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# THERMAL BEHAVIOUR OF GROUND VERMICULITE*

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Thermal behaviour of natural vermiculite (Santa Olalla, Huelva, Spain) was investigated by TG, DTA, emanation thermal analysis (ETA) and high temperature XRD on heating in the temperature range from 30 to 1100°C before and after vibratory mill grinding. Microstructure changes of natural and ground vermiculite samples were characterized by using ETA under in situ conditions of heating. By comparing the ETA and XRD results it was demonstrated that a decrease of radon release rate measured by ETA characterized the decrease in the interlayer spacing of the vermiculite samples that followed the dehydration.

***Keywords:*** *differential thermal analysis, emanation thermal analysis, grinding, interlayer spacing, thermogravimetry, vermiculite, XRD*

## Introduction

Vermiculite is a layered clay mineral of significant commercial importance [1]. In the application of natural vermiculite for preparation of insulation ceramics, thin protection layers and other advanced ceramics a staring material of micron and submicron size has to be used. Methods like wet or dry grinding have been proposed for delaminating and reducing the particle size of the clay minerals [2, 3]. Grinding caused significant modifications in properties of the clays such as surface area, structure, morphology and reactivity [4–6]. Moreover, grinding caused significant modifications in the thermal reactivity of clays [6–10] as well as in high temperature phases formation [11–15]. For vermiculite, it has been observed that grinding caused a considerable particle size decrease, an intense structural degradation resulting in a loss of the lamellar shape and in a progressive amorphization accompanied with the formation of hard agglomerates by cold-welding [16, 17]. The increase in porosity due to grinding of vermiculite has been also studied [18]. The increase in the amount of micropores and mesopores due to gliding and folding borders of the layers during the grinding process was reported. It has been shown that forces between layers weakened allowing penetration into inter-layers of nitrogen used in the surface area measurements [18].

The aim of this work is to compare the thermal behaviour of natural vermiculite before and after grinding. The thermal behaviour has been characterized by conventional methods like DTA, TG or high temperature XRD, as well as by a less common emanation thermal analysis (ETA). The ETA has been already advantageously used in the characterization of thermal reactivity due to microstructure changes of clays [19, 20]. Information obtained by methods used in this study should contribute to a better understanding of changes induced by dry grinding of vermiculite clay mineral.

## Experimental

### *Materials and methods*

Vermiculite from Santa Olalla (Huelva, Spain) was used as starting material having a half-unit cell composition of $(Si_{2.64}Al_{1.36}Mg_{2.48}Fe^{3+}_{0.324}Fe^{2+}_{0.036}Al_{0.14}Ti_{0.01}Mn_{0.01})O_{10}(OH)_2Mg_{0.439}$ [21].

Grinding. Large flakes of the natural vermiculite were cut using a knife-mill (Retsch 25SM-1) and sieved to get a fraction under 80 μm. The grinding of the sample was carried out by a vibratory mill (Herzog ZM-100) at 1500 rpm using the grinding time of 0.5, 2.0, 3.0 and 10 min, respectively.

Surface area was determined by B.E.T. method, based on $N_2$ adsorption measurements carried out by an equipment produced by Micrometrics, Model 2200A (USA).

Low angle laser light scattering (LALLS) equipment model Mastersizer, produced by Malvern (UK), was used for particle size analysis. Volume percentages of 50% known as the mass median diameter ($D_{v50}$) were calculated.

Differential thermal analysis (DTA) and thermogravimetry (TG) measurements were performed in air

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at a heating rate 10 K $min^{-1}$ by Seiko TG/DTA 6300 equipment.

ETA measurements were performed on heating in air at the rate of 6 K $min^{-1}$ using an upgraded Netzsch ETA-DTA 404 instrument. Sample amount of 0.1 g and corundum crucible was used. Details of the ETA measurements have been described elsewhere [22–25]. The surface of the samples for ETA was labelled by trace amount of $^{228}$Th and $^{224}$Ra. Atoms of $^{224}$Ra and $^{220}$Rn were incorporated to the depth of 80 nm into the subsurface of the sample particles due to recoil energy that the atoms gained by spontaneous α-decay of $^{228}$Th [26].

