

## **EFFECT OF Na<sup>+</sup> AND NH<sub>4</sub><sup>+</sup> CATIONS ON MICROSTRUCTURE CHANGES OF NATURAL VERMICULITE DURING HEAT TREATMENT**

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### **Abstract**

Emanation thermal analysis (ETA), DTA, SEM, and XRD were applied for the characterization of the effect of Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions used for saturation of natural Mg-vermiculite on the microstructure during heating. The microstructure changes were characterized by ETA under *in situ* conditions of samples heating in air in the temperature range 20–1300°C. It was found that Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions have a significant effect on the microstructure changes during heat treatment of the natural Mg-vermiculite sample saturated with these ions. For Mg-vermiculite and Na<sup>+</sup> saturated vermiculite the temperatures of the onset of the collapse of interlaminar space were determined by ETA. Differences in thermal stability of the microstructure of dehydrated vermiculite samples were observed by ETA: the microstructure of dehydrated Mg-vermiculite, and Na-vermiculite was found stable until 650 and 350°C, respectively. For dehydrated NH<sub>4</sub>-vermiculite the annealing of the microstructure started at 730°C. The onset temperatures of the formation of new crystalline phases were indicated by ETA as the increase of the radon release rate. The onset temperatures of the ordering of the vermiculite structure or sintering under presence of the glassy stage (for Na-vermiculite), respectively, were determined from the decrease of the radon release rate. The ETA results were confirmed by DTA, XRD and SEM.

**Keywords:** emanation thermal analysis, microstructure changes, vermiculite

### **Introduction**

Vermiculite is a clay mineral of great practical importance. The natural exfoliated vermiculite is used as acoustic and thermal insulator, as an additive in concrete and plaster, as fertilizer carrier, adsorbent, etc. [1–4]. The refractory properties of vermiculite are also utilized in metallurgy [5].

Mg<sup>2+</sup> ions originally present in the interlayer space of natural vermiculite are usually exchanged with various cations to modify the properties of this clay mineral.

The presence of these exchangeable cations may significantly influence the formation of high temperature phases on heating above 900°C.

Emanation thermal analysis (ETA) [6–9] is, as already demonstrated by Balek [9], a sensitive tool for the investigation of the microstructure changes under *in situ* conditions of heating. The aim of this study is to characterize the effect of the Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> ions, respectively, on the microstructure changes of natural Mg-vermiculite, taking place on heating of ion exchanged vermiculite samples in the temperature range 20–1300°C in air.

ETA has been used for the determination of the temperature intervals of the formation of new phases as well as thermal annealing of the phases formed during heating of the vermiculite saturated with Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> cations. Scanning electron microscopy (SEM) and X-ray diffraction (XRD) were used for the identification of the phases formed by heating to selected temperatures. DTA results were used for the comparison with ETA results.

## Experimental

### Materials

Vermiculite from Santa Olalla (Huelva, Spain) was used as the starting material [10, 11] having a half-unit cell composition [12] of Mg<sub>0.439</sub> (Si<sub>2.64</sub> Al<sub>1.36</sub>) (Mg<sub>2.48</sub> Fe<sub>0.324</sub><sup>3+</sup> Fe<sub>0.036</sub><sup>2+</sup> Al<sub>0.14</sub> Ti<sub>0.01</sub> Mn<sub>0.01</sub>) O<sub>10</sub> (OH)<sub>2</sub>. Large flakes were lightly ground using a knife-mill (Retsch ZM-1, Germany) and sieved under 80 μm.

From this material Na<sup>+</sup> and NH<sub>4</sub><sup>+</sup> saturated samples were prepared by repeated contact at room temperature with a 1 M NaCl and 1 M NH<sub>4</sub>Cl solution, respectively. Finally, the samples were washed with distilled water until Cl<sup>-</sup> free solution was obtained. The three vermiculite samples were annealed at 900, 1000, 1100, 1200, 1300 and 1400°C for 1 h in static air.

### Methods

ETA [6, 8] involves the measurement of radon release rate from samples previously labeled. The samples were labeled three weeks prior to ETA measurements using the adsorption of traces of <sup>228</sup>Th and <sup>224</sup>Ra on the sample surface from acetone solution. The specific activity of a sample was 10<sup>5</sup> Bq per mL. Atoms of radon, <sup>220</sup>Rn, were formed by the spontaneous alpha decay of <sup>228</sup>Th and <sup>224</sup>Ra. <sup>224</sup>Ra and <sup>220</sup>Rn atoms were incorporated into the sample to a maximum depth of 80 nm due to the recoil energy (85 keV/atom) which the atoms gained by the spontaneous α-decay.

