Journal of Thermal Analysis and Calorimetry, Vol. 92 (2008) 1, 191–197

THERMAL CHARACTERIZATION OF MONTMORILLONITE CLAYS SATURATED WITH VARIOUS CATIONS

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Emanation thermal analysis (ETA), thermogravimetry and high temperature XRD were used to characterize the thermal behavior during dehydration of natural Na montmorillonite (Upton Wyoming, USA) and homoionic montmorillonite (MMT) samples saturated with different cations, i.e. Li^+, Cs^+, NH_4^+, Mg^{2+} and Al^{3+}. ETA results characterized radon mobility and microstructure changes that accompanied the mass loss of the samples due to dehydration on heating in air. A collapse of interlayer space between the silicate sheets after water release from the MMT samples was characterized by a decrease of the radon release rate, ΔE. Decreases in c-axis basal spacing (d_{001}) values determined from XRD patterns for the different montmorillonite samples follow the sequence:

$$\text{Mg-MMT}>\text{Al-MMT}>\text{Li-MMT}>\text{Na-MMT}>\text{NH}_4\text{-MMT}>\text{Cs-MMT}$$

The decrease of the radon release rate (ΔE) determined by ETA that characterized microstructure changes due to collapse of interlayer space corresponded well to differences in the c-axis basal spacing (Δd_{001}) values determined from the XRD patterns before and after samples dehydration.

Keywords: *collapse of interlayer space, dehydration, emanation thermal analysis, Na-montmorillonite saturated with various cations, radon mobility, thermogravimetry, XRD*

Introduction

In order to understand the environmental behaviour of montmorillonite clay minerals their dehydration and dehydroxylation on heating has been studied by several authors [1–7]. It was found that differences in the montmorillonite dehydration are due to a more or less strong polarizing power of the exchangeable cation. The hydration number of the exchangeable cations can be expressed by a basic spacing of the clay structure characterized by c-axis basal spacing d_{001} [1]. Mackenzie [5] suggested that the amount of interlayer water depends on hydration energy of the adsorbed cations and on hydration of the surface, and that thermogravimetry results can be interpreted to give relative values for these amounts of water. He stated that for most of divalent cations (e.g. Mg^{2+} and Ca^{2+}) the ion is more important that the interlayer surface, but for larger divalent cations as well as for monovalent cations the influence of the layered surface on the hydration is dominant. Glasser *et al.* [7] showed that polyvalent ions tend to detach themselves from the silicate surface and incorporate in the water layers. They stated that the complete loss of the interlayer water is accompanied by a reduction in the c-axis dimensions (0.94–1.00 nm) with exact value depending on the size of interlamellar ions. Several authors [8–10] demonstrated that the decrease of c-axis basal spacing d_{001} as the result of the montmorillonite dehydration is dependent on the exchanged cation and the temperature used for the samples dehydration.

In this study thermogravimetry, emanation thermal analysis and high temperature X-ray diffraction methods were used to characterize the thermal behavior during dehydration of natural Na-montmorillonite and homoionic montmorillonite samples prepared by a saturation of Na-montmorillonite with cations of Li^+, Cs^+, NH_4^+, Mg^{2+} and Al^{3+}, respectively. The high temperature X-ray diffraction was used to determine the c-axis basal spacing parameters of the montmorillonite samples.

Emanation thermal analysis (ETA) [11, 12], based on the measurement of radon release from samples previously labeled, was used to characterize microstructure changes during ‘in situ’ heating of the samples. The ETA has been previously used in the characterization of the thermal behavior of various

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1388–6150/$20.00

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minerals, such as kaolinite [13], saponite, beidelite [3], vermiculite [14–16], boehmite [17], pyrophyllite talc [18], brannerite [19] and hematite [20].

Experimental

Samples

Natural Na-montmorillonite (Upton, Wyoming, USA) was used as a starting material. Homoionic montmorillonite samples saturated with Li^+, Cs^+, NH_4^+ and Mg^{2+}, respectively, were prepared from Na-montmorillonite sample as follows: the amount of 10 g of the Na-montmorillonite was mixed with 800 mL of water and stirred during two days. After decantation 0.2 M chloride solution (200 mL) of the respective cation was added. The suspension was stirred for two days, several times washed by distilled water until the negative reaction for chlorides (using Ag^+ ions). The samples prepared by this way were dried at the temperature of 40°C in air.

