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Controlled rate thermal analysis and differential scanning calorimetry of sepiolites and palygorskites

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Abstract

A series of sepiolites, palygorskites and “Rocky Mountain Leather” (RML) clay minerals have been analysed by controlled rate thermal analysis and differential scanning calorimetry (DSC). Eight weight loss steps are observed and are structure and composition dependent. Three dehydration steps and five dehydroxylation steps are observed. The mass spectrometric curve mimicked the differential thermogravimetric (DTGA) curve enabling the detailed determination of the dehydration and dehydroxylation steps.

Keywords: Attapulgite; Palygorskite; Sepiolite; Rocky Mountain Leather; Dehydration; Dehydroxylation; Controlled rate thermal analysis; Differential thermogravimetric analysis

1. Introduction

Sepiolites and palygorskites form an important group of clay minerals, which have many industrial, catalytic and environmental applications [1–3]. Because of their structural morphology, sepiolites and attapulgites have received considerable attention with regard to the adsorption of organics on the clay surfaces [4–6] and to their use as support for catalysts [7–10]. Sepiolites, attapulgites and various forms of “Rocky Mountain Leather” (RML) (also known as rocky mountain cork, mountain leather or mountain wood) all have a fibrous like morphology with a distinctive layered appearance. Attapulgite has the structural formula $[(OH_2)_4(Mg, Al, Fe,)_5(OH)\cdot 2Si_8O_{20}]\cdot 4H_2O$ and sepiolite the formula $[(OH_2Mg_8(OH)\cdot 4Si_{12}O_{30}]\cdot 8H_2O$. The formulas are written as such to indicate the two types of water present, magnesium co-ordinated water and adsorbed water [11,12]. Both sepiolite and attapulgite are chain minerals: attapulgite consists of two double chains of the pyroxene-type $(SiO_3)^{2-}$ like amphibole $(Si_4O_{11})^{6-}$ running parallel to the fibre axis. Unlike the amphiboles, the attapulgite units are connected to one another by shared oxygen atoms and not cations such as Ca or Mg. Sepiolite consists of three pyroxene-type chains instead of two as in attapulgite; the oxygens linking the chains together are doubly linked as opposed to the singly linked attapulgite oxygen atoms. The structure of these two minerals results in zeolite-like channels, which are approximately 3.7 Å × 6.0 Å and 5.6 Å × 11.0 Å wide, respectively. These channels may be filled with water or organic molecules. The water is partly arranged (ordered) in these channels and water molecules are also bound to the magnesium cations of the Mg (Al, Fe) brucite-like

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ribbon edges that border the channels running along the length of the crystals.

The dehydration and dehydroxylation [13–16] of the palygorskite clays have been studied in detail by thermogravimetric techniques [17–19]. Indeed a review of the thermal analysis of these types of clay minerals has been published [20]. Differential thermal analysis (DTA) in combination with other techniques such as X-ray diffraction and Fourier transform-infrared spectroscopy (FT-IR) proved most useful for the study of the dehydration process [11,12]. It was found that dehydration of sepiolite and attapulgite take place in a series of four steps [19]. Up to 200 °C both hygroscopic and zeolitic water were lost. Between 250 and 450 °C bound water was lost; more strongly bound water (co-ordinated water) and the hydroxyl units were lost in the temperature range 450–610 °C. All of the dehydration/dehydroxylation steps were endothermic in DTA. For both minerals, the partial dehydration of bound H_2O in the ranges 250–610 and 210–550 °C resulted in the formation of sepiolite anhydride and palygorskite anhydride, respectively. Dehydration of the bound H_2O in two steps was attributed to the difference in bonding position of H_2O in the structure of these minerals. With the advances in thermal analysis technology, and the invention of new and novel techniques such as controlled rate thermal analysis, it was considered worthwhile to remeasure the thermal characteristics of a selection of sepiolites and palygorskites. This research reports these analyses based upon the CRTA of sepiolites. A comparison is made with the results of differential scanning calorimetry (DSC).

1.1. Clay minerals

The clay minerals used in this research are (a) Source Clay Minerals Repository Standard Attapulgite PFl-1, (b) sepiolite (Sepsp-1) from Vallecas, Spain, (c) sepiolite from Marschaum and (d) RML collected from the F7 field trip of the 11th International Clay conference (Ottawa, June 1997) [1]. Samples of sepiolite and palygorskite were obtained from the van Der Marel collection. The RML sample was collected from the Nicholson Silica mine near Golden, British Columbia, Canada, in the sandstones of the Ordovician Mount Wilson formation. The clays were analysed by X-ray diffraction for phase purity and dried in a desiccator to remove adsorbed water before being submitted for thermal analysis. The clay minerals were ground to a fine powder of <0.5 μm particle size for thermal analysis.