ETA-DTA measurements were carried out on heating in air at the heating rate of 6 K min<sup>-1</sup>, using a modified Netzsch DTA 404 equipment. During ETA measurements, the labeled sample of 0.1 g was situated in a corundum crucible overflowed by a constant flow of dry air (flow-rate 40 mL min<sup>-1</sup>) which carried the radon release from the sample into the measuring chamber of radon radioactivity.

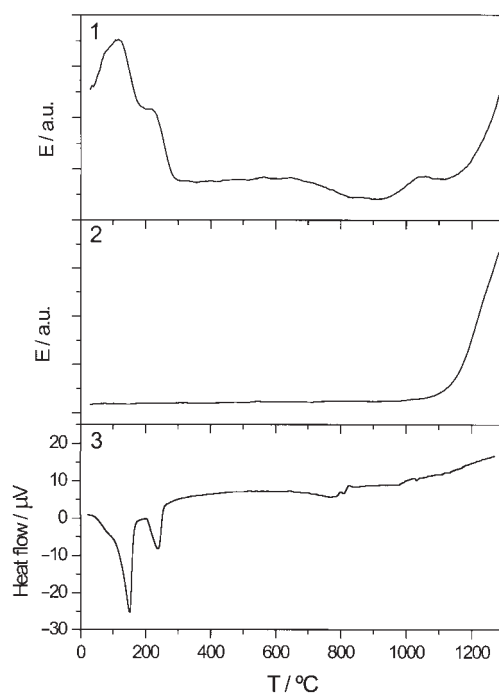
XRD patterns were obtained by means of a SIEMENS equipment (Model D 5000) using Ni-filtered  $\text{CuK}\alpha$  radiation.

For scanning electron microscopy (SEM) the JEOL JSM-5400 equipment was used.

Evolved gas analysis (EGA) experiments were performed under vacuum ( $\sim 10^{-5}$  torr) using a quadrupole mass spectrometer (Quadrupac Q100, LH) during heating at the rate of  $6 \text{ K min}^{-1}$ .

## Results and discussion

Results of the emanation thermal analysis of the natural Mg-vermiculite are presented together with the corresponding DTA curve in Fig. 1. As it follows from our previous study [13] the dehydration on heating of the Mg-vermiculite sample takes place in two steps up to  $240^\circ\text{C}$ . ETA results presented in Fig. 1, made it possible to determine the onset temperature of the partial collapse of the interlayer space partially dehydrated during the previous heating of vermiculite. A good agreement was found between the temperatures of the break indicated on ETA curve at  $140^\circ\text{C}$  and the results of DTA/TG [13] indicating the temperature range  $25\text{--}140^\circ\text{C}$  of the release of water. The decrease of the radon release rate,  $E$ , observed above  $240^\circ\text{C}$  indicated the collapse of the interlayer space of the vermiculite structure, which took place simultaneously with the release of remaining water

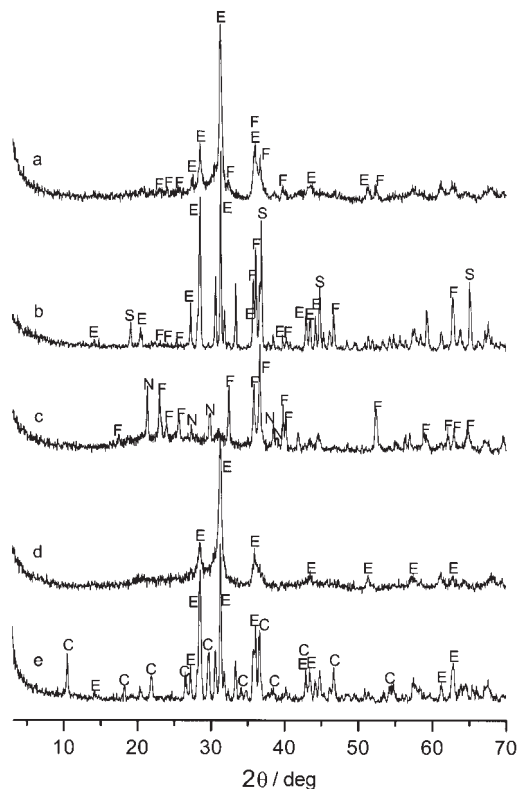


**Fig. 1** ETA and DTA curves of natural Mg-vermiculite. 1 – ETA curve during heating; 2 – ETA curve during cooling; 3 – DTA curve

molecules from the interlayer space. In this way ETA enabled us to determine the onset temperatures of the microstructure changes which followed after the water release from Mg-vermiculite sample.

