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COMPARISON OF ATTAPULGITES FROM DIFFERENT SOURCES USING TG/DTG AND FTIR

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ABSTRACT

Several samples of attapulgites from different sources were analyzed by TG/DTG and FTIR. The thermal behaviour of these clay minerals varies within certain limits according to their origin. For some attapulgite samples, dehydration (bound water) and dehydroxylation occur within the same range of temperature. These differences in thermal behaviour could be related to the various crystal structures, and/or to the chemical compositions of these minerals. We have also observed that associated carbonates in attapulgites decompose in the same temperature zone as the dehydroxylation step.

These results could explain the disagreements found in the literature with respect to the quantity of constituent water when comparing the chemical composition of different attapulgite clay minerals.

INTRODUCTION

Attapulgite, or palygorskite, is a crystalline hydrated magnesium aluminium silicate which has useful colloidal and sorption propterties [1]. This fibrous clay mineral possesses a rigid three-dimensional structure presenting open microchannels [2], and differs from other clays with respect to the structural organization of its water molecules [3]. Previous studies [2,4–6] have shown that attapulgite contains three forms of water in its structure: zeolite water, crystallization water coordinated at two positions to the magnesium/aluminium ions in the crystal lattice, and hydroxyl water linked to the structure of the mineral. However, considering the existing controversy over the ideal formula based on the thermal behaviour of this mineral, the present work reports on the heterogeneity of the relationship between the hydration status of the attapulgite structure and its thermal behaviour (TG/DTG). Infrared absorption spectra are also presented.

LITERATURE REVIEW

Figure 1 presents the attapulgite structure after Bradley [3]. The identification and quantification by thermal methods of several kinds of water

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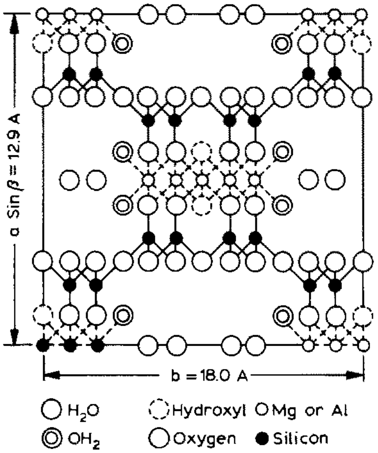

Fig. 1. Schematic representation of the structure of attapulgite $(OH_2)_4(OH)_2Mg_5Si_8O_{20} \cdot 4H_2O$ (after Bradley [3]).

TABLE 1

Observed water losses of attapulgite after Hayashi [4]

	Dehydration step				Total loss
	1	2	3	4	
Temperature range (° C)	< 210	210–350	350–580	580–800	–
Weight Loss (%)	8.0	4.1	5.2	2.1	19.4

TABLE 2

Observed water losses (%) compared with those for ideal attapulgite, after Caillère and Hénin [2]

	U.S.A.	Algeria	Morocco	France	Ideal
Zeolitic water, below 200 ° C	10.8	10.7	8.0	9.8	8.6
Bound water, 250–400 ° C	3.6	2.7	4.0	4.0	8.6
Hydroxyl water, above 400 ° C	4.2	6.2	6.2	6.5	2.15
Total water	18.6	19.6	18.2	20.3	19.35

TABLE 3

Ideal structural formula of attapulgite

Bradley [3]	$(OH_2)_4$	$(OH)_2$	$Mg_5Si_8O_{20}\cdot 4H_2O$
Gard and Follett [7]	$(OH_2)_3$	$(OH)_3$	$MgAl_3Si_8O_{20}\cdot 4\text{–}5H_2O$

TABLE 4

Observed water losses from Niger attapulgite, after Rautureau and Mifsud [8]

	Dehydration step			Total loss
	1	2	3	
Temperature range (°C)	0–150	150–325	325–650	–
Weight loss	8.4	3.4	3.5	15.3

Ideal formula has to be: $(OH_2)_{1.4}(OH)_{1.55}Mg_{2.22}Al_{1.35}Si_{7.93}\cdot 3.55H_2O$.

molecules in attapulgite have been performed by various investigators. However different opinions have been expressed, and the authors are not in agreement about the ideal formula and structure of this mineral. Tables 1–4 show some of these results.

