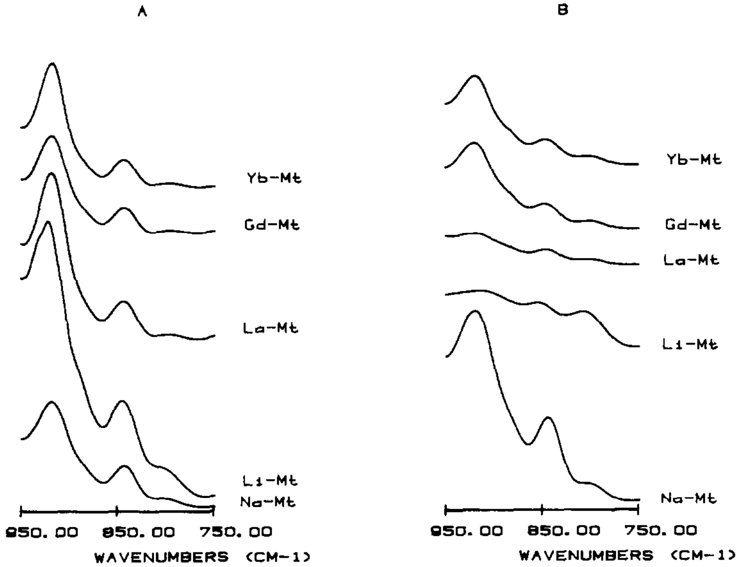

Fig. 5. FT-IR spectra (950–750 cm^{-1}) of M–montmorillonites (M ≡ Na^{I}, Li^{I}, La^{III}, Gd^{III} or Yb^{III}): A, unheated samples; B, air-heated samples (300 °C).

weight loss of 0.4%. This process requires previous hydrolysis of the hydrated interlayer cations, which has been demonstrated to occur even during the preparation of the lanthanide montmorillonites and to be enhanced by air-heat pretreatment. The values in the interval 4.5–4.6% for the heated lanthanide montmorillonites agree with the Fe^{III} content and express a lower limit of this magnitude. From diverse parallel TG measurements on heated Ln–montmorillonite, an accuracy of $\pm 0.1\%$ has been estimated for the experimental weight losses of dehydroxylation in Table 2.

On heating lithium montmorillonite, migration to octahedral positions and hydrolysis of the exchangeable ions occurs as well as entrapping of these ions [13]. The LiOH decomposes at temperatures above 500 °C, so that the high value for dehydroxylation observed in Table 2 (5.6%) must correspond to lithium hydroxide in excess of that reacting via process (1). The transformation of all the interlamellar Li^{I} cations into LiOH, which is not the case, could correspond to an additional weight loss on the theoretical 4.9% value, of 1.6%.

The intensity of the OH bending bands has also been examined (Fig. 5). The FT-IR spectra of Na–Mt show no decrease in intensity on heating; in fact an increase is observed which is known to be caused by a change in the molar absorption coefficient when montmorillonite air-dried films are heated. However, the montmorillonite saturated with Li shows a large decrease in the OH bending intensities. This implies that the air-heat treatment causes the same effect as interactions with LiOH in the Li saturated montmorillonite. It can be deduced that, under heating, the hydrated exchangeable Li ions cause deprotonation of the smectite. In order to maintain electrical neutrality, the Li^{I} cations must be retained as close as possible to the structural oxide ions and, because of the small size of Li^{I} cations (radius 0.60 Å), they can approach the oxide ion through the hexagonal holes in the structural tetrahedral sheets. This occurs with a slight disturbance of the positions of the silicon or oxygen atoms and a decrease in the intensity of OH bending bands.

The intensities of the OH bending bands for the air-heated Na–Mt and Li–Mt samples are not influenced by the relative humidity within the interval studied here. Nevertheless, for the lanthanide-saturated montmorillonites a decrease is observed on heating, which depends on the degree of hydration. The trivalent lanthanide cations are known to form coordination compounds with crown ether ligands having 6 oxygen donors, whose ion-size/crown-size ratio is close to the ion size/hole(smectite)-size ratio [14]. Therefore, the trivalent lanthanide cations can approach the structural oxide ions through the hexagonal holes in the tetrahedral sheets. However, under sufficiently high water pressures the hydration enthalpies of these cations [15] are sufficiently high, compared with that of Li^{I} [16], to shift reaction (1) partially to the left-hand side and to return the cations to their exchange positions. In order to check this statement, FT-IR spectra have been obtained using the vacuum cell already described. Films of the various lanthanide montmorillonites were heated at 300 °C for 24 h in a vacuum cell to pressures of about 10^{-4} Torr. Figures 6 and 7 show the spectra of the montmorillonites saturated with Na, La, Gd or Yb, before and after heating.