From the ETA curve in Fig. 1 it followed that no microstructure changes took place on heating in the temperature range 400–650°C. Consequently, it can be supposed that the microstructure of dehydrated Mg-vermiculite is thermally stable up to 650°C. This information is important when characterizing the thermal stability of the disordered structure.

As concerns the thermal behavior of Mg-vermiculite above 700°C, it followed from the endothermal-exothermal double effect on the DTA curve observed in the temperature range between 780 and 850°C, (Fig. 1, curve 3) that the formation of the new crystalline phases (mainly enstatite) took place after the OH groups were released from the sample. XRD patterns of the sample heated for 1 h at 900°C (Fig. 2a) gave the evidence of the presence of enstatite as the major component and forsterite as minor component. From the XRD pattern of the Mg-vermiculite sample heated for



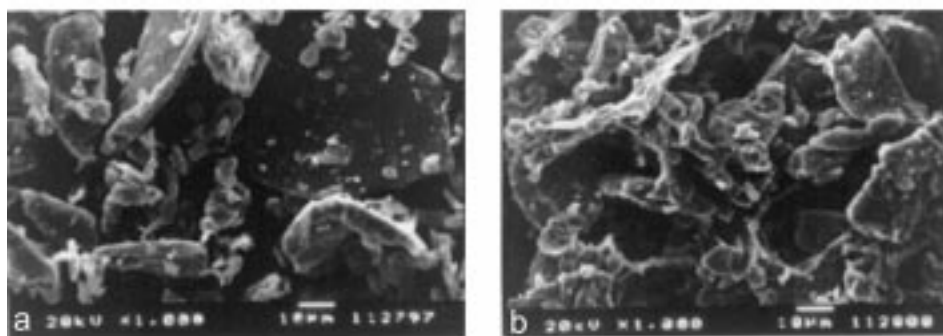
**Fig. 2** Powder XRD patterns of: a – Mg-V heated for 1 h to 900°C; b – Mg-V heated for 1 h to 1300°C; c – Na-V heated for 1 h to 900°C; d – NH<sub>4</sub>-V heated for 1 h to 1000°C and e – NH<sub>4</sub>-V heated for 1 h to 1260°C. V=vermiculite, E=enstatite, F=forsterite, S=sapphirine, C=cordierite, N=nepheline

1 h to 1300°C (Fig. 2b) it became obvious that the formation of enstatite and forsterite took place, in addition the presence of sapphirine was detected in the sample heated above 1100°C.

From the ETA curve of Mg-vermiculite (Fig. 1, curve 1) it followed, that on further heating above 950°C the enhanced radon release rate indicated the formation of new high temperature phases.

It was shown by Balek *et al.* [9] that the onset of the formation of new crystalline phases is usually indicated by the increase of the radon release rate, due to the formation of new radon diffusion paths in the sample in this initial stage of phase transition. On the other hand, the decrease of the radon release rate,  $E$ , observed on the sample heating, usually indicates the onset of the thermal annealing/ordering of the structure.

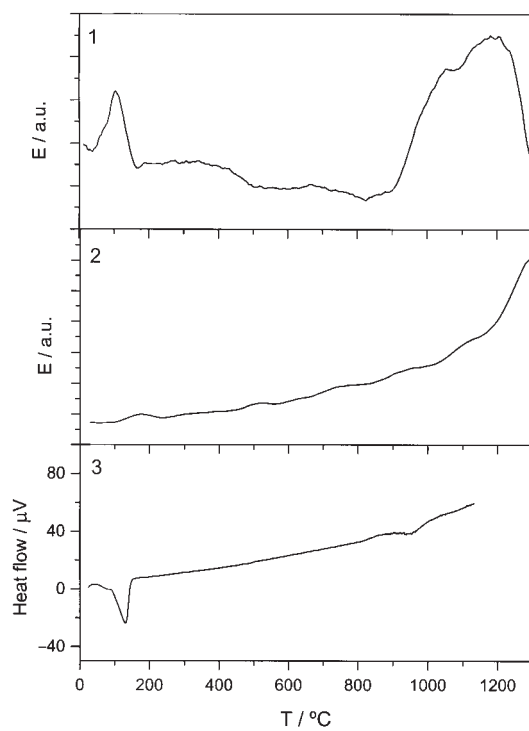
SEM study did not show noticeable morphology changes in the sample heated between 900 and 1260°C (Fig. 3a). No glassy phase was detected. Sample sintering was observed on the SEM micrograph after heating at 1300°C (Fig. 3b). These results confirmed the characterization of the microstructure changes obtained by ETA (Fig. 1, curve 1).



