THERMAL ANALYSIS OF SEPiolite AND PALYGORSKITE TREATED WITH BUTYLAMINE

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ABSTRACT: The thermal behaviour of sepiolite and palygorskite treated with butylamine was investigated by DTA, TG and EGA-MS under a flow of air and N₂. It was shown that the amine was adsorbed by the clays, penetrating into the pores and replacing zeolitic and bound water. The presence of amine in the pores shifted the dehydroxylation peak to temperatures higher than for the untreated clays. Under N₂ the thermal desorption of the amine from sepiolite was observed at 175, 275 and 525°C, and from palygorskite at 170 and 270°C. In addition to desorption, reactions of pyrolysis and condensation to charcoal were detected by the evolution of NH₃, CH₄ or H₂, respectively. In air, oxidation of the organic matter led to the appearance of exothermic peaks, the temperatures of the most intense peaks being determined by the rate of C oxidation, but the shape of the DTA curves and the temperatures of exothermic shoulders were determined by the rate at which H from the organic molecules combined with O from the air.

Sepiolite and palygorskite are closely related clay minerals differing mainly by their unit-cell values, pore dimensions, and the Mg to Al ratio in the octahedral sheet (Nagy & Bradley, 1955; Brauner & Preisinger, 1956; Bradley, 1940). The thermal analysis of these minerals has been thoroughly investigated (see e.g. reviews by Martin-Vivaldi & Fenoll Hach-Ali, 1970, and Singer, 1989). It has been found that organo-clay complexes frequently give rise to characteristic DTA curves which are diagnostic for the clay (Yariv, 1985). However, most of the thermal analysis work on clay-organic associations has been carried out on montmorillonites, whereas little work has been performed on sepiolite and palygorskite treated with organic substances. Martin-Vivaldi & Fenoll Hach-Ali (1970) published DTA and TG results of ethylene glycol, hexanol and hexylamine adsorbed on sepiolite, and also of ethylene glycol adsorbed on palygorskite, showing characteristic exothermic peaks in air. Yariv & Heller-Kallai (1984) in a study of the adsorption of stearic acid by hormites, showed that the DTA exothermic peaks can indicate the formation of organo-sepiolite and organo-palygorskite complexes.

In the present investigation DTA and TG techniques were used to study the thermal behaviour of sepiolite and palygorskite treated with n-butylamine (BA), both in an air atmosphere and nitrogen. In order to obtain a better understanding of the nature of the DTA curves, DTA was simultaneously supplemented by mass spectrometry (MS) of the evolved gases and vapours.

When the heating takes place in an inert atmosphere, the organic material undergoes diagenetic alteration consisting of a pyrolytic degradation (cracking) which occurs simultaneously with condensation. Thermodynamically, the thermal alteration of amines
should lead to the formation of methane, ammonia and graphite. In reality, the residual organic matter tends to be transformed into charcoal. In order to study these changes, the thermal evolution of BA, CH₄, NH₃ and H₂ were followed by MS. In an IR thermospectrometry study on the adsorption of BA by sepiolite and palygorskite, it was shown that most of the amine is adsorbed by forming hydrogen bonds with zeolitic water. Part of the amine is adsorbed by forming hydrogen bonds with bound water and only a small fraction of the adsorbed amine is protonated (Shuali et al., 1989).