Methods

ETA measurements were carried out by using a modified NETZSCH Equipment Type DTA 404. The samples were heated at the rate of 6 K min^{-1} in a constant air flow of 75 mL min^{-1}. Samples for ETA measurements were labeled by a surface adsorption of trace amount of ^{228}Th as nitrate in acetone solution. The specific activity of the sample was 10^4 Bq g^{-1}. Atoms of radon ^{220}Rn were formed by a spontaneous α-decay of ^{228}Th and ^{224}Ra. The ^{220}Rn atoms were implanted into the subsurface of the samples by recoil energy of 85 keV $atom^{-1}$ to a maximum depth of 80 nm, as calculated by the Monte Carlo method using TRIM code [21]. More details about emanation thermal analysis as a less common method are given elsewhere [11, 12].

TG/DTG measurements were carried out by using NETZSCH Equipment Type STA 429 on heating at 6 K min^{-1} in air. XRD equipment (PHILIPS PW 1050/25) using CuK_α Ni-filtered radiation and equipped with a high temperature chamber was applied to obtain XRD patterns and to determine *c*-axis basal spacings (d_{001}) under in situ conditions of heating. Samples were directly heated at a rate of 6 K min^{-1} in air inside the high temperature changer while the XRD patterns were measured at selected temperatures.

Results and discussion

Thermogravimetry results (TG/DTG curves) of Na-montmorillonite and homoionic montmorillonite samples saturated with Li^+, Cs^+, NH_4^+, Mg^{2+} and Al^{3+} ions, respectively, are presented in Figs 1a–f. The mass loss observed on heating from about 50 up to about 200°C corresponds to the release mainly of water molecules of the hydrophobic hydration zone situated between the silicate sheets. The amount of released water as well as the temperature of dehydration process are affected by the interlayer cation [5, 6]. Li^+, Mg^2 and Al^{3+} are small cations with a high polarizing effect. It was demonstrated by Yariv [22] that the hydration water in the interlayer space of the respective montmorillonite samples form H-bonds with the clay-oxygen plane. Similar association can be supposed with exchangeable Na^+ cations and in a smaller extent also with the NH_4^+ cations.

TG results in Figs 1a–f are in agreement with the results of other authors [8–10] demonstrating that temperatures higher than 200°C are needed for a complete dehydration and collapse of the interlayer space initially filled with water molecules. For Li-, Na-, NH_4-, Mg- and Al-montmorillonite samples the values of basal spacings d_{001} of 0.96–1.00 nm were found [8, 9].

Figures 2a–f depict high temperature XRD patterns of the investigated montmorillonite samples. The decrease in basal spacings d_{001} of montmorillonite samples on heating up to 200°C can be attributed to the loss mainly of water molecules situated in the interlayer space with hydrophobic character [22]. The d_{001} values obtained are similar or slightly higher to data reported in [8] for the montmorillonite samples heated at 375°C/3 h. The conditions used for the samples preparation in [8] differed from the conditions used for the high temperature XRD in this study.

For the Al^{3+}-montmorillonite as well as for other samples the d_{001} value obtained in this study is higher than in the paper [8]. This can be ascribed to the fact that a small portion of the intercalated water remained in the samples investigated in the present study.

The d_{001} value found in this study for Cs^+-montmorillonite after heating to 150°C was 1.33 nm , i.e. similar to the value of 1.17 nm found in [8] for the Cs^+-montmorillonite sample after heating at 375°C/3 h. It should be mentioned that the d_{001} value for the Cs^+-montmorillonite that contained no intercalated water should be about 0.99 nm [10]. In the case of Cs-montmorillonite the large monovalent Cs^+ cations are not hydrated. However, they break the structure of the interlayer water. According to Yariv [22] a special shape of water molecules bridging between parallel layers is responsible for the postponement the collapse of interlayer space in the Cs-montmorillonite to higher temperatures, namely up to 420°C.

