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Dedicated to Dr. Robert Mackenzie on the occasion of his 75th birthday

THE STUDY OF THE DEHYDRATION AND DEHYDROXYLATION OF SMECTITES BY EMANATION THERMAL ANALYSIS

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Abstract

The dehydration and dehydroxylation of the smectites, beidellite and montmorillonite (dioctahedral) and saponite and laponite (trioctahedral), were investigated by ETA, DTA, TG and X-ray diffractions. There are differences between the behaviors of di- and trioctahedral clays which are due to the differences in the ability of the exchangeable cations to migrate into hexagonal holes of the SiO_4 network and due to the fact that the dehydroxylation and recrystallization of dehydroxylated trioctahedral smectites occur simultaneously, whereas there is a temperature gap of about 300°C between the dehydroxylation and the recrystallization of dioctahedral smectites.

Keywords: DTA, ETA, smectite clay minerals, TG, X-ray

Introduction

The dehydration and dehydroxylation of smectite clay minerals have been studied for many years due to the importance of these reactions in natural systems and for many technologies [1–7]. Differences in the dehydroxylation of the different smectite minerals has been known for many years. However, only in the last few years have scientists paid attention to differences in the thermal dehydration of the different smectite minerals [8]. The differences in the behavior were related to differences in the surface basicity of the oxygen plane of the smectite layer and its ability to form hydrogen bonds with interlayer water molecules [9]. Yariv *et al.* [10] studied by DSC the thermal dehydration of montmorillonite and laponite, saturated with a large hydrophobic organic cation, which serves as water structure breaker. They showed that the molar dehydration energy is higher in montmorillonite than in laponite. This was related to the tetrahedral substitution of Si by Al, which results in increasing basic strength of atoms of the oxygen plane [9]. A very small tetrahedral substitution was found in most samples of montmorillonite [11, 12], which is a natural clay, but not in laponite which is a synthetic clay. Consequently, hydrogen bonds are formed between water molecules and the oxygen plane in montmorillonite, but not in laponite.

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Water in the interlayer space of smectites can be divided into three zones, A_m, B_{om} and A_o [9]. Water molecules which form the hydration sphere of the exchangeable metallic cation belong to zone A_m. Water clusters which fill the space between the hydrated cations belong to zone A_o. This water forms a boundary layer at the flat oxygen plane. Both these zones contain structured water. Between these two structured zones there is a non-structured zone, containing disordered water molecules (zone B_{om}). Water of zone A_m is acidic due to the strong polarizing power of the exchangeable cation. In the case of smectites with a high basic strength of the oxygen plane, water molecules of zone A_m form hydrogen bonds with the oxygen planes of the silicate layers which serve as electron pair donors. In this case the basal spacing of the clay is determined by the hydration number of the exchangeable cation. It is ~1.5 nm with hydration number 6 and ~1.2 nm with hydration number 3 or 4 (planar). In the case of smectites with a low basic strength of the oxygen planes (such as laponite), where no hydrogen bonds are formed between water molecules of zone A_m and the oxygen plane of the silicate layer, the basal spacing of the clay is determined by the size of the clusters which form zone A_o. Since these clusters are of different sizes the 001 X-ray peak in the diffractogram of laponite is very broad.

In the present paper we describe the study of the dioctahedral smectites, montmorillonite and beidellite and of the trioctahedral smectites, laponite (a synthetic hectorite) and saponite by the emanation thermal analysis (ETA). In this method the release of the inert gas radon (^{220}Rn) from the solid samples, previously labeled with trace concentrations of its parent nuclides ^{228}Th and ^{224}Rn, is measured as a function of temperature [13, 14]. The inert gas does not react with the clay and its release is controlled mainly by diffusion in matrix and pores but increased with increasing temperature. If the latter is taken into consideration, this method makes possible the continuous in-situ study of morphological and microstructural changes which take place during a thermal treatment of the clay. ETA study was supplemented by DTA, TG and X-ray study. These methods can give information on the thermal dehydration of the smectites and on the collapse of the clay.

Experimental

Laponite XLG (a synthetic Na-hectorite) was kindly donated by Laporte Industries, Inc., UK. Wyoming bentonite (Na-montmorillonite) was supplied by Ward's Natural Science Establishment, Inc. Saponite and beidellite, both from California (Ca clays) were supplied by Source Clay Minerals Repository, Columbia, Missouri.