EXPERIMENTAL

Materials

Sepiolite from Vallecas, Spain, and palygorskite from Quincy, Florida, were supplied by Ward’s Natural Science Establishment. The clays were ground manually and sieved to <37 μm (400 mesh). The external specific surface area as determined with N₂ by the BET method (measured on a Quanta Chrome instrument at 77 K, after 1 h degassing at 450 K) was 269.0 ± 21.9 and 158.3 ± 8.3 m²/g for sepiolite and palygorskite, respectively. Mineralogical analysis by X-ray diffraction (XRD) showed that both samples contained traces of quartz, and a very small endothermic peak at 570°C due to quartz was observed on the DTA curve of palygorskite but not on that of sepiolite. From XRD of the palygorskite it seems that this sample contained trace amounts of montmorillonite, kaolinite and calcite, but these minerals were not detected in the sepiolite sample. Carbon analysis of the natural clays showed that palygorskite contained 0.3% C whereas the C content of sepiolite was below the detection limit of the instrument. Very small amounts of CO₂ were evolved when the thermal analysis of natural sepiolite or palygorskite was carried out in air, due to the presence of organic matter. The ion current signal for the most intense evolved gas analysis-mass spectrometry (EGA-MS) peak of CO₂ for both minerals was 4.5 x 10⁻¹² amp. In the presence of N₂, the ion current signals for the most intense EGA-MS peaks were 2.5 x 10⁻¹² and 4 x 10⁻¹² amp for sepiolite and palygorskite, respectively, these peaks probably being due to the presence of trace amounts of carbonate minerals. In both cases these peaks are very small and do not interfere with the peaks of CO₂ evolved during the thermal analysis of BA-treated clays. In agreement with XRD and the C analysis, the CO₂ evolution peaks are much smaller on the EGA curves of sepiolite than on those of palygorskite.

BA was purchased from Aldrich and was redistilled before use according to a method described by Perrin et al. (1966).

Methods

Adsorption of BA on the clay minerals was carried out from the liquid phase. Samples of 0.5 g were suspended in 3 ml of the base and subsequently sealed in ampules under N₂. The ampules containing the clay and the amine were shaken twice a day, and after 1 month the excess liquid was separated from the clay by suction and the clay was dried under vacuum (pressure of 0.01 Torr) at 50°C, for 6 h. The samples were stored in dark bottles permeable to the atmosphere. Determination of the adsorbed amine was carried out by total C analysis using a Perkin Elmer 240c C,H,N Analyser.

Thermoanalytical experiments were carried out on a Mettler TA-1 thermal analysis instrument coupled with a Baltzers’ quadrupole mass spectrometer using the method
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described by Muller-Vonmoos et al. (1977). Samples of 50 mg were used for each run, and parallel analyses were carried out either under a flow of air or N2 (33 cm³/min) with a heating rate of 10°C/min. Calcined kaolinite was used as the reference material. Gas evolution curves of the following masses were recorded: H₂O, 17 and 18; CO₂, 22 and 44; CH₄, 15 and 16; NH₃, 16 and 17; H₂, 2; and BA, 30 (Heller & Milne, 1978). Total pressure in the mass spectrometer unit during all the experiments was 4 x 10⁻⁶ mbar. The ion currents produced by the various masses are indicated in the legends of the Figures for the most intense peak. No quantitative calibration of the system for the different masses was carried out and consequently the EGA curves should be considered from a qualitative point of view only.

A few mass spectrometric measurements of evolved gases were carried out with a VG Quadrupoles Ltd. Micromass PC. For this purpose 50 mg of BA-treated sepiolite and palygorskite were heated at 10°C/min in a glass tube to 500°C under a flow of He. The composition of the evolved gases was determined by using the library of spectrograms in the computer memory of the instrument.

RESULTS AND DISCUSSION

Carbon analysis

The %C adsorbed by sepiolite and palygorskite was 5.4 and 3.0, and the calculated amounts of adsorbed amines were 112.5 and 62.5 mmol/100 g clay, respectively. It is obvious that the amount of BA sorbed by sepiolite is almost twice than that sorbed by palygorskite.

Thermal analysis—sepiolite

The DTA curve of untreated sepiolite displays four endothermic reactions with the following peak maxima: (1) 135°C; (2) 315 and 360°C (two small peaks) in air or 345°C in N₂; (3) 515°C; and (4) 825°C followed by a sharp exothermic peak at 830°C (Fig. 1). The endothermic peaks are accompanied by weight loss and evolution of water.

