THERMAL STUDY OF VERMICULITES AND MICA-VERMICULITE INTERSTRATIFICATIONS

A. Justo, J. L. Pérez-Rodríguez and P. J. Sánchez-Soto

INSTITUTO DE CIENCIA DE MATERIALES, CENTRO MIXTO CONSEJO SUPERIOR ˙
DE INVESTIGACIONES CIENTIFICAS-UNIVERSIDAD DE SEVILLA, P.O.BOX 1115,
41080-SEVILLA, SPAIN

Simultaneous DTA-TG has been carried out on a set of natural vermiculite samples. Based on their dehydration behaviour the samples can be divided in two groups: (a) those with DTA endothermic peak temperatures at 140°–150°C and 240°–270°C (pure vermiculites) and (b) those with peak temperatures at 95°–115°C (vermiculite with mica or mica-vermiculite interstratifications). The low temperature at which the endothermic effect in group (b) appears is discussed on the basis of dilution due to the inert layers of mica, differences in chemical composition, and lowering of interlamellar water bond energy.

Keywords: layer silicates, vermiculites and mica-vermiculite interstratifications

Introduction

Much work on the thermal behaviour of layer silicates has been reported in the literature [1–4]. Vermiculites show characteristic DTA endothermic effects in the range 20°– 300°C. The origin of these effects has been discussed in detail [1, 2]. Walker and Cole [1] identified three endothermic effects in the dehydration region corresponding to three stages of water elimination; temperatures of these effects, as well as their intensities and shapes were found to be strongly dependent on the nature of the interlayer cation and the relative humidity of the atmosphere in equilibrium with the sample prior to DTA. For Mg-vermiculites, no marked changes were observed over a considerable range of relative humidity [1].

The term vermiculite used in industry covers not only the mineral vermiculite, but also materials containing mica/vermiculite interstratifications and mixtures of mica and vermiculite. Mica-vermiculite interstratifications show large variability in composition from low to high ratios of vermiculite to biotite layers and Walker

and Cole [1] demonstrated the similarity of their DTA curves to those produced by equivalent mechanical mixtures of vermiculite and biotite.

This paper describes simultaneous DTA-TG of a set of natural vermiculite samples and shows that dehydration temperatures depends on the detailed mineralogy.

Experimental

Materials

Samples were selected from different geological formations in Southern Spain (Andalusia and Badajoz), and have been described previously [4]. Table 1 gives sample locations.

Table 1 Locations of samples studied

Samples	Location	Number of samples
SO	Santa Olalla, Huelva	5
ALC, EA	Almonaster, Huelva	5
RJ	Real de la Jara, Sevilla	2
N, C, P, T, N–LP	Ojén, Málaga	11
Ro	El Ronquillo, Sevilla	1
Bu	Burguillos del Cerro, Badajoz	1
Be	Benahavis, Málaga	1

Methods

Prior to mineralogical characterization, samples were wet-ground in an agate mortar and pestle to avoid excessive structural damage. X-ray diffraction (XRD) patterns were recorded on a Siemens Kristalloflex D-500 diffractometer, using Ni-filtered CuK_α radiation. Chemical analyses were performed by atomic absorption spectrometry, after complete dissolution of the samples with a mixture of $HF-HNO_3-HCl$. FeO contents were determined by the o-phenantroline method [5].

DTA and TG were carried out simultaneously using a Rigaku PTC-10A Thermoflex analyzer, with a sample weight of 40 mg, static air atmosphere, calcined alumina as reference, and platinum sample cups. The heating rate was normally 15 deg/min but a rate of 5 deg/min was also employed. Care was taken to keep

constant the initial humidity, particle size and packing density. Mg-saturated samples were used.

Results

Based on the XRD results, samples were divided into two groups: pure vermiculites (samples SO-1c, SO-2, SO-3 EA-1, EA-2, A, ALC-SO, ALC-SC, Be, N-1, N-2, N-3, N-4, N-5, C-1, C-2, P-1, P-2, T, and RJ-2), and vermiculites with mica or mica (biotite)/vermiculite interstratifications (samples Bu-1, Ro-1, RJ-1, N-LP, SO-1a and SO-1b). Pure vermiculites gave similar XRD patterns [4], showing reflections corresponding to trioctahedral vermiculites [3], and all behaved simularly to diagnostic treatments. After potassium-saturation and heating to 110° and 550°C, all of the 14 Å mineral contracted to 10 Å, and no 14 Å reflections remained, indicating that chlorite was absent. In oriented samples, very weak and broad reflections at 10.3–10.5 Å were observed, indicating relicts of mica in the vermiculites.