1.2. Thermal analysis

Differential thermogravimetric analysis (DTA) was conducted on TA® Instruments Thermogravimetric Analyser (TGA, Q500) equipped with evolved gas analysis (EGA) furnace, which was connected to a quadrupole mass spectrometer (PFEIFFER, QMS 200 Prisma) through a 1/8 in., in diameter, transfer line. Nitrogen was used as the purging gas and the flow rate was controlled precisely at 80 ml/min. For each run, sample powders were loaded onto platinum sample pan and heated to 1000 °C at high-resolution heating rate of 2 °C/min, where the heating rate was dynamically and continuously modified in response to the changes in the rate of sample's weight loss, termed as controlled rate thermal analysis (CRTA). DSC was performed on a TA® Instrument DSC Q10 analyser. Sample powders were loaded into sealed alumina pan and heated to 500 °C at heating rate of 2 °C/min. The empty alumina pan was used as reference and the heat flow between the sample and reference pans was recorded.

2. Results and discussion

2.1. Thermogravimetic analysis and differential thermogravimetric analysis

The thermogravimetric and DTA curves of a sepiolite from Spain are shown in Fig. 1. Four distinct weight losses are observed. Two are ascribed to dehydration and two to dehydroxylation. The first step occurs at 50 °C and is attributed to the loss of adsorbed water (Fig. 2). The second step is observed at 246 °C. The third step is complex with two overlapping weight loss steps observed at 450 and 494 °C. The final step is also complex and two weight loss steps are observed 787 and 820 °C. Nagata et al. proposed a set of steps for the dehydration and dehydroxylation of a sepiolite [19]. These steps correspond to (a) the loss of adsorbed water, (b) the loss of hydration water, (c) the loss of co-ordination water, (d) the loss

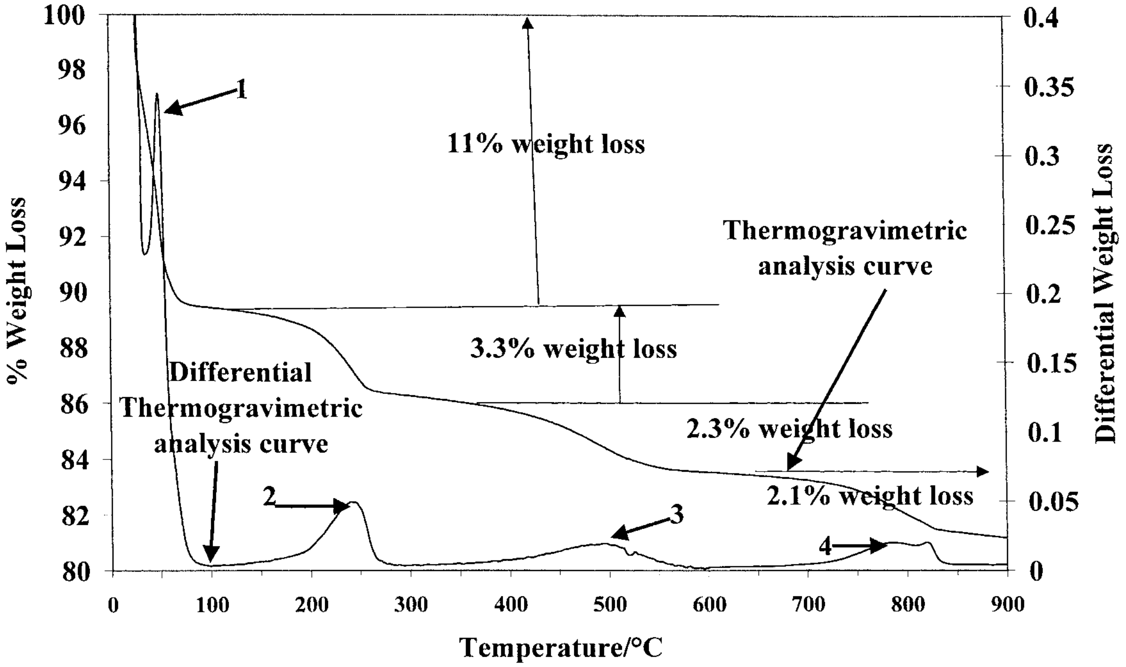

Fig. 1. Thermogravimetric and differential thermogravimetric curves for the controlled rate thermal analysis of sepiolite from Vallecas (Spain).