The DTA curves obtained for sepiolite treated with BA under flow of air or N₂ are presented in Figs. 2A and 3A, respectively. They can be divided into three regions: (1) up to 225°C, both curves showing the endothermic dehydration reaction; (2) from 225–800°C the curve recorded in air differs from that under N₂, oxidation reactions leading to the development of broad exothermic peaks in air, whereas in N₂, endothermic peaks are recorded; (3) above 800°C the thermal recrystallization of the dehydroxylated clay (meta-sepiolite) leads to a significant exothermic peak. The gas evolution curves of the amine-treated sepiolite are shown in Figs. 2B and 3B. Thermal weight losses derived from the TG curves are listed in Table 1.

As water is evolved, in part due to the oxidation of organic matter and in part due to the dehydration and dehydroxylation of the clay, conclusions on the combination of hydrogen atoms originating from BA with oxygen should be obtained by subtracting the H₂O evolution curve of the amine-treated sepiolite recorded under N₂ from that recorded in air. The difference between the two curves may give the required information on the oxidation of organic matter. The water evolution curve obtained under N₂ is called the 'inorganic water evolution curve', whereas the evolution curve obtained in air is called the 'total water evolution curve'. The calculated curve is called the 'organic water evolution curve', and is shown in Fig. 2C.
The gas evolution curve of mass 16 is characteristic of both NH$_3$ and CH$_4$. On the other hand, the curve of mass 15 is characteristic, mainly, of CH$_4$. The difference between the two curves may give the desired information on the evolution of NH$_3$ and is called the ‘ammonia evolution curve’ (Fig. 3C). Figs. 2C and 3C should be considered qualitative rather than quantitative.

(a) The first region of the DTA curve. The thermal analysis of BA-treated sepiolite (Fig. 2A) shows a weight loss starting at 70°C with DTG and DTA peaks at 120°C, lower than the peak temperature recorded on the curves of the untreated sepiolite (Fig. 1A). EGA shows that the endothermic peak is associated with the evolution of BA (175°C) and NH$_3$ (125°C) in addition to zeolitic and interparticle H$_2$O (135°C).

The most significant difference between the DTA curves of the untreated and treated sepiolite, recorded either in air or in N$_2$, is the relative intensity of the endothermic peak. In the untreated clay this peak is the most intense among the four endothermic peaks, and according to the TG curve, is associated with a weight loss of 11.4%. The weight loss of the amine-treated sepiolite in this region is significantly smaller by ~60%, indicating that a great part of the zeolitic and interparticle water was substituted by the amine. A small peak appears at 125°C in the CO$_2$ evolution curve resulting from the desorption of CO$_2$ which was adsorbed by the amine-treated clay from the atmosphere prior to the DTA study. Similar peaks are obtained with all the BA-treated samples studied, either in air or under N$_2$. 
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Fig. 2. DTA and DTG curves (A), and EGA curve (B) obtained by thermal analysis of BA-treated sepiolite, under flow of air. Ion current signal of gas in the most intense EGA-MS peak is $54 \times 10^{-12}$ amp for $M/Z = 18$ (at 140°C), and $26 \times 10^{-12}$ amp for $M/Z = 44$. C is a calculated 'organic water evolution' curve (see text).

Fig. 3. DTA and DTG curves (A) and EGA curve (B) obtained by thermal analysis of BA-treated sepiolite, under flow of N₂. Ion current signal of gas in the most intense EGA-MS peak is $17.5 \times 10^{-12}$ amp for $M/Z = 2$; $3.6 \times 10^{-12}$ amp for $M/Z = 15$; $8.4 \times 10^{-12}$ amp for $M/Z = 16$; $50 \times 10^{-12}$ amp for $M/Z = 18$; $1.0 \times 10^{-12}$ amp for $M/Z = 30$; $4.1 \times 10^{-12}$ amp for $M/Z = 44$. C is a calculated 'ammonia evolution' curve (see text).