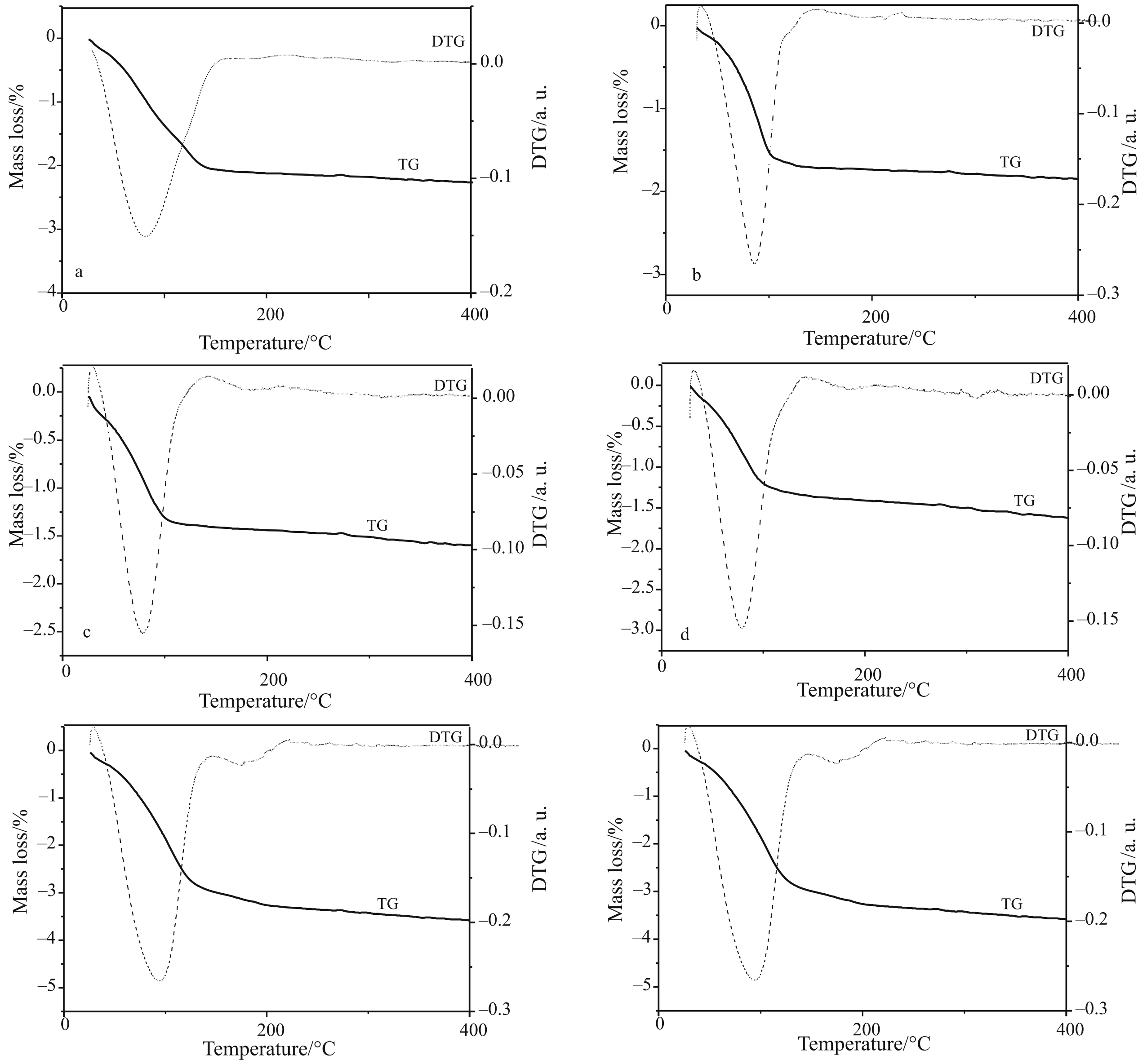

Fig. 1 Thermogravimetry results of montmorillonite samples measured in air at the rate 6 K min^{-1}. a – Li^+-exchanged montmorillonite, b – Na-montmorillonite–natural sample (locality Upton, Wyoming, USA), c – Cs^+-exchanged montmorillonite, d – NH_4^+-exchanged montmorillonite, e – Mg^{2+}-exchanged montmorillonite, f – Al^{3+}-exchanged montmorillonite

Figures 3a–f depict emanation thermal analysis results of Na-montmorillonite and homoionic montmorillonite samples prepared by saturation of Na-montmorillonite with Li^+, Cs^+, NH_4^+, Mg^{2+} and Al^{3+} ions, respectively. These figures showed an enhanced radon release rate, $E(T)$, at the beginning of the heating due to the surface exposure after the water release from the samples, followed by a decrease of radon release rate $E(T)$ that characterized the collapse of the interlayer space between the silicate sheets, initially filled with water molecules. It is obvious that the mobility of radon atoms in the montmorillonite sample decreased due to the collapse of the interlayer space between the silicate sheets.

