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THERMAL ANALYSIS STUDY OF THE ADSORPTION OF D_2O BY SEPIOLITE AND PALYGORSKITE.

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ABSTRACT

D_2O treated sepiolite and palygorskite were studied by DTA, TG and EGA. The adsorption was carried out by wetting the clays with D_2O prior and after heating sepiolite to 430 and 600°C, and palygorskite to 360 and 600°C. Optimal conditions for adsorption of D_2O are obtained after the temperate heating. Heating to 600°C blocked the porous structure and the adsorption took place on the external surface. Gas evolution curves showed that HDO is evolved during the recrystallization stage of sepiolite but not of palygorskite. It appears that during the first stages of dehydroxylation of sepiolite deuterium is trapped by the amorphous meta sepiolite and is released at higher temperatures during the recrystallization stage. It was concluded that the second stage of dehydroxylation of sepiolite is not associated with the decomposition of residual TOT units but results from the decomposition of secondary units which have been formed during the first stage of the dehydroxylation of this clay.

INTRODUCTION

Sepiolite and palygorskite are fibrous clay minerals with a porous

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structure [1-3]. When subjected to thermal treatments they undergo several endothermic reactions (dehydration and dehydroxylation) and an exothermic reaction (recrystallization). The DTA and DTG curves can be divided into four regions. Each region is associated with a characteristic peak. The first region (and the first DTA endothermic peak) is due to the dehydration of interparticle and zeolitic water. The second region (and the second DTA endothermic peak) is due to the loss of part of the water molecules coordinated to the cations located at the edges of the octahedral sheets, inside the zeolitic pores ("bound water"). At this stage the dehydration is reversible. The phase which is obtained at this stage is sometimes called "sepiolite anhydride" or "palygorskite anhydride", respectively.

The remainder of the "bound water", together with H_2O molecules resulting from the dehydroxylation of the clays, are evolved during the third stage giving one endothermic peak. As a result of the dehydroxylation, the so called "sepiolite anhydride" or "palygorskite anhydride" is transformed into amorphous phases named "meta-sepiolite" and "meta-palygorskite". This stage of dehydration is irreversible. At the high temperature region, above 800°C, (the fourth region) an endothermic effect occurs which is followed by an exothermic one. These effects are distinct for most of the sepiolites reported in the literature and less pronounced in the case of palygorskites. The endothermic phenomenon is attributed to dehydroxylation of residual OH groups , while the exothermic peak results from the recrystallization of the "meta-clay" into clinoenstatite [4,5]. The various regions as well as the corresponding peaks will be assigned by A, B, C and D, respectively.

EXPERIMENTAL

Sepiolite from Vallecas, Spain and palygorskite from Quincy, Florida, were supplied by Ward's Natural Science Establishment.

The saturation of both clays by D_2O was carried out by three methods. In the first method (the "mild treatment") 50 mg samples of the ground clays were covered by several drops of D_2O. The wet samples were equilibrated for 60 hours in small covered beakers. In the second method (the "temperate treatment") 50 mg samples of the ground sepiolite or palygorskite were gradually heated in the DTA furnace to 430 and 360°C, respectively. Each sample was covered by several drops of D_2O and equilibrated for 24 hours in the covered beakers. In the third method (the "extensive treatment") 50 mg of the clay samples were gradually heated to 600^0C in the DTA furnace and then treated with several drops of D_2O as in the "temperate treatment".

Thermal analyses of the D_2O treated clays were carried out on a Mettler TA-1 instrument coupled to a Baltzers quadrupole mass spectrometer, for evolved gas analysis [6]. Each run was carried out under flow of air (1.9 liter x hr^{-1}). Heating rate was 10^0 min^{-1}. Gas evolution curves for the masses 18 (H_2O), 19 (DHO) and 20 (D_2O) were recorded.

RESULTS

Samples prepared by the "mild treatment"

The DTA curves of D_2O treated sepiolite and palygorskite are similar to those of the untreated clays [4,5]. The temperatures of the peak maxima, the range of each peak and the corresponding weightloss are presented in Table 1.

TABLE 1

The assignment of peaks, peak maxima (from DTA), temperature range of peaks (from DTG) and weightloss during each peak (from TG).