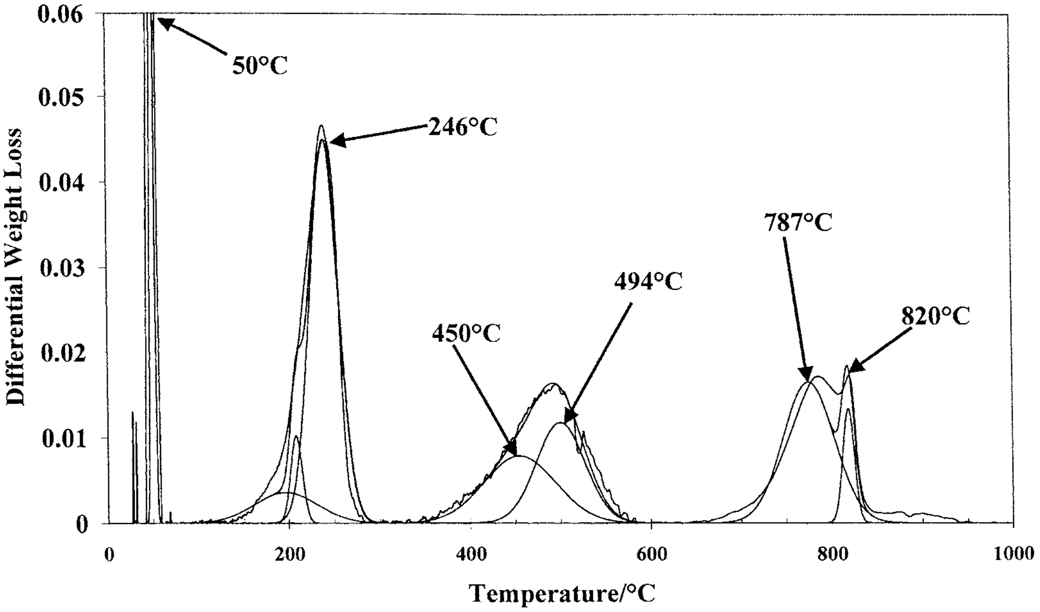

Fig. 2. Component analysis of the DTGA curves for sepiolite.

of water through dehydroxylation. Such a scheme is represented by the following chemical equations:

- Step 1: $Mg_8Si_{12}O_{30}\ (OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O \rightarrow Mg_8Si_{12}O_{30}\ (OH)_4{\cdot}(H_2O)_4 + 8H_2O$
- Step 2: $Mg_8Si_{12}O_{30}\ (OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O \rightarrow Mg_8Si_{12}O_{30}\ (OH)_4{\cdot}(H_2O)_2 + 2H_2O$
- Step 3: $Mg_8Si_{12}O_{30}\ (OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O \rightarrow Mg_8Si_{12}O_{30}\ (OH)_4 + 2H_2O$
- Step 4: $Mg_8Si_{12}O_{30}\ (OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O \rightarrow 8MgSiO_3 + 4SiO_2 + 2H_2O$

Such a scheme is an apparent oversimplification as each of these steps may be subdivided into component weight loss steps. If one uses the formula ($Mg_8Si_{12}O_{30}\ (OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O$) for sepiolite then the theoretical weight loss for step 1 should be 11.0%. The % weight loss observed for the TGA curve for sepiolite was 11%. The theoretical weight loss for step 2 is 2.76% compared with the observed value of 3.3%. The third step theoretical weight loss also should be 2.76% and a value of 2.3% is observed. The final weight loss step should be 5.21%. However, only 2.1% weight loss is found. Thus, there is reasonable agreement with the predicted and the observed weight loss values. The observation that the experimentally determined weight loss step is less than that predicted is an indication that some dehydroxylation has taken place in the previous steps with the evolution of the bound water. It has been found that sepiolite folds to the anhydride like form when about half the H_2O of co-ordination is removed, at <200 °C in vacuum or at approximately 300 °C in air. Removal of the remaining H_2O at 530 °C under reduced pressure produces little further structural change. Infrared evidence suggests that partially dehydrated sepiolite is a folded structure with H_2O of co-ordination trapped in hexagonal holes. The remaining H_2O is lost, without significant structural change, at approximately 500 °C under vacuum to give a true anhydride [21–24].

2.2. Relationship between the mass spectrum of evolved water vapour and the DTGA curve

The integral of the peaks in the DTGA curve in Fig. 1 should be equivalent to the % weight loss for each of the steps. The summary of these results for a series of sepiolites and palygorskites are reported in Table 1. A second method of estimating weight loss is to measure the evolved water vapour from each of the steps shown in the reactions in 3.1 using mass spectrometry. Fig. 3 displays the mass spectrum of evolved water together with the DTGA curve. Fundamentally this mass spectrum follows the DTGA curve with precision. Hence, the percentage relative area under the MS curve will provide a second set of results for the weight changes. Table 1 also reports these weight changes.