On further heating above 200°C the radon mobility remained low for most of investigated samples. However, for Cs^+ montmorillonite (Fig. 3c) an enhancement of the radon release rate $E(T)$ was observed on heating above 200°C, due to the release of still remaining water and opening the new diffusion path for radon release. As expected, no radon release enhancement was observed with other montmorillonite samples on heating above 200°C; by this way the ETA results characterized the thermal

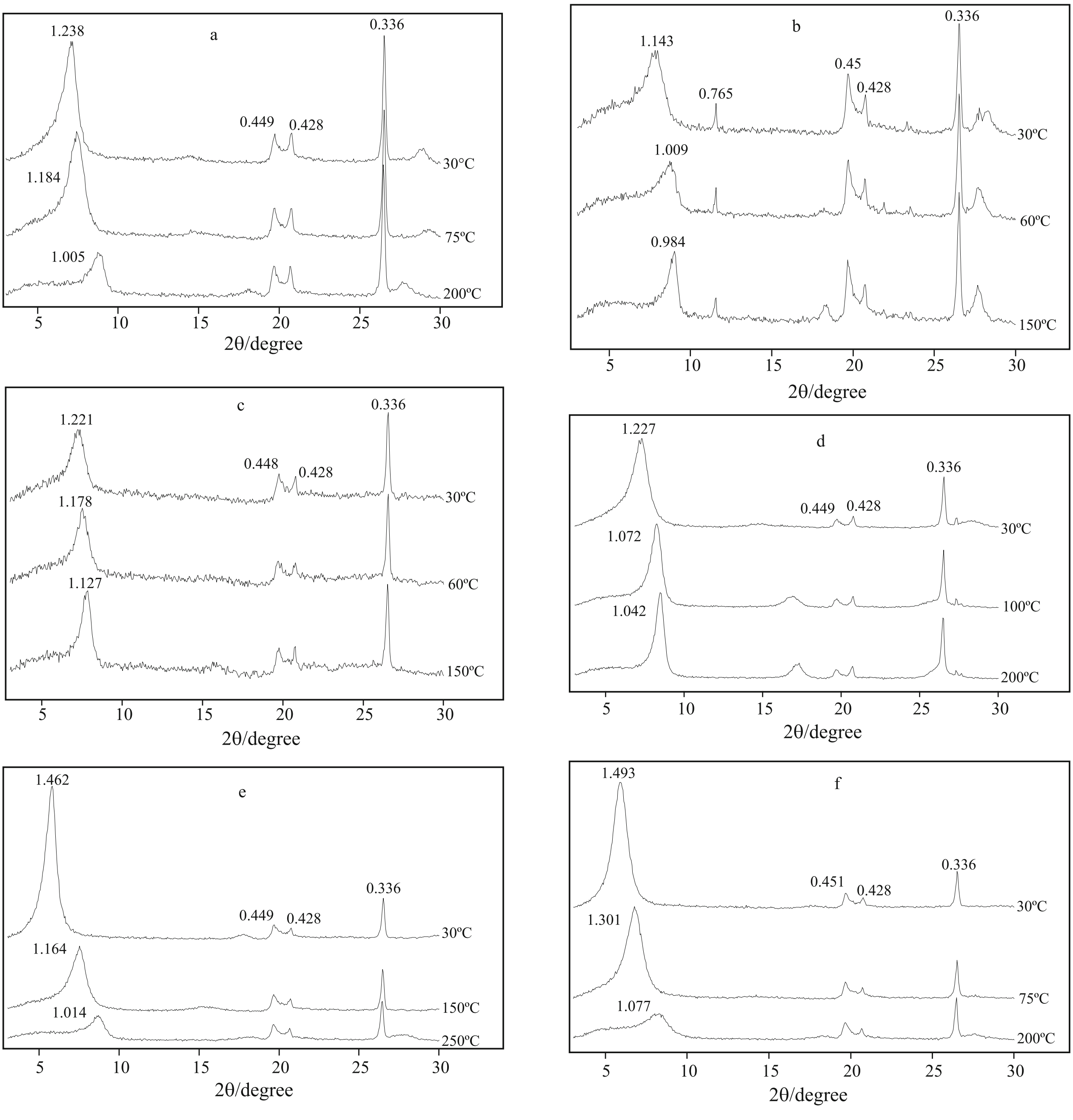

Fig. 2 High temperature XRD patterns obtained on heating of the montmorillonite samples. a – Li^+-exchanged montmorillonite, b – Na-montmorillonite–natural sample (locality Upton, Wyoming, USA), c – Cs^+-exchanged montmorillonite, d – NH_4^+-exchanged montmorillonite, e – Mg^{2+}-exchanged montmorillonite, f – Al^{3+}-exchanged montmorillonite

stability of the collapsed interlayer space between the silicate sheets of the samples after the water release.

According to the ETA results presented in Figs 3a–f the intensity of the radon mobility changes observed on air heating of various ion-exchanged montmorillonite samples differed. The results obtained in this study can be compared with the results of our previous study [4] characterizing thermal behaviour on argon heating of Na-montmorillonite saturated with cations of Li^+, Mg^{2+} or Al^{3+}, respectively.

The theoretical model proposed by Beckman and Balek [23] was used to evaluate the ETA experimental data and to compare the mobility of radon atoms during heating of the montmorillonite samples. The temperature dependence of the radon release rate, $E(T)$, can be expressed as

$$E(T) = E_{25} + E_D(T)\Psi(T) \qquad (1)$$

where the term E_{25} is radon release rate measured at room temperature, the term E_D is radon release rate due to the diffusion, depending on the number of