Table 2 Variability in chemical composition of samples studied

|	Maximum	Minimum
SiO_2	45.20	36.17
Al_2O_3	16.93	10.90
Fe_2O_3	7.03	1.07
FeO	5.27	1.15
TiO_2	3.07	0.15
MgO	20.05	13.67
K_2O	8.31	0.03
H_2O*	25.24	18.50

* Loss on ignition at 1000°C

Table 2 shows the variability in chemical composition of the samples. The data presented correspond to the extreme values found by chemical analysis. The total iron content is low to moderate, not exceeding 10 wt% (Fe_2O_3 + FeO) in any sample. The content of potassium is due to the presence of small amounts of interstratified mica, all pure vermiculites showing about 0.03% K_2O.

Figures 1 and 2 show representative DTA-TG curves of these samples, DTA curves of pure vermiculites (Fig. 1a) show large endothermic effects at 145°–150°C with smaller ones at 260°–270°C, and correspond to Mg-vermiculites [1, 2]. Some samples (Fig. 1b, c) show a small endothermic effect at about 550°C and a corresponding weight loss on the TG curve. These effects are attributed to dehydroxylation of mica relicts present in the vermiculite. Other

samples show two endothermic effects (Fig. 1d) at 110° and 205°C, which are characteristics of Mg-vermiculites but lower than those of pure vermiculites. This probably arises from interstratification present in these samples. The weight loss on the TG curve associated with the endothermic effect at 575°C may be attributed to dehydroxylation of partially altered mica comprising this interstratification.
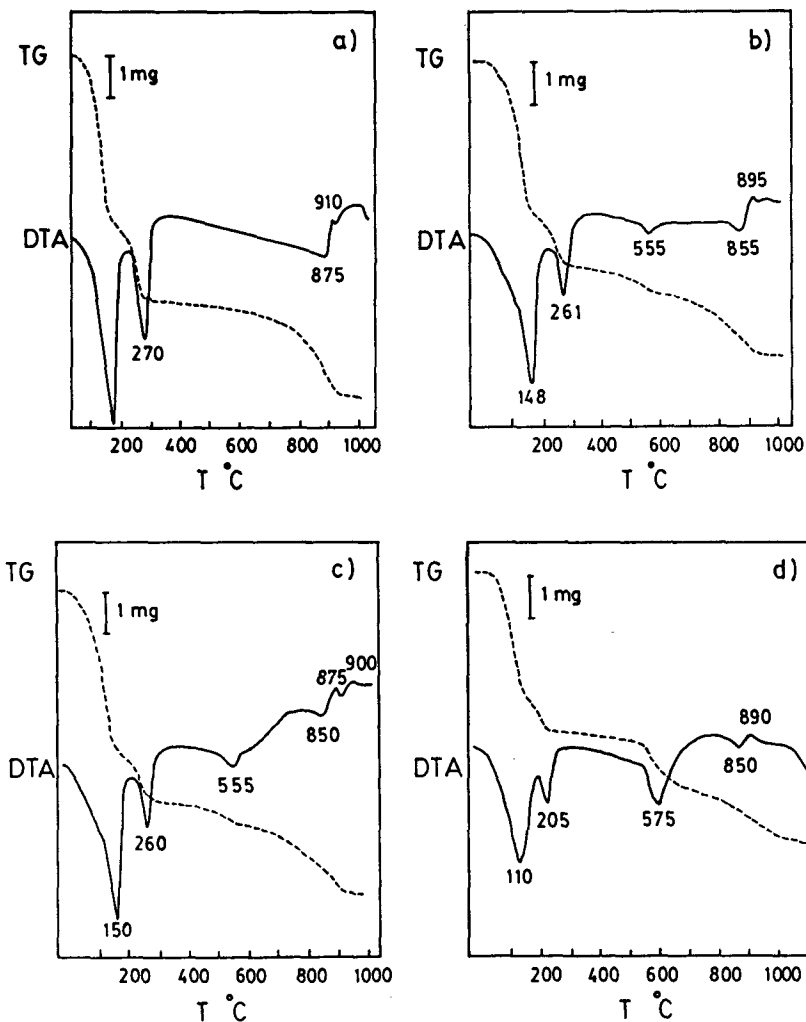
Fig. 1 Simultaneous DTA-TG curves of (a) pure vermiculite, (b, c) vermiculite with relict mica, (d) interstratified vermiculite-mica. Heating rate 15 deg/min
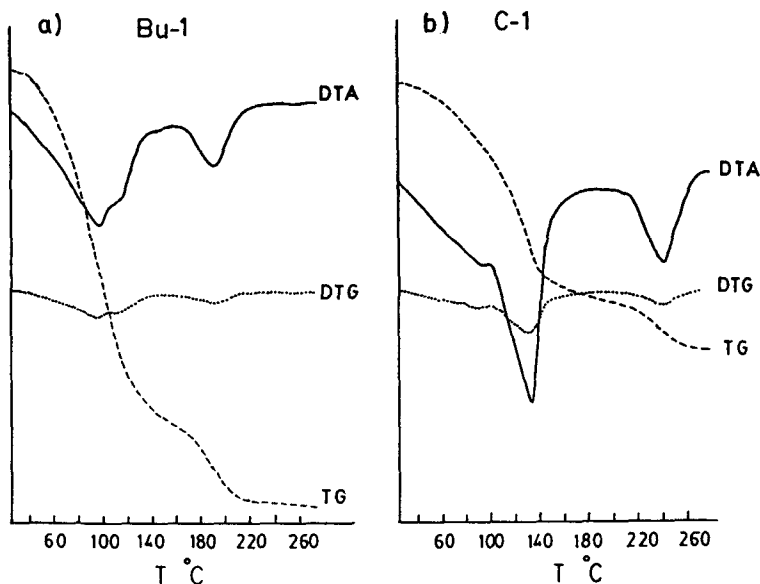
Fig. 2 Simultaneous DTA-TG curves of (a) sample Bu-1 (vermiculite with mica-vermiculite interstratification) and (b) sample C-1 (pure vermiculite). Heating rate 5 deg/min