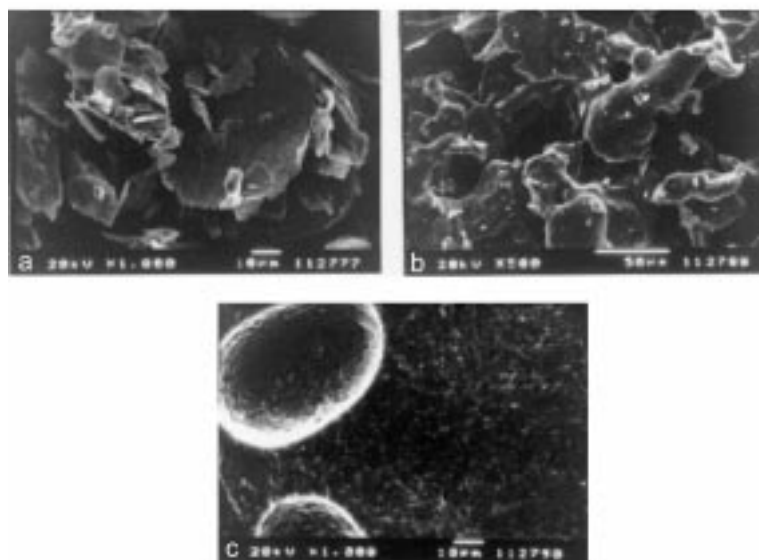
**Fig. 3** SEM micrographs of Mg-vermiculite heated for 1 h to: a – 1000°C; b – 1300°C

In Fig. 4, ETA and DTA curves characterized the thermal behavior of Na<sup>+</sup> saturated vermiculite. From curve 1 it followed that the onset temperature of the collapse of the interlayer space is 110°C. The remaining water molecules present in the interlaminar space of Na-vermiculite were released simultaneously to the decrease of  $E$  during sample heating. From DTA results, curve 3, it followed that the total release of the interlaminar water surrounding Na<sup>+</sup> ions took place at  $\cong 150^\circ\text{C}$  [14].

ETA curves in Figs 1 and 4 revealed the differences in the onset temperatures of the collapse of the interlaminar space in Mg-vermiculite and Na-vermiculite, respectively. Moreover, from curve 1 in Fig. 4 it followed that the thermal stability of the microstructure of the dehydrated Na-vermiculite is considerably lower as compared with that of dehydrated Mg-vermiculite. The temperature of 350°C can be considered as the onset temperature at which the annealing of the microstructure of dehydrated Na-vermiculite took place. In both cases, the annealing of the microstructure was



**Fig. 4** ETA and DTA curves of Na-vermiculite. 1 – ETA curve during heating; 2 – ETA curve during cooling; 3 – DTA curve