The ETA instrument has been previously described [14]. Parent nuclides of radon, i.e. ^{228}Th and ^{224}Ra, were used in trace concentrations for the labeling of the clay samples by their adsorption from aqueous solutions and subsequent drying at 80°C in air. ^{220}Rn atoms are formed as the consequence of spontaneous alpha radioactive decay. The labeled samples were stored for three weeks in dry air before the ETA measurements were made. The samples were heated from room temperature to 1200°C and cooled back to room temperature in a dynamic dry air atmosphere. The heating rate was 5°C min^{-1}.

Simultaneous DTA-TG curves were recorded in flowing air using a Stanton-Redcroft apparatus (STA 781). Calcined alumina was used as reference material. Cylindrical alumina crucibles (5×5 mm) were used for the specimen (20 mg) and the reference material. The samples were heated from room temperature to 1000°C in a dynamic dry air atmosphere (50 ml min^{-1}). The heating rate was 10°C min^{-1}.

X-ray analysis of powder samples was carried out by a Philips Automatic Powder Diffractometer (PW 1710) with a Cu tube anode.

Results and discussion

ETA curves of laponite, saponite, montmorillonite and beidellite are shown in Figs 1–4. The ETA curves describe the temperature dependence of radon release showing either an increase in the rate of the release of radon or a decrease in this rate which correspond to increase and decrease in the surface areas and nanoporosity of the examined solid samples, respectively. In the temperature range where there are no changes in the morphology and microstructures of the clay, the ETA curves show a smooth character of the release of radon. Figures 1–4 also show the DTA and TG curves of these minerals. In Fig. 5 X-ray diffractograms of clay samples heated at 300°C under vacuum are shown.

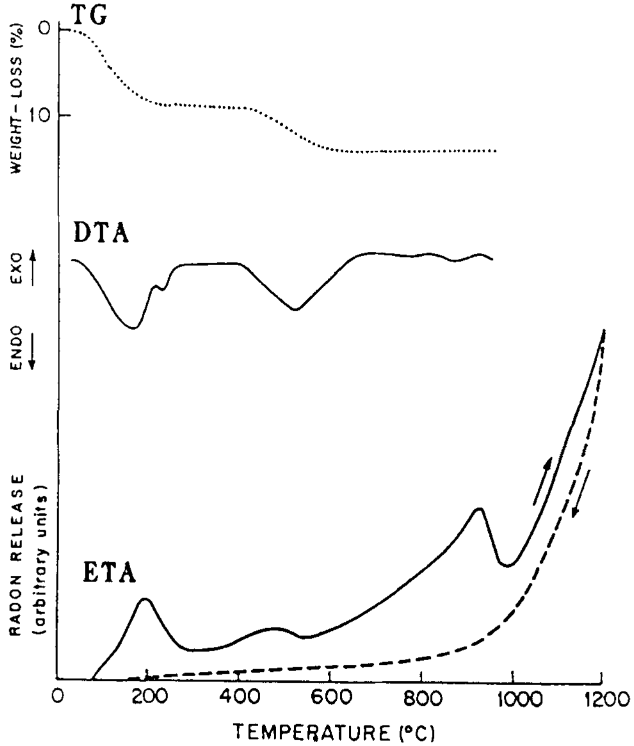

Fig. 1 ETA (heating and cooling curves), DTA and TG curves of beidellite

The dehydration of the smectites

The first increase in the rate of radon release in the ETA curve results from an endothermic reaction which is associated with weight-loss, as can be seen from the DTA and TG curves. This is the dehydration process in which water is evolved from the interlayer space. There are significant differences between the ETA curves of di- and trioctahedral clays and they will be discussed separately.

Dioctahedral smectites

ETA curves of beidellite and montmorillonite show that the highest emanation occurs at 200 and 100°C, respectively (Figs 1 and 2). This can be interpreted as follows. Before the thermal treatment the interlayer space is filled by different types of water and the basal spacing of the smectite is determined by the size of the hydrated cation. In the first thermal stage mainly weakly adsorbed water molecules are evolved (non-structured water of zone B_{om}) leaving vacancies in the interlayer space, thus leading to an increase in the rate of release of radon. At higher temperatures the exchangeable cations are dehydrated. This process leads to a collapse and decrease of the basal spacing thus leading to a decrease in the rate of radon release. This process terminates at 300 and 200°C according to the ETA curves of beidellite and montmorillonite, respectively. This is in agreement with our X-ray study of the