DTA-TG curves recorded at low heating rate (Fig. 2) revealed a shoulder on the first endothermic peak that for vermiculite with mica or vermiculite with mica-vermiculite interstratifications (sample Bu-1) is located towards the lower-temperature side of the peak. For pure vermiculite (sample C-1) a shoulder occurred on the higher temperature side of the DTA peak. TG and DTG curves showed weight losses in the region in which the above DTA effect was observed. Mechanical mixtures of samples from group (a (vermiculites) with group (b) (interstratifications), showed DTA curves with four clearly defined DTA effects. Two of them appeared at 68° and 170°C (heating rate = 5 deg/min) corresponding to dehydration of vermiculite in the interstratification, and 98° and 215°C corresponding to the dehydration of the lamellae of pure vermiculite.

Discussion and conclusions

The samples can be divided into two groups, depending on the temperatures at which the first DTA peak appears:

(a) Samples with peak temperatures at 140°– 150°C an d 240°– 270°C. This group comprises only the pure vermiculites. ·

(b) Samples with peak temperatures at 95°–115°C. This group comprises samples of vermiculite with mica, or vermiculite with mica-vermiculite interstratifications.

There is no single explanation for the thermal behaviour of this set of natural vermiculites. Although related to loss of water, the mechanism must differ from one sample to another depending on chemical composition and partial structural breakdown during dehydration. Thus, the presence of interstratifications produces thermal effects at lower temperatures compared with pure vermiculites. It has been shown previously [7] that the sudden release of water (dehydration and dehydroxylation) causes the expansion of vermiculite, the highest expansibilities being shown by samples containing mica or mica-vermiculite interstratifications [8]. However, the sudden release of interlayer water is not the only factor influencing expansion, as the effects of the presence of relicts of altered mica, loss of OH structural groups and chemical composition remain to be properly evaluated. Kinetic measurements on similar samples (clay fractions <2 μm, see reference [9]) indicated that dehydration and dehydroxylation reactions proceed through an interfacial mechanism based on first-order kinetics. Differences in dehydroxylation temperature were associated with different degrees of interstratification in the starting vermiculites, as observed in the present investigation.

The low temperature at which the endothermic effect in samples of group (b) appears could be attributed to lowering of water bonding energy associated with differences in chemical composition (possibly potassium or iron). However, the water-bonding energy in the interlamellar space of vermiculites mainly depends on the interlamellar cation. As all the samples studied in this work were homoionic (Mg-saturated), this fact would explain the similarity of DTA curves of samples from group (a), despite differences in chemical composition of tetrahedral and octahedral sheets.

For mica-vermiculite interstratifications, the mica layers are inert from the thermal point of view. However, the higher expansibilities measured in these materials [8] produces more porous powders in the sample holder than pure vermiculites. This higher porosity allows easier release of water molecules from the sample to the atmosphere, thus lowering the temperature of the endothermal effects.

References

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Zusammenfassung —An einer Reihe von natürlichen Vermikulitproben wurde simultane DTA-TG durchgeführt. Anhand ihres Dehydratationsverhaltens können diese Proben zwei Gruppen zugeordnet werden: (a) jene mit endothermen DTA-Peaktemperaturen von 140°–150°C und 240°–270°C (reine Vermikulite) und (b) jene mit Peaktemperaturen von 95°–115°C (Vermikulit mit Glimmer oder Glimmer-Vermikulit Zwischenlagerungen). Die niedrige Temperatur, bei der in Gruppe (b) der endotherme Effekt auftritt, wird anhand der Verdünnung durch inerte Glimmerschichten, den Unterschieden der chemischen Zusammensetzung und der Erniedrigung der interlamellaren Wasserbindungsenergie besprochen.