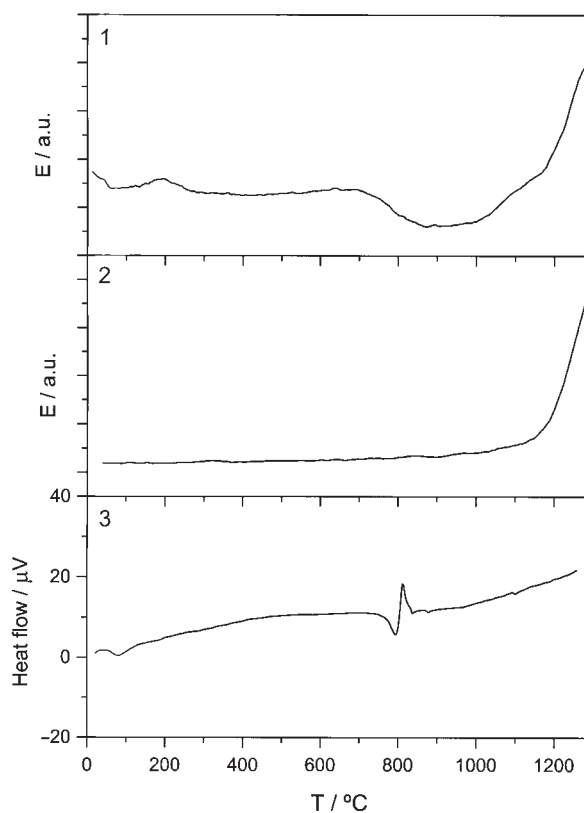


**Fig. 5** SEM micrographs of Na-vermiculite heated for 1 h to: a – 1000°C; b – 1200°C; c – 1300°C

characterized by the decrease of the radon release rate observed on the ETA curve in the corresponding temperature range.

The strongly enhanced radon release rate observed for the  $\text{Na}^+$  saturated vermiculite in the temperature range 900–1050°C may be associated with the formation of new diffusion paths after the release of structural OH groups. The break starting at 1050°C characterized the onset of the densification and the annealing of newly formed diffusion paths for radon in the sample. The effects of the increasing trend of radon release rate  $E$  indicated the temperatures at which new phases appeared. Finally, the decrease in  $E$  starting at 1180°C may be associated to the formation of the glassy melt. The results of ETA are in a good agreement with the results of XRD.

XRD patterns of  $\text{Na}^+$  saturated vermiculite heated to 900°C indicated the presence of nepheline and forsterite (Fig. 2c). The presence of only forsterite was detected in the samples heated to 1100 and 1200°C, respectively.

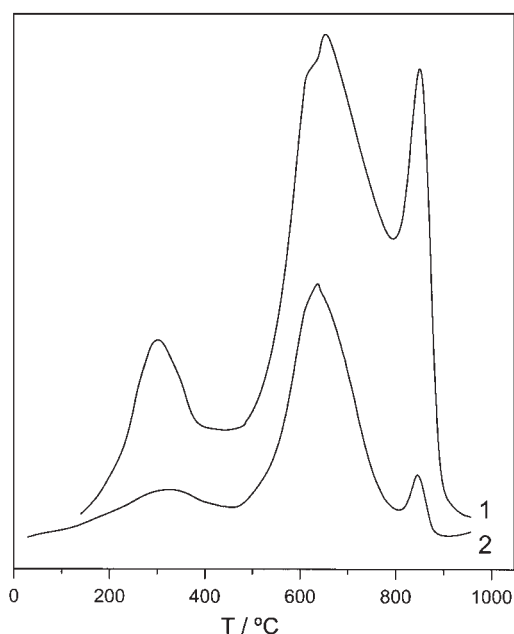


**Fig. 6** ETA and DTA curves of  $\text{NH}_4$ -vermiculite. 1 – ETA curve during heating; 2 – ETA curve during cooling; 3 – DTA curve

The SEM micrographs characterizing the microstructure of the Na-vermiculite sample heated to 1000, 1200 and 1300°C (Fig. 5) confirmed the microstructure changes char-

acterized by ETA. The Na-vermiculite retained the lamellar morphology until 1000°C, whereas the sample heated to 1300°C can be characterized as molten glass. The glassy character was confirmed by SEM micrograph for the sample heated to 1200°C.

In Fig. 6 ETA and DTA curves characterized the thermal behavior of NH<sub>4</sub>-vermiculite. From curve 1 it followed that no significant changes in the microstructure took place from 50 to 700°C. This is in a good agreement with the previous characteristics of this sample [13] as it contains only collapsed layers in which practically no interlayer water was present [14]. It was indicated by TG results [13] and mass spectrometry detection (MS) that on heating above 500°C the sample was losing ammonia and OH groups from the vermiculite structure (Fig. 7).