XRD diffraction patterns were measured under in situ heating of the sample at the rate 10 K $min^{-1}$ by using the Philips X'Pert Pro device equipped with a goniometer θ–θ and the high temperature chamber Anton Paar HTK-1200. The $CuK_\alpha$ radiation of 40 kV and 40 mA was used.

## Results and discussion

The surface area (*s.a.*) of the un-gound vermiculite sample was smaller than 1 $m^2$ $g^{-1}$. After grinding for 2 min the *s.a.* of the sample increased to 39 $m^2$ $g^{-1}$ and after 10 min grinding its *s.a.* was 20 $m^2$ $g^{-1}$. As to the particle size calculated by the LALLS method the values of the mass median diameter ($D_{v50}$) were 24.6 μm for the un-ground sample and 9.2 μm for the 2 min ground sample. It was observed by XRD patterns (Fig. 1) that a decrease in intensity and a broadening of diffraction peaks took place due to grinding, being caused by the crystal size decrease and an increase of crystal disorder. An amorphization was observed in the sample ground for 10 min. These findings are in agreement with previous results demonstrating that grinding of phyllosilicates caused delamination, breaking of the layers, rearrangement of the coordination polyhedra and diffusion within the structure of atoms that after progressive grinding may give rise to amorphous materials [2–10].

To characterize the thermal behaviour of ground vermiculite the sample prepared by 2 min grinding was used. This sample was characterized by a relatively large surface area value and still remained crystalline (Fig. 1). From the TG results (Fig. 2a) it follows that dehydration and dehydroxylation of unground and ground vermiculite samples substantially differ: (*i*) for the un-ground sample two dehydration steps on heating up to 250°C and one single dehydroxylation step completed at about 900°C were well resolved (curve 1, Fig. 2a); (*ii*) for the ground sample the dehydration and dehydroxylation steps were not well resolved as in the case of the un-ground sample. A continuous mass loss took place in the temperature range from 50 to 350°C, and the dehydroxylation was completed at 800°C (curve 2, Fig. 2a). The DTA results presented in Fig. 2b confirmed the TG results.

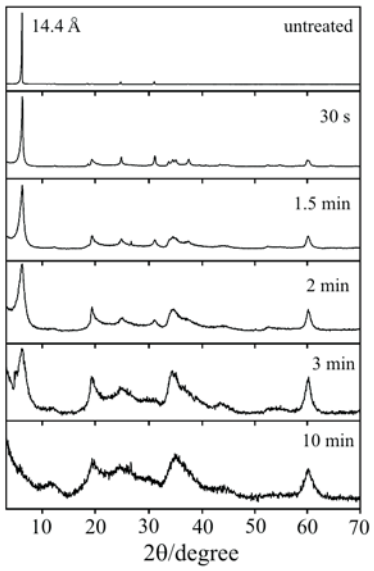


**Fig. 1** XRD patterns of vermiculite samples ground for different time periods

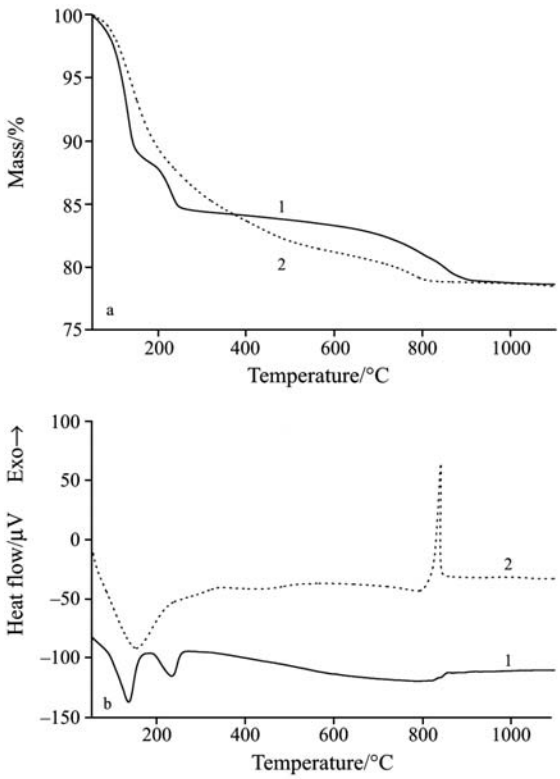


**Fig. 2** Results of a – TG and b – DTA of vermiculite samples: curve 1 – un-ground sample, curve 2 – sample ground for 2 min