The temperature for the first dehydration step was found to be 50 °C by DTGA and 48.3 by mass spectrometry. However, as may be observed in Fig. 3, some variation in determining the weight loss for this step is experienced. Two overlapping weight loss steps are observed at 222 and 246 by DTGA method and at 216 and 254 °C by mass spectrometry. Two weight loss steps are observed at 450 and 494 °C by the DTGA method and at 466 and 531 °C by MS method. The total areas for these two steps are 32.7% by DTGA and 32.2% by MS. Two further dehydroxylation steps are observed at 787 and 820 by DTGA and at 785 and 823 °C by MS methodology. The % relative weight losses by the two methods are very comparable.

2.3. DTGA and TGA of palygorskite

The principal difference between the formula of sepiolite and palygorskite rests with the formula. Sepiolite [$Mg_8Si_{12}O_{30}\ (OH)_4{\cdot}(H_2O)_4{\cdot}8H_2O$] is a trioctahedral type mineral with three divalent magnesium cations filling the three positions of the octahedron. On the other hand, palygorskite with the formula $[(OH_2)_4(Mg,\ Al,\ Fe)_5(OH){\cdot}2Si_8O_{20}]{\cdot}4H_2O$ has some of the magnesium cations replaced with trivalent cations such as Al or Fe, thus, palygorskites tend towards a dioctahedral structure. Fig. 4 displays the TGA and DTGA curves for a palygorskite. Five steps may be observed in the DTGA curve. The first step occurs at 63.4 °C and a % water loss of 12.7% is observed. The second dehydration step occurs at considerably lower temperatures than for sepiolites and is observed at 168 °C. A 16.3% relative weight loss is observed for this step. Two weight loss steps are observed for the palygorskite at 357 and 415 °C. It is possible to speculate that these two temperatures represent the dehydroxylation of the OH units from the octahedral Fe and Al, respectively. However, such a concept needs further proof using for example

Table 1

Results of the thermal analysis of the differential thermal analysis patterns of sepiolites and palygorskites as measured by the controlled heating rate experiment and in comparison with the mass spectrum of evolved water vapour

Sepiolite	Sepiolites 1		Sepiolites 2		Sepiolites 3		Sepiolites 4		Palygorskite 1		Palygorskite 2		Palygorskite 3		Rocky 1	
	DTG	MS	DTG	MS	DTG	MS	DTG	MS	DTG	MS	DTG	MS	DTG	MS	DTG	MS
Dehydration, °C (%) (step 1)	50 (18.4)	48.3 (3.3)	51.4 (14.3)		57.7 (22.2)	57.7 (8.1)			63.4 (12.7)	65.8 (7.9)	57.7 (22.2)			50	55	
Dehydration, °C (%) (step 2)	222 (13.3)	216 (10.0)	207 (13.7)	211 (14.8)	157 (16.6)	158 (27.0)			168 (16.3)	131 (8.9)	157 (16.6)	157 (16.6)	160 (3.1)	198 (8.4)		216 (21.0)
Dehydration, °C (%) (step 3)	246 (14.3)	254 (31.2)	248 (19.4)	248 (29.8)	226 (1.6)	231 (4.9)	246 (37.1)	251 (34.0)		171 (28.8)	226 (1.6)	226 (1.6)	241 (22.8)	245 (32.5)	231 (13.2)	237 (30.3)
Dehydroxylation, °C (%) (step 4)	450 (3.9)	466 (14.1)	388 (5.9)		339 (2.9)	353 (5.2)	386 (6.5)		357 (17.7)	348 (15.8)	339 (2.9)	339 (2.9)	356 (1.5)	392 (3.2)	364 (6.6)	353 (9.2)
Dehydroxylation, °C (%) (step 5)	494 (28.8)	531 (18.1)	444 (11.0)	435 (23.8)	418 (17.9)	423 (18.2)	440 (24.9)	433 (27.7)	415 (50.5)	407 (38.7)	418 (17.9)	418 (17.9)	450 (9.0)	464 (8.6)	428 (16.6)	433 (13.7)
Dehydroxylation, °C (%) (step 6)	787 (19.3)	785 (18.9)	672 (8.3)		489 (38.3)	486 (36.4)			591 (1.9)		489 (38.3)	489 (38.3)	569 (17.7)		475 (16.4)	
Dehydroxylation, °C (%) (step 7)			740 (24.5)	745 (31.5)	682 (0.5)		749 (32.4)	732 (14.1)			682 (0.5)	682 (0.5)	600 (24.2)	695 (14.9)	573 (21.8)	59.4 (25.4)
Dehydroxylation, °C (%) (step 8)	820 (2.0)	823 (4.3)	806 (2.8)						864 (0.95)						613/673 (4.0)	
Dehydroxylation, °C (%) (step 9)															821 (21.0)	