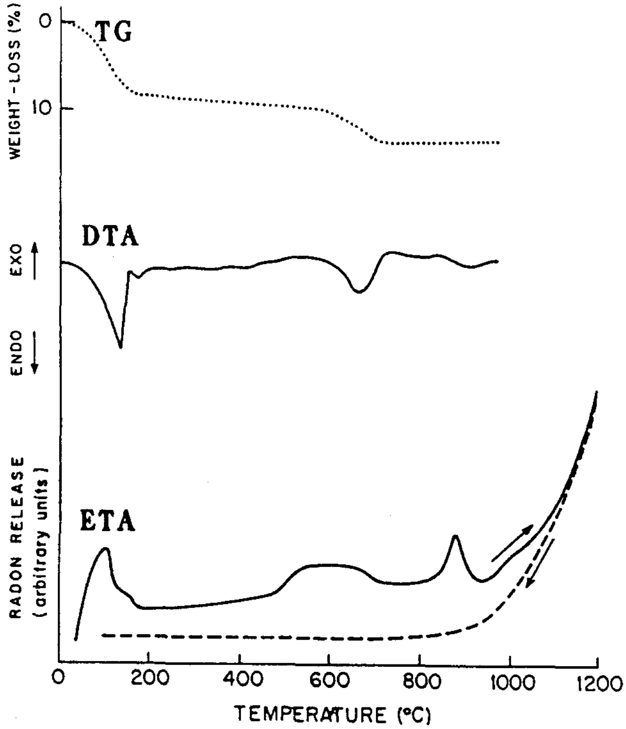

Fig. 2 ETA (heating and cooling curves), DTA and TG curves of montmorillonite

Table 1 Basal spacings (in nm) of smectites equilibrated at room temperature (*r.t.*) at 40% humidity and heated under vacuum at 300°C

Mineral	Temperature/°C	
	r.t.	300°C
Beidellite	1.42	0.99
Montmorillonite	1.25, 1.52 sh	0.96
Laponite	1.23	1.08
Saponite	1.50	1.26

samples. Diffractograms which were recorded after heating the samples at 300°C for 24 h showed that their *c*-spacing dropped to 0.99 and 0.96 nm, respectively (Table 1 and Fig. 5). It should be noted that during this thermal treatment the exchangeable cations were fixed by migrating into the hexagonal holes of the silicate layers and any rehydration of the samples after removal from the furnace was not observed.

Trioctahedral smectites

The ETA curve of laponite differs from those of the dioctahedral smectites (Fig. 3). It shows a rise in the emanation rate up to 130°C indicating that up to this temperature laponite behaves similarly to the dioctahedral clays. This is followed by a small decrease of the emanation rate. From 200°C an almost constant rate of radon release is observed. The figure shows that the rate of radon release starts to drop only at 600°C. According to the TG curve most of the water was evolved below 300°C. An X-ray diffractogram of this clay heated 24 h at 300°C under vacuum showed a very broad basal spacing ranging between 3 and 10 2θ with a maximum at 1.08 nm (Fig. 5). The broad peak indicates an inhomogeneous interlayer with spacings ranging between 0.95 and >2.0 nm. This behavior is associated with the presence of non-fixed exchangeable cations and water clusters of zone A_0 in the interlayer space of laponite, which were readsorbed from the atmosphere. It was necessary to heat the laponite at 400°C for 3 days in order to obtain a *c*-spacing of about 1.0 nm. Above 600°C the exchangeable cations migrated into the silicate layer and the clay collapsed, leading to a slower emanation. The ETA clearly indicated the highly disordered structure of the laponite sample before the temperature reached 600°C, when the structure transition takes place which will be discussed in the latter part of this paper.

Saponite is less basic than both dioctahedral smectites which are studied here, but is more basic than laponite, due to the tetrahedral substitution of Si by Al which occurs in the former. The thermal dehydration of this mineral is between that of the dioctahedral clays and that of laponite. The ETA curve shows a sharp increase in the emanation rate with a maximum at 100°C, due to the evolution of non-structured water (zone B_{onl}), followed by a sharp decrease, which terminates at about 200°C due to the dehydration of the exchangeable cations. An additional weak de-