Caillère and Hénin [2] calculated the structural formula of these minerals of different origin, on the basis of 26 oxygens, dividing the water according to the percentage weight loss within the various ranges of temperature. Their results are presented in Table 2; the ideal formula is different from that given by Bradley.

Tables 3 and 4 illustrate other controversial results obtained by Gard and Follett [7] and Rautureau and Mifsud [8].

EXPERIMENTAL

In this work, six samples of attapulgite, listed in Table 5, were investigated.

TABLE 5

Attapulgites studied in the present work

American attapulgite (Quincy, Florida), obtained through World's Natural Science Establishment Inc., Rochester, NY.
French attapulgite (Marmoiron), kindly supplied by Dr. M.C. Jaurand
Two Spanish attapulgites (unknown origin), kindly supplied by Dr. J. Dunnigan
Attapulgite from England (unknown origin)
Russian attapulgite (unknown origin), kindly supplied by Dr. J. Dunnigan

The following experimental conditions were used during the TG/DTG analysis: sample weight 7–20 mg; heating rate 20 °C min^{-1}; dynamic flow rate of dry nitrogen or CO_2 50 cm^3 min^{-1} on a Perkin-Elmer TGS2 apparatus.

The FTIR analyses were performed using a Nicolet MX-1 instrument.

RESULTS AND DISCUSSION

Thermal analysis

Dynamic nitrogen and CO_2 were used in the thermogravimetric analysis of the attapulgite samples. Use of the nitrogen atmosphere allowed us to identify the presence of carbonates, which are usually associated with these minerals as impurities.

Figure 2 and Table 6 show the differences in thermal behaviour of these minerals under a nitrogen atmosphere. We can see that the thermal traces of the six kinds of attapulgite are all different, for example in the percentage of various types of water in the structure. Further, it is apparent that in the case of Spanish attapulgite No. 2 the two-stage loss of water, characteristic