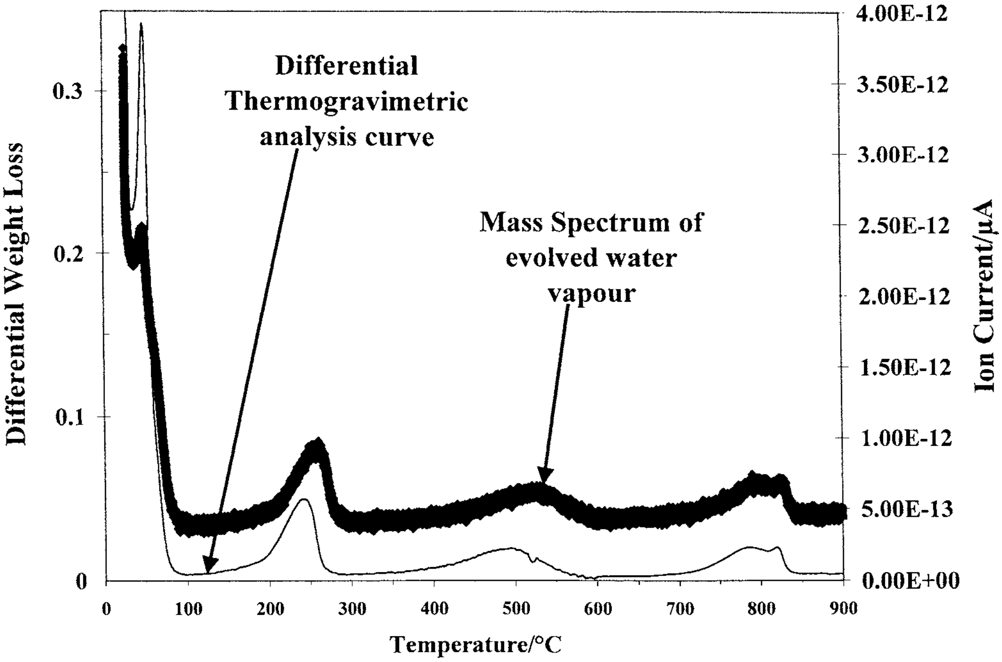

Fig. 3. DTGA curve and the mass spectral curve of evolved water from sepiolite from Vallecas (Spain).

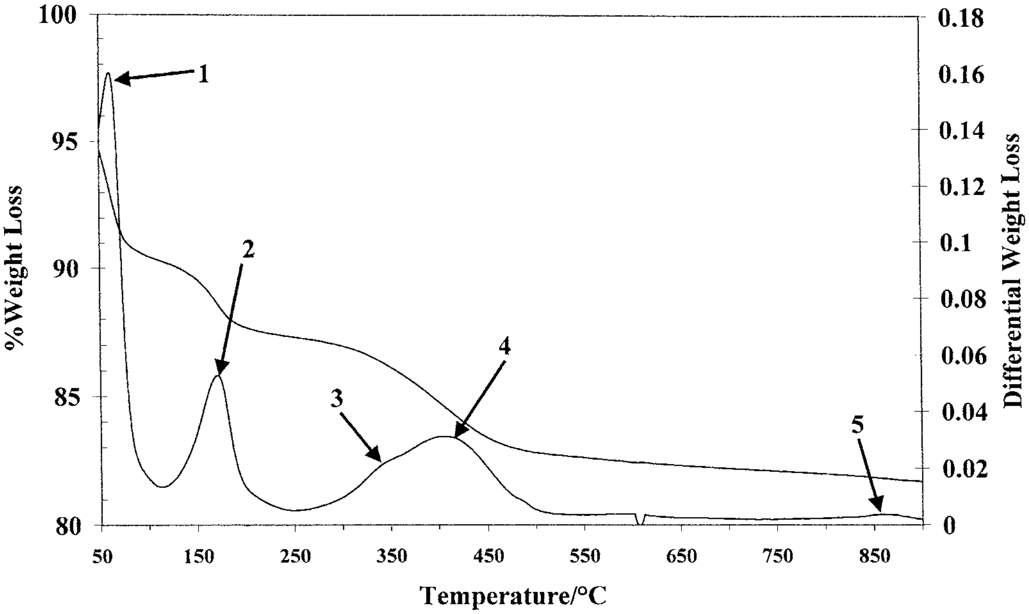

Fig. 4. TGA and DTGA of palygorskite with high magnesium substitution.