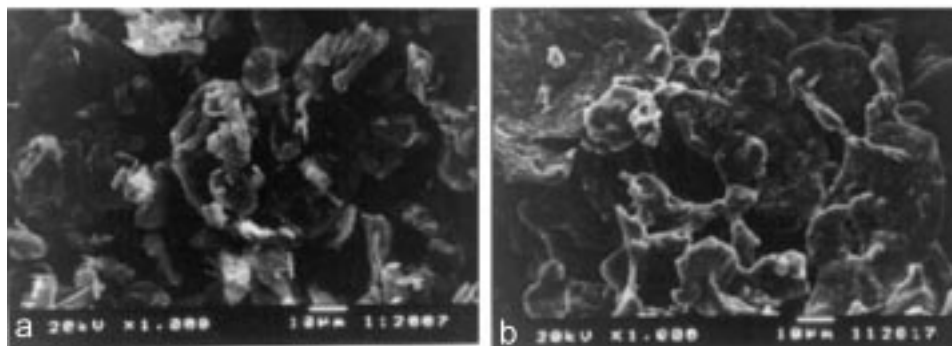
**Fig. 7** Evolved water and ammonia profiles from NH<sub>4</sub>-vermiculite. 1 – H<sub>2</sub>O; 2 – NH<sub>3</sub>

From the onset of decrease of the radon release rate observed on the ETA curve in Fig. 6 it follows that the temperature of 730°C corresponds to the onset temperature of the annealing of the vermiculite structure. From Fig. 7 it is obvious that at this temperature the sample lost a great proportion of OH groups and ammonia bound in the structure. It can be supposed from the ETA results, curve 1, that the process of the vermiculite structure annealing was terminated at 900°C, i.e. at the temperature at which the MS results indicated the release of the remaining ammonia and OH groups (Fig. 7).

XRD patterns of NH<sub>4</sub>-vermiculite heated between 900 and 1200°C showed the presence of enstatite (Fig. 2d). In the samples heated to 1200 and 1300°C, respectively, cordierite was detected in addition to enstatite (Fig. 2e).



It was observed by SEM (Fig. 8) that the  $\text{NH}_4$ -vermiculite heated to the temperatures in the range 1000–1300°C retained the lamellar morphology, however the morphology of the sintered sample was observed after heating to 1300°C.



**Fig. 8** SEM micrographs of  $\text{NH}_4$ -vermiculite heated for 1 h to: a – 1000°C, b – 1300°C

ETA characterized the  $\text{NH}_4^+$  saturated vermiculite in a similar way as that of natural Mg-vermiculite during heating above 850°C (Figs 1 and 6, curves 1). The formation of diffusion paths for Rn formed on heating to high temperatures enhanced the release of Rn from the sample.

In both  $\text{NH}_4$ - and Mg-vermiculite samples heated to the temperatures of 900°C and 1300°C only crystalline phases with similar mineralogical composition were detected. This determined the similar shape of ETA curves for both samples in this temperature range. The formation of a glassy melt in the Na-vermiculite was indicated by the decrease of the radon release rate in the temperatures higher than 1180°C.

ETA curves measured during cooling of the investigated Mg-, Na- and  $\text{NH}_4$ -vermiculite (Figs 1, 3, 7, curves 2) confirmed that the processes which took place during heating of these samples up to 1300°C were irreversible.

Following characteristics were proposed for the investigated vermiculite samples obtained after heat treatment to 1300°C: a porous ceramics resulted from samples prepared from Mg-vermiculite and  $\text{NH}_4$ -vermiculite, whereas the glassy character was observed with the sample prepared from the Na-vermiculite.

## Conclusions

It was demonstrated by ETA that  $\text{Na}^+$  and  $\text{NH}_4^+$  ions have significant effects on the microstructure changes observed during heating of the natural Mg-vermiculite sample saturated with these ions. For  $\text{Na}^+$  saturated and Mg-vermiculite the ETA made possible to determine the temperatures of the onset of the collapse of interlamellar space followed after the release of water molecules from the interlamellar space. Moreover, the thermal stability of the microstructure of dehydrated vermiculite samples was determined. It followed from the values of Rn release rate measured during constant rate heating that microstructure of dehydrated Mg-vermiculite is stable up to

650°C, and that on further heating the annealing of the irregularities of the structure takes place. On the other hand, for the dehydrated Na-vermiculite the annealing of the microstructure started already at 350°C. For dehydrated NH<sub>4</sub>-vermiculite the annealing of the microstructure started at 730°C. ETA results were in a good agreement with the results of TG and DTA.

From the comparison of the results of ETA, SEM and XRD it followed that the ETA enabled us to determine the onset temperatures of the formation of new crystalline phases, indicated by the increase of the radon release rate. The onset temperatures of the ordering of the structure, sintering under presence of the glassy stage (for Na-vermiculite) were determined from the decrease of the radon release rate observed under *in situ* conditions of the sample heating. ETA can be recommended as a tool for characterization of the microstructure changes during *in situ* conditions of heating of clay minerals saturated with various ions.

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