(b) The second region of the DTA curve. In air (Fig. 2A) this region represents the oxidation of most of the organic substance as confirmed by the evolution of the CO₂. The DTA curve shows several exothermic peaks, characteristic of the oxidation of the organic material. These peaks are not observed when the DTA was performed under a flow of N₂ (Fig. 3A). In N₂ the second region represents desorption, pyrolysis and charcoal formation which are identified by the evolution of BA, CH₄, NH₃ and H₂.

The organic water evolution curve (Fig. 2C) shows one peak at 355°C with a shoulder at 330°C. The CO₂ evolution curve of BA-treated sepiolite (Fig. 2B) shows that the oxidation of the amine and formation of CO₂ commences at ~ 250°C, reaching a maximum rate at 360°C and staying at the same level up to 720°C. Only three small peaks are observed above this plateau. This is in agreement with the thermal weight loss (Table 1) which reaches a constant rate during the heating. The CO₂ evolution decreases above 720°C and at the same time the H₂O evolution curve shows the development of another small peak at 750°C.

The profile of the DTA curve seems to be determined by the oxidation of both C and H. For the BA-treated clay, due to the fact that the organic molecule has a high H to C ratio, the DTA curve has a profile similar to that of the organic water evolution curve (Fig. 2C). However, the principal exothermic peak on the DTA curve (360°C) and the following
shoulders (600 and 725°C) are at the same temperatures as the corresponding features in the organic water evolution curve.

The DTA curve (Fig. 3A) recorded under N₂ shows three small broad endothermic peaks. The first endothermic peak extends from 250 to 350°C with a maximum at 310°C, and is associated with peaks in the BA-, H₂O- and NH₃-evolution curves at 275, 310 and 320°C, respectively. The DTG curve (Fig. 3A) shows a diffuse peak with a broad maximum extending from 275 to 310°C. It should be mentioned that the untreated sepiolite showed H₂O evolution peak at 370°C due to desorption of part of the bound water (Martin-Vivaldi & Fenoll Hach-Ali, 1970; Singer, 1989). The shift of this peak to 310°C suggests the penetration of the amine into the pores of the clay. The size of this peak recorded in N₂, where all the evolved water originates from the clay, is much smaller than that recorded in air where water originates in part from the clay and in part from the oxidation of BA. This peak is very small relative to its size on the curves of untreated sepiolite indicating that some bound water has been replaced by the amine.

Two broad endothermic peaks (extending from 430 to 530°C, and 530 to 640°C) appear on the DTA curve recorded under N₂, associated with the evolution of H₂O (maxima at 475 and 540°C), BA (maximum at 525°C), CH₄ (575°C), NH₃ (at 550°C) and H₂ (at 525°C). It should be mentioned that the H₂O-evolution curve of the untreated sepiolite shows only one peak at 515°C (Fig. 1B) which represents the final stage of the bound water evolution and the beginning of dehydroxylation of the clay (Martin-Vivaldi & Fenoll Hach-Ali, 1970; Singer, 1989). In the BA-treated sepiolite this dehydration stage splits into two peaks, the first peak associated mainly with the final stage of bound water evolution, and the second with dehydroxylation. The splitting of the dehydration peak and the rise in the temperature of the dehydroxylation peak prove that the organic matter is present inside the pores.

Thermal analysis combined with mass spectrometry was previously used for the study of the adsorption of BA by zeolites (e.g., Jacobs & Uytterhoven, 1972; Ghosh & Curthoys, 1984; Ghosh et al., 1985; Parker et al., 1985) and by silica-alumina (Guil et al., 1984; Takahashi et al., 1976). These studies showed that when these solids sorbed with BA were heated, the adsorbed molecule decomposed into ammonia and butene by the Hofmann degradation:

\[
\text{CH}_3\text{–CH}_2\text{–CH}_2\text{–NH}_3 + \text{O–Zeol.} \rightarrow \text{NH}_3 + \text{CH}_3\text{–CH}_2\text{–CH} = \text{CH}_2 + \text{HO–Zeol.}
\]