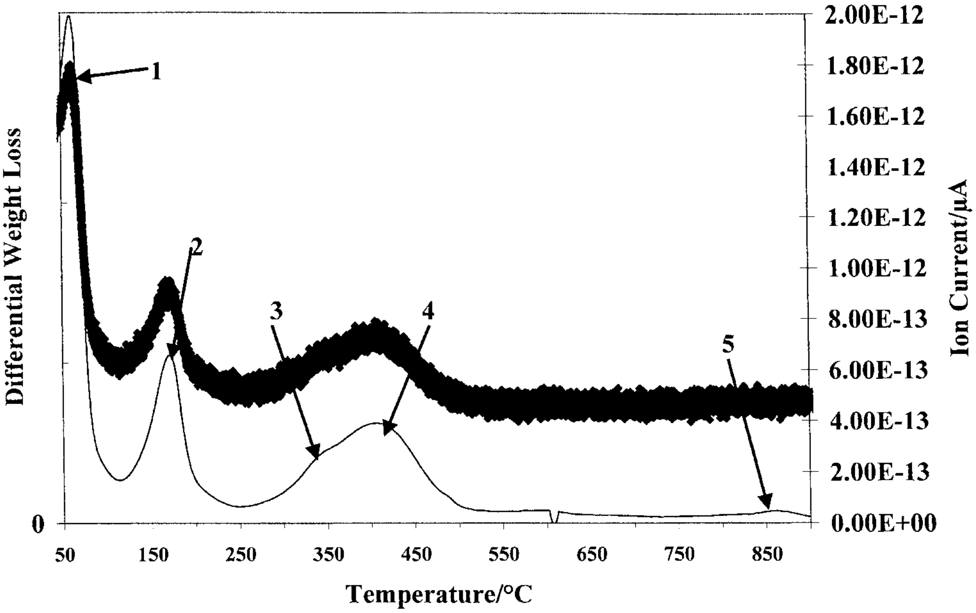

Fig. 5. Mass spectrum of evolved water vapour and DTGA curve of palygorskite with high magnesium substitution.

infrared spectroscopy as the cations are randomly distributed in the octahedral layer. Another more likely consideration is that these two temperatures represent the irreversible dehydration of residual bound water and the folding of the tunnels (at 357 °C) and the dehydroxylation (at 415 °C). A minor dehydroxylation step is also observed at 864°C and is ascribed to the dehydroxylation of OH units from the remnant magnesium.

The mass spectrum of evolved water together with the DTGA pattern of the palygorskite is illustrated in Fig. 5. Again the MS curve follows with precision the DTGA curve. The first weight loss step according to the MS pattern is observed at 65.8 °C, which is slightly higher than the value from the DTGA result. The mass spectrum shows two weight losses at 131 and 171 °C. Two further weight losses corresponding to steps 3 and 4 in Fig. 5, are observed at 348 and 407 °C. Because of the wide variation in the mass spectrum ion current, step 5 could not be observed in the mass spectrum.

2.4. DTGA and TGA of "Rocky Mountain Leather"

A powder X-ray diffraction study of 52 samples having the mountain leather texture of a fibrous, matted intergrowth of asbestiform crystals, shows that 41 are either sepiolite or palygorskite (attapulgite) or some mixture of the two clay minerals [15]. Fig. 6 displays the TGA and DTGA curves for a "RML". The thermal analysis pattern at first appears complex, however, the pattern appears as a combination of the two minerals sepiolite and palygorskite. The RML sample shows a strong loss of water of hydration at ~50 °C both by MS and by DTGA. The difficulty of determining the amount is attributed to the sloping baseline in both the DTGA and MS curves. MS shows a dehydration step at 216 and 237 °C in which 50% of the total water is lost. Two dehydroxylation steps are observed at 364 and 428 °C (DTGA) and 353 and 433 °C (MS). The weight loss by DTGA is 6.6 and 16.6% for these two steps and 9.2 and 13.7% by MS. A further step is observed at 573 °C (DTGA) and 594 °C (MS) in which 21.8% weight loss is observed.