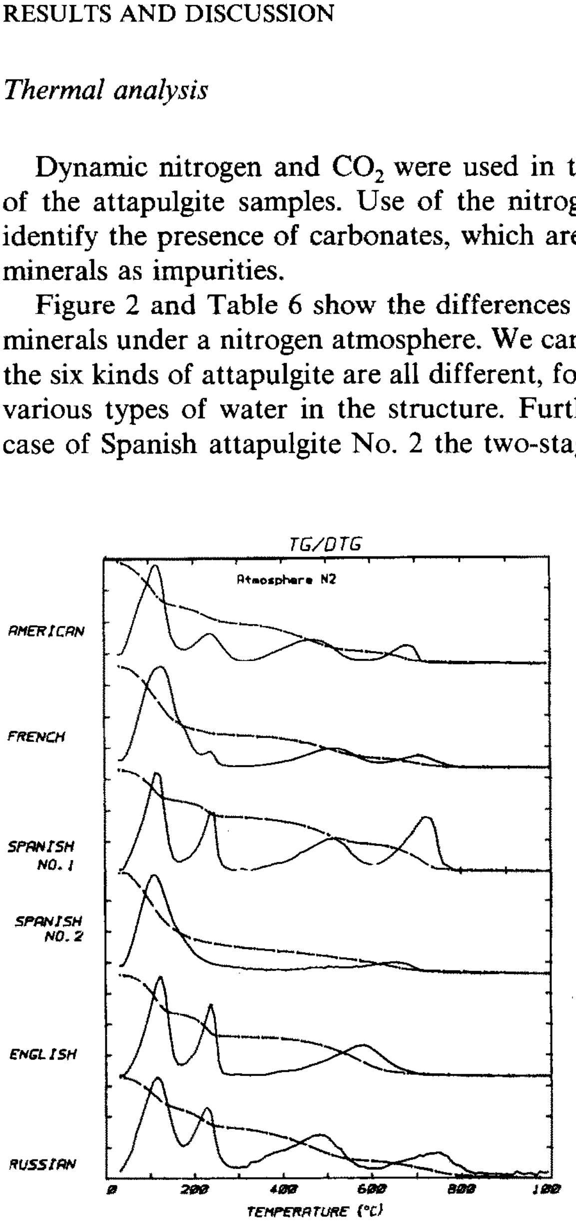

Fig. 2. TG/DTG curves of attapulgites from different sources (under N_2 atmosphere).

TABLE 6

Observed water losses (%) from thermal analysis of attapulgites using dynamic nitrogen gas

Attapulgite	Dehydration step				Total Loss
	1	2	3	4	
	Zeolitic + hygroscopic water	Bound water crystallisation water		Hydroxyl water + carbonates decomposition	
American	8.2	2.9	5.1	2.2	18.4
French	9.4	0.8	3.5	1.3	15.0
Spanish No. 1	5.0	2.8	4.7	4.2	16.7
Spanish No. 2	8.5	–	–	1.9	10.4
England unknown origin	7.0	4.3	–	6.7	18.0
Russian	6.0	3.3	6.4	3.2	18.9

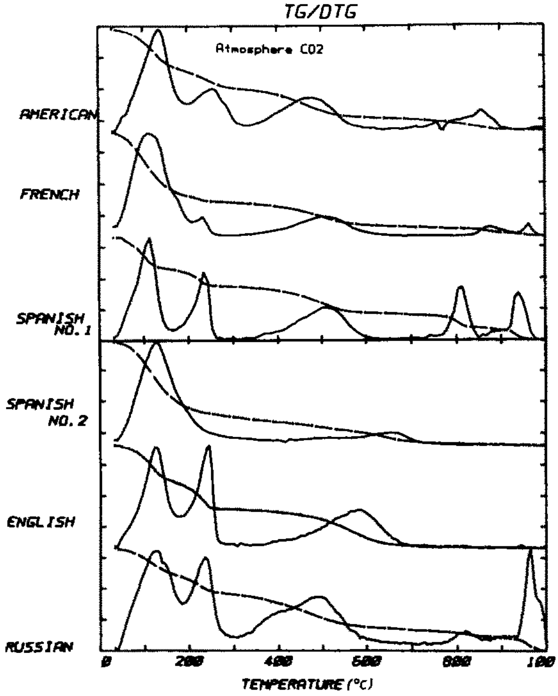

Fig. 3. TG/DTG curves of attapulgites from different sources (under CO_2 atmosphere).

of crystal water, is absent. In addition, only a single-stage loss of crystal water is observed in the case of English attapulgite.

These differences in the thermal behaviour of attapulgites from different sources can be ascribed to their varied crystal structures, and/or differences in chemical composition.

These effects may explain the disagreement between the results of Michel Rautureau et al. [8] (from thermal analysis) and the structural model proposed by Bradley [3]. Figure 3 illustrates the TG/DTG curves of these minerals using a CO_2 atmosphere. These thermal traces show the presence of carbonates when they are associated with attapulgite. As shown on the DTG curves, the decomposition of carbonates is located towards higher temperatures and it is separated from the dehydroxylation of these minerals under a CO_2 atmosphere. Under a nitrogen atmosphere, however, dehydroxylation of attapulgite and decarboxylation of associated carbonates (when they are present) occur over the same temperature range (600–800 ° C). The former effect shows to what extent care must be taken when using thermogravimetric analysis for quantitative calculations concerning these compounds. This may explain why there is disagreement between various authors about the quantity of constituent water, or water linked to the