The degradation is followed by isomerization and polymerization which is accompanied by the evolution of CH₄:

\[
\begin{align*}
\text{C}_4\text{H}_8 & \xrightarrow{\text{cracking & isomerization}} \text{alkanes and alkenes (C}_3 \text{ – C}_4) \\
& \text{polymerization} \rightarrow \text{CH}_4 \\
& \text{aromatics (e.g., toluene, xylene)}
\end{align*}
\]

Another parallel decomposition reaction occurs together with hydrolysis leading to the evolution of CO, CO₂ and propane:

\[
\begin{align*}
\text{CH}_3\text{–(CH}_2\text{)₃–NH}_3 + \text{Zeol.} & \rightarrow \text{NH}_3 \rightarrow \text{CH}_3\text{–(CH}_2\text{)₃–OZeol.} \\
\text{CH}_3\text{–(CH}_2\text{)₃–OZeol.} & \xrightarrow{\text{hydrolysis}} \text{C}_3\text{H}_8, \text{CO, CO}_2
\end{align*}
\]
TABLE 1. Thermal weight loss (%) at various stages of the thermal analysis of untreated and BA-treated sepiolite and palygorskite (data obtained from TG curves).

<table>
<thead>
<tr>
<th>Temp. range (°C)</th>
<th>Untreated (air)</th>
<th>BA-treated (air)</th>
<th>BA-treated (N₂)</th>
<th>Untreated (air)</th>
<th>BA-treated (air)</th>
<th>BA-treated (N₂)</th>
</tr>
</thead>
<tbody>
<tr>
<td>25-175</td>
<td>10.50</td>
<td>4.00</td>
<td>4.00</td>
<td>8.60</td>
<td>4.60</td>
<td>4.75</td>
</tr>
<tr>
<td>175-225</td>
<td>0.25</td>
<td>0.50</td>
<td>1.20</td>
<td>0.45</td>
<td>0.35</td>
<td>0.45</td>
</tr>
<tr>
<td>225-250</td>
<td>0.05</td>
<td>0.40</td>
<td>0.60</td>
<td>0.35</td>
<td>0.45</td>
<td>0.50</td>
</tr>
<tr>
<td>250-300</td>
<td>0.60</td>
<td>0.60</td>
<td>1.40</td>
<td>1.20</td>
<td>0.70</td>
<td>0.95</td>
</tr>
<tr>
<td>300-350</td>
<td>1.00</td>
<td>1.00</td>
<td>1.45</td>
<td>0.80</td>
<td>1.10</td>
<td>1.00</td>
</tr>
<tr>
<td>350-400</td>
<td>0.50</td>
<td>1.10</td>
<td>2.85</td>
<td>0.70</td>
<td>1.20</td>
<td>1.75</td>
</tr>
<tr>
<td>400-450</td>
<td>0.60</td>
<td>1.00</td>
<td>2.40</td>
<td>0.60</td>
<td>0.80</td>
<td>0.40</td>
</tr>
<tr>
<td>450-500</td>
<td>0.80</td>
<td>1.20</td>
<td>0.60</td>
<td>0.30</td>
<td>1.20</td>
<td>1.00</td>
</tr>
<tr>
<td>500-550</td>
<td>0.40</td>
<td>1.00</td>
<td>0.40</td>
<td>0.25</td>
<td>0.80</td>
<td>0.40</td>
</tr>
<tr>
<td>550-600</td>
<td>0.15</td>
<td>1.10</td>
<td>0.60</td>
<td>0.30</td>
<td>0.40</td>
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</tr>
<tr>
<td>600-650</td>
<td>0.20</td>
<td>0.80</td>
<td>0.45</td>
<td>0.40</td>
<td>0.10</td>
<td>0.20</td>
</tr>
<tr>
<td>650-700</td>
<td>0.20</td>
<td>0.90</td>
<td>0.30</td>
<td>0.40</td>
<td>0.10</td>
<td>0.15</td>
</tr>
<tr>
<td>700-750</td>
<td>0.60</td>
<td>0.90</td>
<td>0.30</td>
<td>0.20</td>
<td>0.10</td>
<td>0.25</td>
</tr>
<tr>
<td>750-800</td>
<td>1.00</td>
<td>0.85</td>
<td>1.10</td>
<td>1.75</td>
<td>1.50</td>
<td>1.70</td>
</tr>
<tr>
<td>Total weight loss</td>
<td>17.85</td>
<td>17.05</td>
<td>20.60</td>
<td>17.80</td>
<td>15.30</td>
<td>17.10</td>
</tr>
</tbody>
</table>