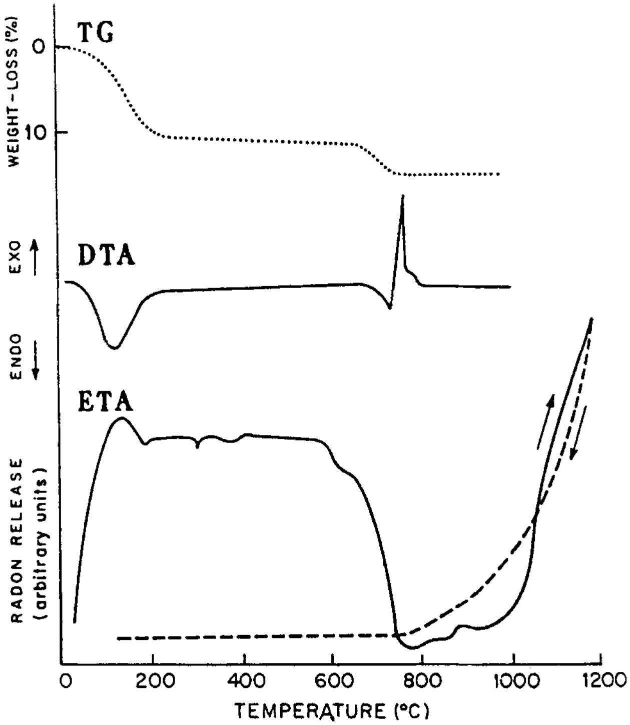

Fig. 3 ETA (heating and cooling curves), DTA and TG curves of laponite

crease in the emanation rate appears in the range 500–700°C. From X-ray data (Fig. 5) it is obvious that this mineral readsorbed water from the atmosphere after being dehydrated at 300°C. It requires temperatures higher than 400°C and a long heating period to loose the ability to readsorb water from the atmosphere. The readsorbed water molecules coordinated the exchangeable cations and were hydrogen bonded to the oxygen planes [9]. Thus a *c*-spacing of 1.26 nm was obtained after heating the clay at 300°C. The differences in the dehydration between di- and trioctahedral clays is associated with the differences in the migration of the interlayer cations into hexagonal holes of the SiO_4 network on thermal dehydration and their fixation. In montmorillonite and beidellite a temperature of 300°C is sufficient for this fixation. In saponite and laponite, on the other hand, the fixation occurs only with the first stages of the dehydroxylation of the clay [15].

Dehydroxylation of smectites

The DTA and TG curves show endothermic dehydroxylation peaks at 530, 650, 730 and 810°C for beidellite, montmorillonite, laponite and saponite, respectively. In the case of the dioctahedral clays, beidellite and montmorillonite, the ETA curves show that the dehydroxylation is associated with an increase in the rate of the

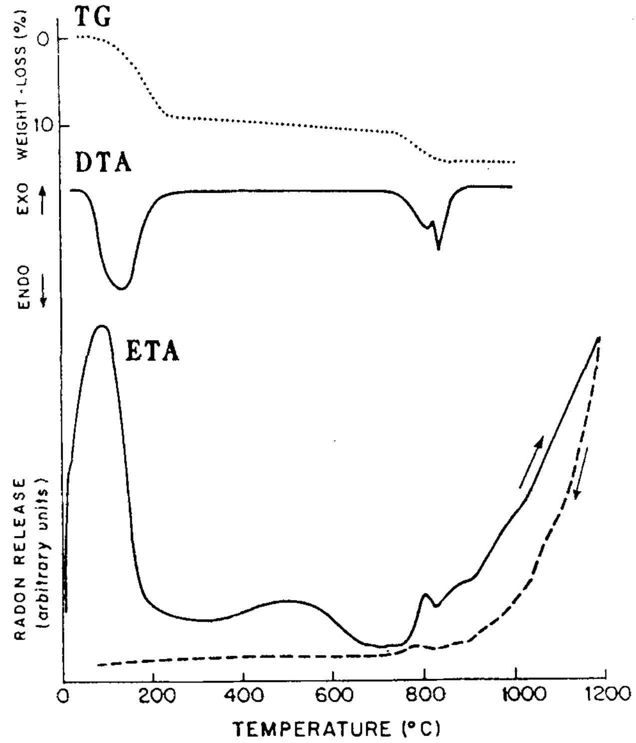

Fig. 4 ETA (heating and cooling curves), DTA and TG curves of saponite

release of radon. This is due to the fact that the dehydroxylation process results in the formation of amorphous meta-beidellite and meta-montmorillonite, respectively, which are rich with lattice vacancies. On further heating, the annealing of the amorphous particles takes place. Above 900°C the DTA curves of the dioctahedral smectites show *S*-shaped endothermic exothermic effects which are not accompanied by any weight-loss and are ascribed to recrystallization of the amorphous meta clays [1]. The sharp rise in emanation rate which is observed above 900°C is mainly due to an increased radon mobility caused by thermal diffusion. However, the changes in the emanation rate due to the recrystallization of the clay is clearly shown.