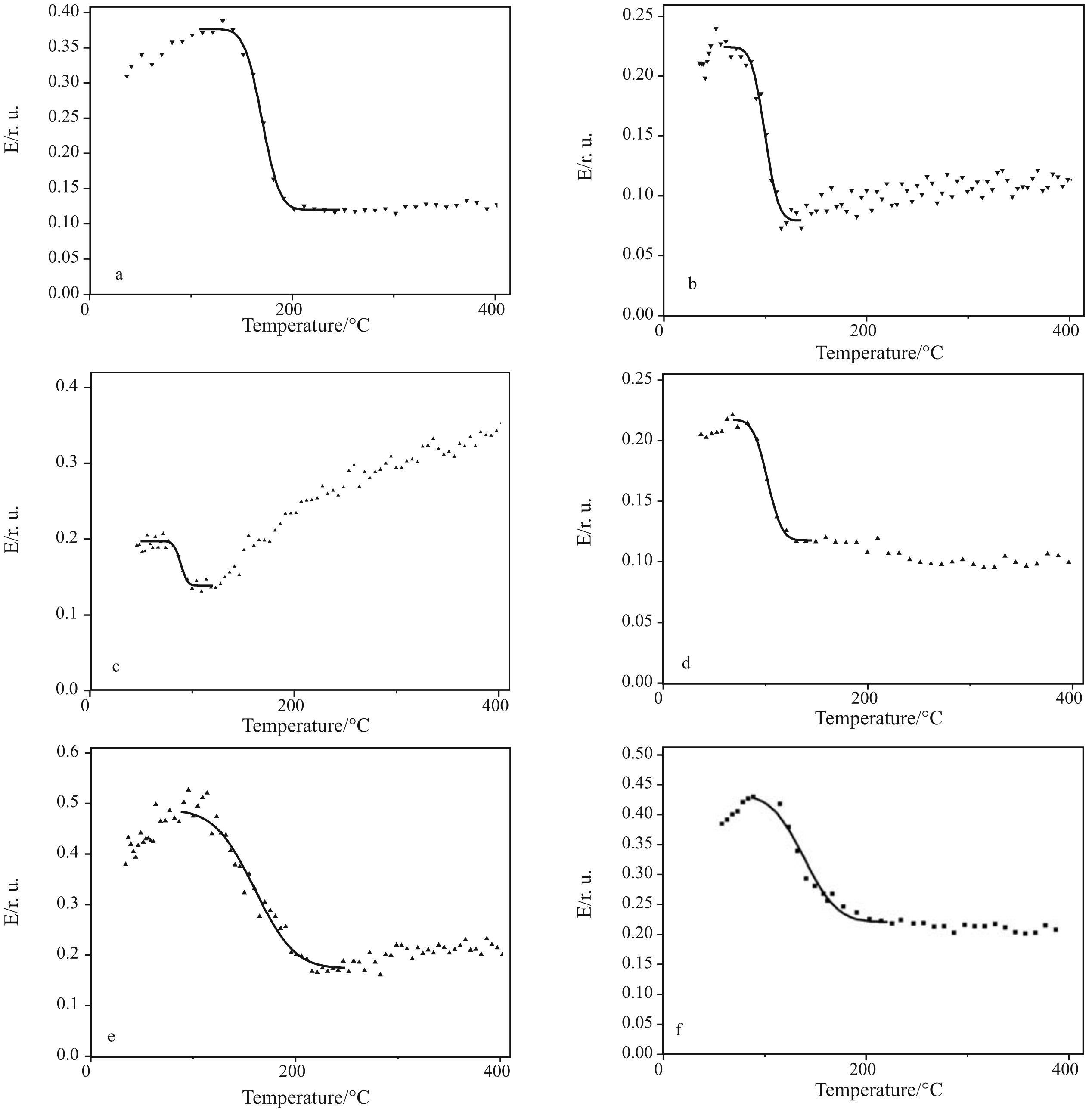

Fig. 3 ETA results of montmorillonite samples measured on heating in air at the rate 6 K min^{-1}. a – Li$^+$-exchanged montmorillonite, b – Na-montmorillonite–natural sample (locality Upton, Wyoming, USA), c – Cs$^+$-exchanged montmorillonite, d – NH_4^+-exchanged montmorillonite, e – Mg^{2+}-exchanged montmorillonite, f – Al^{3+}-exchanged montmorillonite

radon diffusion paths. The term E_D characterizes radon mobility along structure irregularities and $\Psi(T)$ is the function characterizing the decrease of the number of the radon diffusion paths.

The radon release rate, E_D, due to diffusion can be written as

$$E_D = (3/y)(\coth y - 1/y) \qquad (2)$$

where $y(T)=(S/M)\rho/(D/\lambda)^{1/2}$, S/M is surface area and interlayer space between the silicate sheets serving as radon diffusion paths, ρ is density of the sample, (D/λ) is average radon diffusion length, D is radon diffusion coefficient and λ is radon decay constant $\lambda=0.0027\ s^{-1}$),

$$D = D_0\exp(-Q_D/RT)$$

where D_0 is the factor depending on the number of diffusion paths and their availability for radon atoms migration, Q_D is activation energy of radon migration involving both the activation energy of the escape of radon atoms from the traps in the solid sample and that of the migration along diffusion paths in the solid, R=8.314 J mol^{-1} K^{-1} is molar gas constant, T is temperature in K.

Following expression for $\Psi(T)$ functions was proposed [23] to describe the decrease of the number of radon diffusion paths due to sticking of the interlayer space during sample heating