Similar degradations should be responsible for the appearance of NH₃ together with BA at 320 and 550°C. The NH₃ evolution peak is very small at 275°C but is relatively intense at 550°C, indicating that the degradation of BA takes place mainly with the high-temperature desorption of the amine. The evolution of CH₄ at 575°C indicates that the degradation stage is followed by polymerization and the formation of aromatic species. The evolution curve of M/Z = 44 shows very small peaks at temperatures similar to those of H₂O evolution curves (475 and 530°C). It is possible that this curve represents CO₂ and/or C₃H₈ which are formed during degradation of BA, associated with hydrolysis.

The adsorption of BA by sepiolite differs from the adsorption by zeolites in that only a very small fraction of the adsorbed BA is protonated (Shuali et al., 1989). Consequently, only a very small fraction of the adsorbed organic matter is degraded, as can be seen from the ion current signals for M/Z = 15, 16, and 44, indicated in the legends to Fig. 3.

The evolved gases under helium flow were H₂O (from the beginning of the thermal treatment), CO₂ (from 200°C), very small amounts of propane, propanol, ethanol, acetic acid (from 350°C), and traces of butene (from 450°C).

(c) The third region of the DTA curve. The DTA curves of the amine-treated sepiolite, either in air or under N₂, show sharp endothermic and exothermic peaks of dehydroxylation and recrystallization of the sepiolite at 815–830°C and 830–850°C, respectively. This stage is associated with a weight loss similar to that of the untreated clay (Table 1).

The gas evolution curves recorded under N₂ show that in the inert atmosphere this stage is associated with the evolution of H₂O, CO₂ and/or C₃H₈, NH₃ and H₂. This is not surprising
for H₂O which is also evolved during the heating of the untreated sepiolite. The peak in the evolution curve of M/Z = 44 is very small and must indicate that very small amounts of CO₂ and/or C₃H₆ (which were obtained between 400 and 600°C) were trapped and are released at this stage during recrystallization of the amorphous meta-sepiolite phase. The same interpretation applies to the appearance of the small NH₃ peak.

It has been shown that D₂O was trapped by sepiolite during the first stage of the dehydroxylation and released during the recrystallization stage (Shuali et al., 1988). Trapping should be the result of restructuring of the clay silicate TOT units by breaking of different Si–O, Mg–O and Al–O bonds. In the new disoriented structural units of the meta-sepiolite, which is formed during the first dehydroxylation stage, some of the H₂O, CO₂ and NH₃ molecules can interact with newly formed broken bonds. As the new silicate phase grows, these molecules are trapped inside the amorphous phase. At higher temperatures, the recrystallization of meta-sepiolite occurs and Si, Mg, Al and O atoms diffuse from the poorly ordered species to the uniformly ordered silicate units. At this stage the trapped H₂O, CO₂ and NH₃ are evolved. The ion current signal of the evolved CO₂ can give information on the amount of gas which was trapped during the dehydroxylation, and in the thermal analysis of the untreated sepiolite it was 2.5 × 10⁻¹² amp either in air or under N₂. This small amount originates from the thermal decomposition of the trace carbonate minerals in the sample. In the thermal analysis of BA-treated sepiolite it was 4.1 × 10⁻¹² and 10 × 10⁻¹² amp when recorded under N₂ or air, respectively. This is an indication that in the presence of oxygen, where CO₂ is the principal product of the oxidation reaction, considerable amounts of CO₂ are trapped. Evolution of H₂ results from the condensation of organic matter and the formation of residual char. The H₂ evolution curve shows a very strong peak, relative to the other peaks, which indicates that the charcoal formation is very intense.