Clay	Assignment of thermal range	Peak Maximum (°C)	Temperature Range (°C)	Weightloss (%)
Sepiolite	A	140	r.t-240	18.6
	B	325;370	240-430	2.9
	C	525	430-650	2.2
	D	830		
		840 (exo)	650-900	1.8
Palygorskite	A	130	r.t-220	16.0
	B	270	220-370	2.8
	C	475	370-625	4.0
		endo. tail	625-790	1.0
		900 (exo)	no peak	-

The H_2O evolution curves show the most intense peaks compared to those of HDO and D_2O. They are located at the same temperatures as peaks A, B and C in the DTA curves of palygorskite and A,B,C and D in the case of sepiolite. Peaks A and B in the HDO evolution curve appear at the same temperature in which the corresponding H_2O evolution curves show peaks. Peak C appears at temperatutes lower than those recorded for H_2O. While the evolution peak of HDO appears at 500 and 470°C for sepiolite and palygorskite, respectively, the H_2O peak appears at 525 and 480°C. The ratios between the intensities of the differnt peaks in the HDO and the respective H_2O evolution curves are shown in Table 2.

TABLE 2

Intensity ratios of peaks A,B and C in the HDO evolution curves vs. respective peaks in the H_2O evolution curves.

Peak	Sepiolite		Palygorskite	
	I	II	I	II
A	0.50	1.45	0.40	1.20
B	0.45	1.33	0.55	1.46
C	0.35	1.05	0.35	0.95

I- sample prepared by "mild treatment".
II- sample prepared by "temperate treatment".

In region D of D_2O-sepiolite, the HDO evolution curve shows a small peak at 840°C. This peak appears together with an intense H_2O evolution peak and is associated with the recrystallization of this clay. The intensity ratio between the HDO and H_2O is smaller than those found for peaks A, B, and C and is equal to 0.13, indicating that a very small fraction of the OH groups, which persisted at this stage in the clay, was subjected to isotope exchange. No HDO was detected for the D_2O-palygorskite at this stage of the thermal analysis.

D_2O is evolved only during the occurrence of peak A. The ratios between the intensities of the first D_2O and H_2O evolution peaks are 0.26 and 0.17 for sepiolite and palygorskite, respectively, indicating that only a small fraction of the zeolitic and interparticle water was replaced by the D_2O in the present treatment.

Samples prepared by the "temperate treatment"

The DTA and DTG curves of these samples are similar to those of the natural and D_2O-"mild treated" samples. The TG curves revealed that the weightloss corresponding to each peak was slightly smaller (by 10-15%) than that recorded after the "mild treatment".

The D_2O evolution curves of both clays show that peak A is very intense relative to its intensity in the curve of the "mild treated" clay. The intensity ratio between this peak and peak A in the H_2O evolution curve is 0.54. Very small peaks B and C are also detected. Comparoson between the present curves and those obtained from the samples which were prepared by the "mild treatment", shows that the present treatment increases the adsorption of D_2O by both clays. The HDO evolution curves of both clays show that peaks A, B, and C are intensified relative to the mild treatment. The intensity ratios of these peaks relative to those of the H_2O evolution curves are given in Table 2.

Samples prepared by the "extensive treatment"

The DTA and DTG curves show a single endothermic peak at 130°C. This peak is associated with weightloss. Peaks B and C which characterize the evolution of bound water from the zeolitic pores, do not appear in these curves.

The gas evolution curves reveal that the single DTA peak is associated with the evolution of D_2O, HDO and H_2O. From the absence of peaks B and C it may be concluded that the adsorption of D_2O takes place on the surface of the clay particles.

DISCUSSION

The appearance of HDO evolution peaks in the temperature range of the evolution of the bound water (peaks B and C, Table 1) indicates that D_2O is adsorbed into the zeolitic pores where upon it interacts with the bound water by isotope exchange of H by D and perhaps also by ligand exchange of coordinated water molecules ("bound water") by D_2O.

Thermal dehydration of sepiolite and palygorskite, first causes a non-uniform folding of the layers. With further dehydration an ordered folded stage is reached [7-12]. In the present study, after heating palygorskite to 360°C and sepiolite to 430°C, the D_2O molecules penetrate into the non-uniform folded pores. These are optimal conditions for the saturation of these clays with D_2O. Heating up to 600°C blocked the pores to penetration of D_2O and the adsorption took place on the external surfaces.