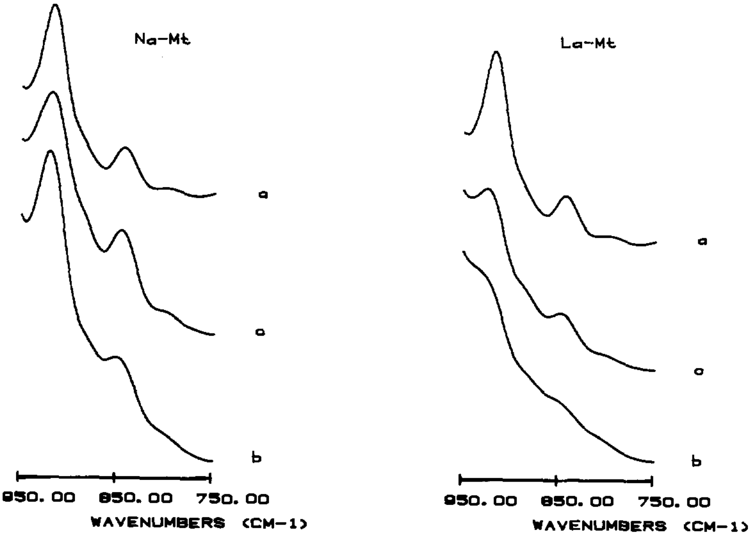

Fig. 6. FT-IR spectra (950–750 cm^{-1}) of M–montmorillonites ($M \equiv Na^{I}$ or La^{III}) in a vacuum cell: a, unheated samples; b, vacuum-heated samples (300 °C, 24 h); c, samples treated as in b, followed by further rehydration at 55% relative humidity.

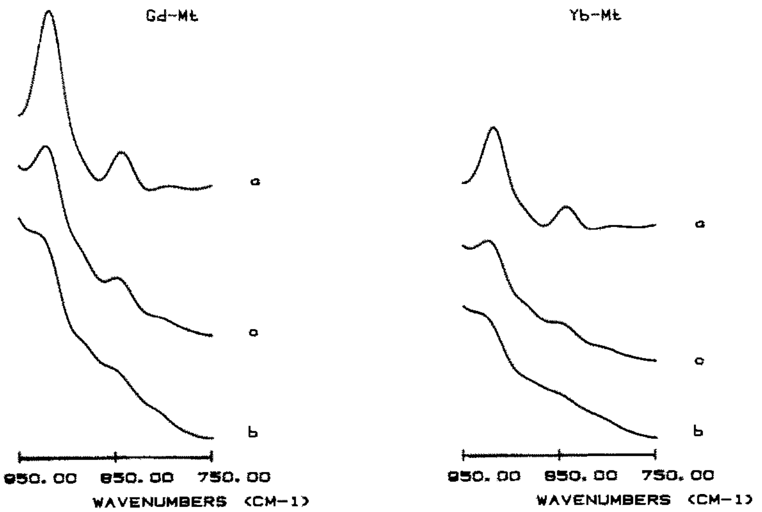

Fig. 7. FT-IR spectra (950–750 cm^{-1}) of M–montmorillonites (M ≡ Gd^{III} or Yb^{III}) in a vacuum cell: a, unheated samples; b, vacuum-heated samples (300 °C, 24 h); c, samples treated as in b followed by further rehydration at 55% relative humidity.

The spectra of the samples rehydrated in air, after heating, are also shown. As suggested above, at a reduced vapour pressure reaction (1) occurs and the lanthanide cations approach the hexagonal holes in the tetrahedral sheets of the montmorillonite, but on rehydration they return to their exchange positions. The intensities of the OH bending bands do not increase with hydration in the case of the Li–Mt samples. This must be interpreted on the basis of the lower value of the hydration enthalpy of Li^{I}.

In connection with the storage of high-level nuclear wastes, the above-mentioned results on the effect of preheating on the thermal dehydration of Ln–montmorillonites afford a description of the fixation of radionuclides by the geologic formations surrounding the waste canisters.

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