In the ETA study the samples were heated to 1200°C and cooling curves were recorded. Comparing heating with cooling curves shows that at each temperature below 1100–1150°C values of the release of radon are lower during sample cooling, indicating that the particles which underwent the cooling process were larger after having passed the heating process. It demonstrated clearly that after the crystallization of the amorphous meta-smectites, particle size of the crystallized material increased with the rise in temperature, up to 1150–1200°C. In the case of the trioctahedral laponite and saponite, the ETA curves show that the dehydroxylation was associated with a decrease in the rate of the release of radon. According to Bradley

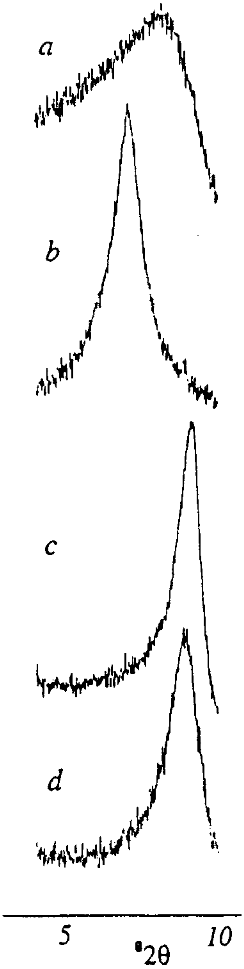

Fig. 5 X-ray diffractograms of (a) laponite, (b) saponite, (c) montmorillonite and (d) beidellite, heated one night at 300°C under vacuum and left 3 h in air atmosphere

and Grim [16] and to Earnest [17, 18] trioctahedral smectites form unstable metaphases which undergo immediate recrystallization during the thermal treatment. A decrease in the rate of the release of radon is due to crystallization of enstatite. In our study its presence has been observed by X-ray study of the samples heated at 1000°C. The ETA cooling curve of saponite shows that in general the release of radon is lower than in the heating curve – an indication that after the thermal crystallization of the dehydroxylated clay, the particles became larger with the rise in temperature, up to 1200°C.

In laponite the high temperature range is complicated as is shown by the fact that between 1200–1050°C the cooling curve was below the heating curve, whereas from 1050°C downwards to 750°C it was above the heating curve. The low rate emanation in the heating curve in the temperature range of 750–1050°C is that of enstatite, which is obtained at >750°C. According to Bradley, Grim and Earnest [16–18] by heating hectorite above 1000°C, diopside, clinoenstatite and forsterite are obtained, in addition to enstatite, and their amounts increase with the rise in temperature. A similar thermal reaction is expected to occur with laponite (which is a synthetic hectorite) at >1000°C. The rates of emanation in the heating curve in the 1050–1200°C temperature range and in the whole cooling curve characterize the radon diffusion properties in these four minerals. The ETA cooling curves of laponite and of the other minerals investigated in this study make it possible to characterize the diffusion properties of the products of the thermal treatments in air up to 1200°C. The apparent activation energy of radon diffusion can be used as a parameter in this characterization which will be discussed in another paper.

Conclusion

The ETA method has been shown as a very suitable method for the *in-situ* characterization of microstructural changes occurring during the heating of clay minerals. In the first stage weakly adsorbed non-structured water (zone B_{0m}) is evolved from the interlayer space, leaving vacancies in the interlayer space, thus enabling the increment of the rate of release of radon. At higher temperatures water from the hydration atmosphere of the cations (zone A_m) is evolved. In the dioctahedral clays the exchangeable cations migrate into the hexagonal holes of the silicate layers and are fixed, the clays collapse and the emanation of radon decreases together with the dehydration of the cations. In the trioctahedral clays, the migration of the exchangeable cations into the hexagonal holes of the silicate layers and their fixation occurs at about 600°C, leading to a collapse of the clay and a decrease in the rate of emanation. Above 500°C, when the dioctahedral clays are dehydroxylated, the release of radon increases because of the lattice vacancies in the amorphous phases. At about 950°C, during the crystallization of the amorphous phase, the particles grow and the radon release rate decreases. In the case of the trioctahedral clays, the amorphous phase which should be obtained with their dehydroxylation, recrystallizes immediately after the dehydroxylation. Consequently an increase in the radon release rate due to the dehydroxylation is not obtained.

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