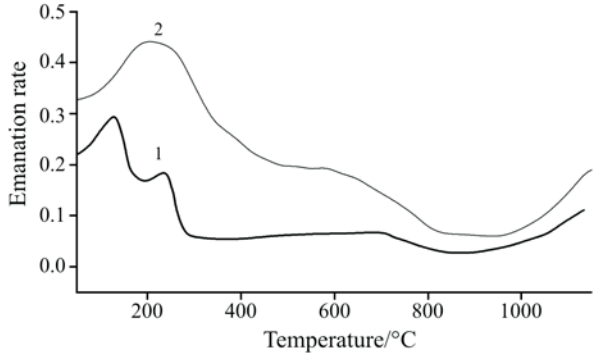


**Fig. 3** ETA results of vermiculite samples: curve 1 – un-ground sample, curve 2 – sample ground for 2 min

The ETA results are presented in Fig. 3 as temperature dependences of the measured radon release rate (called emanation rate *E*) from samples previously labelled [24, 25]. An increase in the emanation rate, *E*, characterize an increase of surface area of interfaces, formation of additional structure defects or grain boundaries that serve as paths for radon diffusion, whereas a decrease in *E* reflects a decrease in surface area of interfaces, losing open pores, and/or closing up structure irregularities that served as radon diffusion paths [27].

By using the ETA (Fig. 3, curve 1), the un-ground sample was characterized in the temperature range from 50 to 300°C by an increase in the emanation rate, *E*, in two steps, namely from 50 to 130 and from 180 to 230°C, respectively; in both cases the increase of *E* was followed by a decrease of *E*. By comparing the ETA results with the results of TG in this temperature range (Fig. 2a) it followed that the release of radon from the samples was enhanced by water release. The sharp decrease in the emanation rate, *E*, observed in two steps, was ascribed to the decrease in the interlayer spacing that followed the dehydration steps. This statement was confirmed by XRD patterns (Fig. 4a) that made possible to determine changes in interlayer spacing that served as the radon diffusion channels: for the un-ground sample before the heat treatment $d_{002}$ was 14.4 Å, it decreased to 11.6 Å after sample heating at 100°C, and to about 10 Å for the sample heated at 300°C. These changes in $d_{002}$ were reflected as a decrease in the emanation rate, *E*.

In its turn, the dehydroxylation that took place on sample heating at temperatures above 800°C caused a decrease in the interlayer spacing (Fig. 4a) due to the collapse of layers, yielding a talc-like structure, which is characterized by the stack layers without water or cations in the interlayer space [20]. This collapse was reflected by a decrease in the emanation rate, *E*.

It was detected by high temperature XRD that on further heating to 900°C and above this temperature new crystalline phases, i.e. enstatite and spinel, were formed (Fig. 4a). The DTA exothermal effect characterized formation of the new phases by an exothermal effect (Fig. 2b). The formation of the new phases was indicated by an increase in the emanation rate, as observed at the temperature range above 900°C (Fig. 3). It has been previously reported [24, 28–30] that the formation of new phases may be accompanied by the formation of additional diffusion paths for radon. From Fig. 3 it followed that the shape of the ETA curves the ground and the un-ground vermiculite samples differed.