2.5. Comparison with other sepiolites

In this work, some four sepiolites and three palygorskites together with an example of a "RML" were studied using thermal analysis techniques. Considerable variation in the temperatures of dehydration and

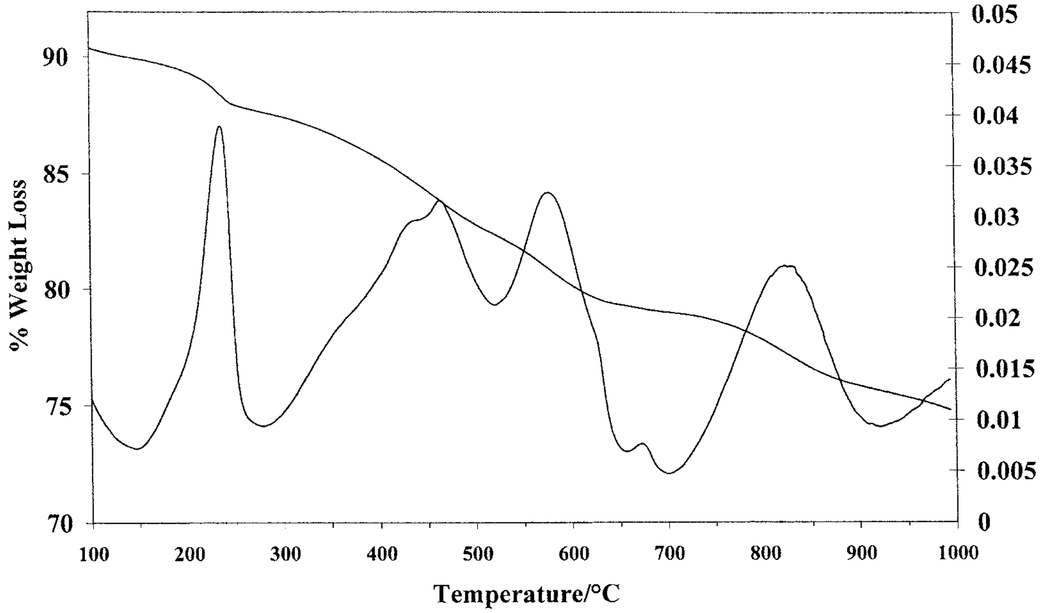

Fig. 6. TGA and DTGA of "Rocky Mountain Leather".

dehydroxylation were obtained (Table 1). Differences are observed between the temperature of dehydration of the sepiolites and the palygorskites. This difference is attributed to the different structure of the two clay minerals. Sepiolites tend towards a trioctahedral structure whereas palygorskites tend towards a dioctahedral structure. These conclusions are in agreement with the findings of Shuali et al. who by deuteration studies of sepiolite and palygorskites showed that the dehydroxylation and crystallisation of the two minerals were different [25]. The temperatures of dehydroxylation of sepiolites and palygorskites are similar except for the last dehydroxylation step, which is higher for the sepiolites. The variation may be attributed to the presence of high amounts of Mg in the sepiolites.

2.6. Differential scanning calorimetry

The differential scanning calorimetric results for a selection of sepiolites and palygorskites are shown in Fig. 7. The results of the heat flow analyses are reported in Table 2. There are six endotherms observed for sepiolites in the 50–500 °C region. The principal endotherm consists of two overlapping endotherms centred upon approximately 83–89 and 100–122 °C. The two endotherms are attributed to adsorbed and zeolitic or 'channel' water. These two endotherms make up some 80% of the heat required to remove water from the sepiolites. The DSC results show that the temperatures for the removal of water for palygorskites are somewhat lower than for sepiolites. The temperatures

Table 2
Results of the differential scanning calorimetry

	Sepiolites 1, °C (%)	Sepiolites 2, °C (%)	Sepiolites 3, °C (%)	Palygorskite 1, °C (%)	RML 1, °C (%)
Heat flow (step 1)	83 (41.7)	89.2 (34.7)	83.0 (44.3)	54.7 (33.3)	67.2 (40.4)
Heat flow (step 2)	122.5 (38.0)	125.9 (24.1)	114 (33.8)	99.0 (53.1)	99.7 (41.7)
Heat flow (step 3)		233.1 (7.0)			
Heat flow (step 4)	282 (5.9)	257 (3.8)	269 (6.6)	300.2 (6.6)	271.9 (4.6)
Heat flow (step 5)	332.5 (14.4)	391.7 (13.9)	335 (13.7)	325 (2.9)	316 (10.0)
Heat flow (step 6)		430.9 (16.5)	452 (1.6)	416 (4.0)	418 (3.2)