$$\Psi(T)=0.5\left[1+\mathrm{erf}\frac{1-\frac{T_\mathrm{m}}{T}}{\frac{\Delta T\sqrt{2}}{T}}\right] \qquad (3)$$

where erf is the sign for the integral Gauss error function, T_m is the temperature of maximum rate of the decrease of radon diffusion paths, ΔT is the temperature interval of the respective solid-state process.

The temperature dependences of the model $\Psi(T)$ functions, calculated by using Eq. (3) can be used for the characterization the radon mobility decrease, due to sticking of the interlayer space of the samples.

The model curves of the temperature dependences of the radon release rate $E_\mathrm{D}(T)$ are presented in Figs 3a–f as full lines, whereas the ETA experimental data are presented as points. A good agreement of the fitted curves and the experimental ETA data was achieved.

The temperature dependences of $\Psi(T)$ functions obtained by fitting the experimental ETA data with the theoretical model [23] have been included in Fig. 3 as solid lines, to characterize the radon mobility decrease due to the collapse of the interlayer space during the dehydration of the investigated montmorillonite samples. The ΔE values that characterized sticking of the montmorillonite (MMT) interlayer space due to dehydration (Table 1) decreased in the following sequence

Mg-MMT>Al-MMT>Li-MMT>Na-MMT>

NH_4-MMT>Cs-MMT

Values of difference in *c*-axis basal spacing (Δd_{001}) that characterize the sticking of the interlayer space of the samples due to their dehydration are also included in Table 1.