The ratio between the intensity of peak B in the HDO and H_2O evolution curves is higher than that of peak C (Table 2). A decrease in the intensity ratios from peak B to C is due to the fact that peak C in the H_2O evolution curve is associated with dehydroxylation in addition to bound water evolution. In sepiolite and palygorskite all clayey OH groups are located inside the crystal structure and it is not expected that isotope exchange between structural OH groups and D_2O molecules occurs [13], especially in the "mild treatment". However, if one assumes that there is no isotope exchange between the clayey OH groups and the D_2O molecules, one would not expect an HDO evolution peak at 840°C (peak D). This peak in the H_2O evolution curve is attributed to the last stages of the dehydroxylation of sepiolite.

In order to understand how it is possible that HDO is found in the gases which are evolved in connection with the terminal stage of the dehydroxylation of sepiolite, one must assume that the deuteration of the bulk silicate phase occurs at lower temperatures. A possible temperature range for the deuteration could be that of region C, the first stage of dehydroxylation. At this stage the ordered folded sepiolite undergoes a transformation into a non crystalline meta-sepiolite phase. This structural transformation is not merely the result of the thermal diffusion of protons and HOH molecules from inside the bulk of the silicate phase towards the outside. The restructuring probably follows the breaking of different Si-O, Mg-O and Al-O bonds in the clayey silicate TOT units. In the new structural units of the meta-sepiolite some of the OH groups are temporarily located at the edges of the species and both isotope exchange and deuteration may occur. The deuterated species will grow while the deuterium atoms are trapped inside the bulk amorphous phase. Similar trapping of CO_2 and NH_3 molecules was observed during the thermal analysis of sepiolite treated with aliphatic amines [14]. At 830°C a recrystallization occurs and at this stage Si, Mg, Al and O atoms diffuse from the poorly ordered meta-sepiolite species to the well uniform ordered units of clinoenstatite. At this stage the trapped H and D atoms are able to escape in the form of H_2O or HDO molecules. The difference between sepiolite and palygorskite is that H or D atoms are not trapped in the latter, probably because the amorphous meta-palygorskite consists of open units in which atoms or groups are not trapped. In conclusion, the second stage of dehydroxylation of sepiolite (peak D) is not associated with the decomposition of residual fractions of TOT units but results from the decomposition of secondary units in which H atoms (or OH groups) were trapped during their formation. The decomposition of the sepiolite TOT units by thermal dehydroxylation has already occurred during the appearance of peak C. However, the evolved gases were trapped by the amorphous meta sepiolite until the recrystallization stage.

REFERENCES

1 W. F. Bradley, Amer Mineral 25 (1940) 405.
2 B. Nagy and W. F. Bradley, Amer Mineral 40 (1955) 885.
3 K. Brauner and A. Preisinger, Mineralog. Petrogr. Mitt . 6 (1956) 120.
4 J. L.Martin Vivaldi and P. Fenoll Hach Ali, in "Differential Thermal Analysis"; Editor: R. C. Mackenzie. Academic Press (1970) chapter 20.
5 A Singer, in "Minerals in Soil Environments", 2nd ed. (1988, in press); Editors: S. B. Weeds and J. B. Dixon, Soil, Sci. Soc. Am., Madison.
6 M. Muller Vonmoos, G. Kahr and A. Rub, Thermochim Acta, 20 (1977) 387.
7 W. Hirsiger and M. Muller Vonmoos, Thermochim Acta, 13 (1975) 223.
8 H. Nagata, S. Susumu and T Sudo, Clays and Clay minerals, 22 (1974) 285.
9 S. Lokanata, B. K. Mathur, K. Samantary and S. Bhattacherjee,
a. Zeitschrift fur Kristallographie, 171 (1985) 69.
b. J. Materials Science Letters, 3 (1984) 1105.
10 Y. Nathan, in "Proceedings of the International Clay Conference", Tokyo 1969, (L. Heller, Editor), Israel University Press, Jerusallem, 1 (1969) 91.
11 C. Serna, J. L. Ahlrichs and M Serratosa, Clays and Clay Minerals, 23 (1975) 452.
12 G. E. VanScoyoc, C. J Serna and J. Ahlrichs, Amer. Mineral. 64 (1979) 215.
13 C. Serna, G. E. VanScoyoc and J. L Ahlrichs, J. Chem Phys. 65 (1976) 3389.
14 U. Shuali, S. Yariv, M. Steinberg, M. Muller Vonmoos, G. Kahr and A. Rub, in preparation.