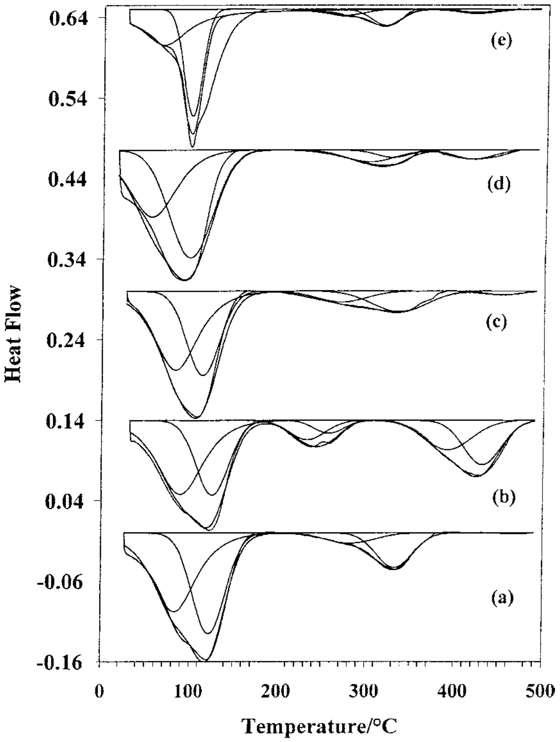

Fig. 7. Differential scanning calorimetry of sepiolite from Vallecas (Spain) (a), sepiolite (Tanzia), (b) sepiolite, (Turkey) (c), palygorskites (Texas, USA), and (d) Rocky mountain leather.

of the endotherms are higher than that observed for the thermogravimetric analyses. The first weight loss step was observed in the 50–60 °C region and the second above 100 °C. This difference may be attributed to the rates of heating of the two experiments. The TGA experiment runs isothermally and at a heating rate of 2 °C. The DSC experiment runs at 2 °C/min. So it could be expected that the results of the slower experiment might be observed at lower temperatures. There is also a fundamental difference between the way the two experiments are conducted. The DSC is a constantly heating experiment whereas the TGA experiment is a high-resolution experiment with the weight loss changes occurring under isothermal conditions.

A third endotherm is observed in the 257–300 °C region. The endotherm appears broad and makes up between 3.8 and 6.6% of the total heat flow. This endotherm is assigned to the heat required to remove chemically bound water. The endotherm corresponds well with the weight loss step observed by both DTGA and MS in the 225–250 °C temperature range. Another endotherm is observed in the 316–335 °C region. This endotherm makes up some 10–14.4% of the heat flow. Again this endotherm is in harmony with the weight loss step observed in the 339–357 °C temperature range. A higher temperature endotherm is observed in the 416–452 °C temperature region. This is a small endotherm and is ascribed to the removal of hydroxyls from the octahedral cation. This endotherm corresponds to the weight loss step 5 (Table 1). The DSC experiment is temperature limited and any higher endotherms are not observed using this technique.

The variation in the DSC results between the different sepiolites and palygorskites may be attributed to a number of factors. Firstly, the variation in chemical composition will effect the position of the endotherm. DSC pattern (a) is typical of a high magnesium sepiolite. The endotherms are more temperature defined for the ‘pure’ sepiolite. If some of the magnesium is replaced with other cations for example Fe and Al, then a DSC pattern as observed in (b) is obtained. Such replacement shifts the structure of the sepiolite from trioctahedral towards dioctahedral. This structural change will then effect the position of the endotherms. For palygorskites and “RML” the endotherms are broad to very broad as is observed in Fig. 7d and e.

3. Conclusions

A number of conclusions may be drawn:

(a) The number of steps in the thermal analysis of sepiolites and palygorskites are greater compared with previous published results when using high-resolution DTGA techniques.
(b) The mass spectrum of water for sepiolites, palygorskites and “RML” follows with precision the DTGA curves in the CRTA experiment.
(c) The CRTA experiment enables the separation of the weight losses for the dehydration steps of sepiolite clay minerals.
(d) Three dehydration steps are observed. These occur around 50–60 and 150–220 °C.
(e) Two dehydroxylation steps are observed in the CRTA experiment. A low temperature weight loss at 350–400 °C and a higher temperature weight loss >500 °C.

(f) Significant differences in the results as determined by the dynamic and CRTA experiment are observed.
(g) The results of the DSC experiment harmonise with the CRTA TGA/DTGA experiment.
(h) Six endotherms are observed in the DSC temperature range from 50 to 500 °C.
(i) Three endotherms are observed at around 80, 120 and 270 °C and are attributed to the removal of water from the sepiolite clay minerals.
(j) Two higher temperature endotherms are observed at around 330 and >400 °C and are assigned to the dehydroxylation of the sepiolites.
(k) This step results in the folding of the sepiolite.
(l) Both the DSC and DTGA patterns of sepiolites differ from those of palygorskites.
(m) RML appears to be a combination of sepiolite and palygorskite.

Acknowledgements

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