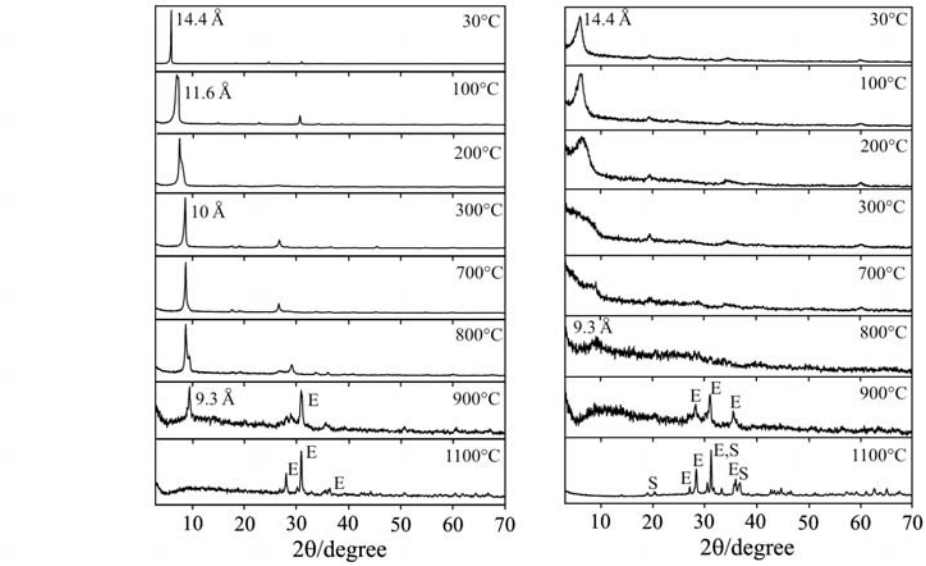


**Fig. 4** XRD patterns of vermiculite samples heated at different temperatures a – un-ground sample, b – sample ground for 2 min. E – enstatite, S – spinel

The emanation rate values of the ground vermiculite in all the temperature range are significantly larger than for the un-ground sample. This can be explained by the increased surface area of the ground sample due not only to the decrease in particle size produced by grinding, but mainly to voids and crevices formed by the alteration of the particle borders that resulted in folding and gliding of the vermiculite layers during grinding [17].

For the ground sample an increase in the emanation rate, $E$, took place up to about 220°C and was followed by a decrease of $E$. It is obvious from the TG results (Fig. 2a) that a continuous mass loss took place on heating of the ground sample in this temperature range. The decrease in $E$ (Fig. 3, curve 2) observed on heating of the ground sample above 220°C was ascribed to a decrease of the interlayer space that accompanied the dehydration of the sample. As it followed from XRD patterns (Fig. 4b) in the ground sample heated above 220°C a significant broadening of the basal diffraction peak took place, suggesting heterogeneity in the interlayer distances produced by random displacement and imperfection in the crystal order mainly due to edge alteration [16, 17]. Although the values of $d_{002}$ spacing were not well resolved for the ground vermiculite sample heated above 200°C a shift in the basal diffraction toward smaller $d_{002}$ values was observed. These effects were characterized by the relative decrease in the emanation rate, $E$, on heating the sample from 220 to 450°C. Further heating above 650°C caused a decrease in $d_{002}$ to 9.3 Å, indicating the collapse of the layers and the formation of a talc-like structure. This collapse was characterized by a decrease in the emanation rate.

In the temperature range above 840°C, an increase in the emanation rate took place due to volume diffusion mechanism. The higher values of the emanation rate, $E$, for the ground sample as compared to the un-ground sample can be also attributed to the fact that the mechanical activation by grinding enhanced the formation of new crystal phases. The high temperature XRD and DTA results confirmed this explanation. Thus, the XRD pattern of the sample heated at 1100°C (Figs 4a and b), showed better resolved peaks for the crystalline phases formed in the ground sample, and the DTA exothermal effect with the maximum at 842°C was more intense for the ground sample than for the un-ground vermiculite sample (Fig. 2b). Consequently a supplementary insight into microstructure development of the vermiculite samples under in situ heating conditions was obtained by ETA.

## Conclusions

Differences in thermal behaviour of vermiculite samples caused by vibratory mill grinding were characterized by TG, DTA, ETA, high temperature XRD and surface area measurements. An agreement between the ETA results characterizing microstructure changes under in situ heating of the samples and the decrease in the interlayer spacing $d$ determined from the XRD patterns was found. A supplementary insight into microstructure development of the vermiculite samples caused by grinding was obtained by ETA. Comparison of the results of different methods contributed to a better understanding of the effect of grinding on vermiculite clay mineral.

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