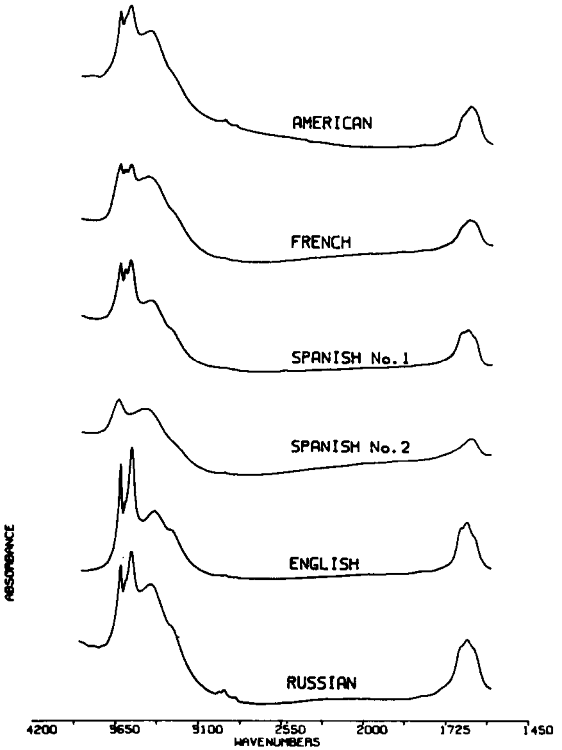

Fig. 4. FTIR of attapulgites from different sources.

TABLE 7

Vibration frequencies (cm^{-1}) of attapulgites in O–H region

Attapulgite	Structural hydroxyl	Bound water				Zeolitic water		Hygroscopic water	
		1		2		Stretching bands	Bending bands	Stretching bands	Bending bands
		Stretching bands	Bending bands	Stretching bands	Bending bands				
American	3616	3550	1672	3580	1625	3404	1645	3270	1645
French	3616	3550	1670	3585	1625	3408	1650	3270	1650
Spanish No. 1	3618	3550	1670	3585	1625	3405	1650	3270	1650
Spanish No. 2	3629	–	–	–	–	3430	1645	3270	1645
English	3615	3542	1672	3580	1630	3400	1650	3275	1650
Russian	3614	3545	1675	3580	1625	3403	1650	3275	1650

structural and chemical composition of attapulgite, when these values are calculated from the amount of water lost between 600 and 800 °C [2,8].

Infrared spectroscopy

In order to clarify the process of thermal behaviour of attapulgites, infrared studies have been carried out on these minerals. Figure 4 and Table 7 show the absorption patterns between 4000–3000 cm^{-1} and 1700–1600 cm^{-1} wavelength region, corresponding to the vibrations of hydroxyl groups. Infrared spectra of attapulgite have already been published [4,9].

Comparing the FTIR spectra of English attapulgite with those from samples of American, French and Russian origin, we can see that all the peaks characteristic of O–H groups are present, while the results obtained from TG/DTG curves show the presence of only one stage weight loss of crystal water for this sample.

Judging from the infrared absorption spectra, we believe that the losses of both the second stage of crystal water and hydroxyl groups associated with the octahedral sheet in the structure, occur in the temperature region between 355 and 793 °C.

The FTIR results for Spanish attapulgite No. 2 provide additional evidence for the absence of crystal water in the structure of this mineral.

In general the FTIR spectra of American, French, Spanish No. 1 and Russian attapulgites show the presence of all characteristic peaks associated with O–H vibration bands, but with different intensities, and the results of TG/DTG analysis coincide well with these infrared results.

CONCLUSION

The thermal behaviour of attapulgite minerals varies within certain limits according to their origin. For some attapulgite samples, dehydration (bound water) and dehydroxylation occur at about the same temperature.

These results also show the presence of hygroscopic water in attapulgites which is lost together with zeolitic water below 200 °C.

Associated carbonates in attapulgites decompose in the same temperature zone as the dehydroxylation step, therefore negating all attempts to quantitatively determine a structural formula derived from water losses occuring in this range of temperatures.

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