In was of interest to compare the experimentally obtained characteristics of the collapse of interlayer space between the silicate sheets after water release from the different montmorillonite samples, namely the decrease of the radon release rate, ΔE, and values for decreases in *c*-axis basal spacing (d_{001}) determined from XRD patterns.

Table 1 Values of radon release rate decrease ΔE and differences c-axis basal spacing Δd_{001} characterizing dehydration of montmorillonite samples saturated with various cations

Montmorillonite	Decrease of radon release rate	Difference in *c*-axis spacing
Cation	ΔE/r. u.	Δd_{001}/nm
Li^+	0.257	0.257
Na^+	0.149	0.159
Cs^+	0.064	0.094
NH_4^+	0.100	0.137
Mg^{2+}	0.349	0.448
Al^{3+}	0.276	0.380

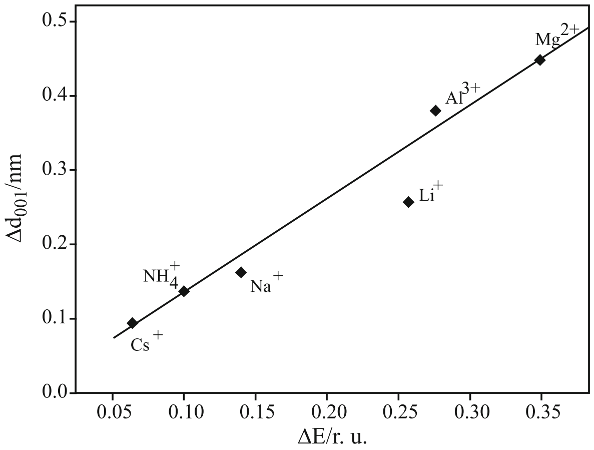

Fig. 4 Relationship between values of differences (Δd_{001}) in *c*-axis basal spacing determined from XRD patterns and corresponding changes of the radon release rate (ΔE) determined from ETA measurements during samples dehydration

Figure 4 depicts the linear relationship between values of the differences Δd_{001} in values of *c*-axis basal spacing and the corresponding values of the radon mobility decrease, ΔE due to sticking of the interlayer space as the results of the samples dehydration. The most intense decrease of the radon mobility, ΔE, was observed with the Mg-montmorillonite (Figs 1b and 3b). The differences in the *c*-axis basal spacing (Δd_{001}) determined from the XRD patterns (Fig. 2b) supported the results.

There is a good agreement between the decrease of radon mobility ΔE, determined from ETA data and values of Δd_{001} determined from XRD patterns due to the collapse of the interlayer space between silicate layers of the investigated MMT samples. Values of the differences in the interlayer space Δd_{001} due to dehydration of the samples followed the same sequence as the corresponding ΔE values characterizing the decrease in the radon mobility due to the sticking of the silicate sheets.

Conclusions

The high temperature X-ray diffraction patterns characterized the collapse of the interlayer space between silicate sheets of montmorillonite samples saturated with various cations due to water release. Values of the *c*-axis basal spacing (d_{001}) decrease determined from XRD patterns for the different montmorillonite samples before and after dehydration follow the sequence: Mg-MMT>Al-MMT> Li-MMT>Na-MMT>NH_4-MMT>Cs-MMT.

ETA characterized of the decrease of the radon mobility in the samples due to collapse of the interlayer space between the silicate sheets after the water release. A good agreement was found between the decrease of radon mobility ΔE and values of the differences Δd_{001} due to the sticking of the interlayer space as the result of the samples dehydration.

The decrease of the radon mobility in the samples corresponded well to differences in the *c*-axis basal spacing (Δd_{001}) values determined from the XRD patterns.

The ΔE values that characterized sticking of the interlayer space due to dehydration of the samples decreased in the same sequence as the differences in the interlayer space Δd_{001}.

The ETA brought about additional information about processes that took place on heating of homoionic montmorillonite samples saturated with various cations.

Acknowledgements

The paper was prepared in the frame of the bilateral cooperation between C.S.I.C and Academy of Sciences of the Czech Republic. Presentation of this work was supported by the Ministry of Education of Czech Republic (Project LA-292) and by the Ministry of Education of Spain (projects MAT 2004-02640 and MAT 2005-04838).

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DOI: 10.1007/s10973-007-8761-9