Thermal analysis—palygorskite

The DTA curve of the untreated palygorskite shows three endothermic reactions with peak maxima at: (1) 150°C; (2) 265 and 285°C in air and N₂, respectively; (3) 465°C, accompanied by weight losses due to the evolution of water (Fig. 4).

The DTA curve of the palygorskite treated with BA, under a flow of air or N₂ (Figs. 5A and 6A), can be divided into three regions: (1) up to 225°C, the curves showing endothermic dehydration reactions; (2) from 225–750°C oxidation reactions in the presence of air lead to the appearance of broad exothermic peaks, whereas in N₂, endothermic peaks are recorded; (3) above 750°C the thermal recrystallization of the dehydroxylated mineral leads to the appearance of a weak exothermic peak. The ‘total’ and ‘organic H₂O’ evolution curves as well as the CO₂, CH₄, NH₃ and H₂ evolution curves are shown in Figs. 5B, 5C, 6B and 6C. Thermal weight loss values determined from the TG curves are listed in Table 1.

(a) The first region of the DTA curve. The DTA curves of BA-treated palygorskite in air and N₂ show one endothermic peak at 135°C which characterizes the evolution of zeolitic and interparticle water. This temperature is lower than that recorded for the untreated clay. In addition to the evolution of H₂O, EGA shows that the reactions occurring in the first region include the evolution of BA (170°C), NH₃ (150°C) and very small amounts of H₂.

Table 1 shows that from room temperature to 225°C, the weight loss of BA-treated palygorskite is ~40% less than the weight loss of untreated palygorskite, indicating that some of the interparticle and zeolitic water was substituted by the adsorbed amine. The weight loss of water should be smaller than that in Table 1 because BA, NH₃ and very small amounts of
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H₂ are also evolved during this stage. More water is substituted by BA in sepiolite than in palygorskite. This is in agreement with the higher adsorption of amines by sepiolite.

(b) The second region of the DTA curve. The DTA curve recorded under air (Fig. 5A) shows an exothermic peak at 390°C and two shoulders at 280 and 590°C. The ‘total H₂O’ evolution curve (Fig. 5B) shows two peaks in this region located at 295 and 530°C. From the location of the first peak (295°C) it seems plausible to relate it, at least in part, to the loss of bound water. This is supported by the fact that a peak also occurs at 270°C in the H₂O evolution curve recorded under the stream of N₂ (‘inorganic water’ evolution curve, Fig. 6B), but this peak is very weak in the inert atmosphere indicating that in an air atmosphere it results mainly from the oxidation of BA hydrogen. The DTG curve of the untreated palygorskite shows that the evolution of the first part of the bound water takes place between 250 and 350°C. The BA-treated palygorskite lost 1.8% at this stage, which is only slightly less than the 2% lost by the untreated clay in this temperature range. In reality the weight loss of H₂O is less than 1.8% because BA, NH₃ and CO₂ are also evolved. The difference between the untreated and BA-treated palygorskite indicates that some of the bound water was replaced by the amine or evolved at higher temperatures. This may serve as evidence that the adsorbed amine is located in the pores of palygorskite.

The CO₂ evolution from BA-treated palygorskite (Fig. 5B) starts at 240°C as a result of the oxidation of the BA carbon. The rate of C oxidation increases rapidly with the rise in temperature up to 390°C. From this point the CO₂ evolution curve appears as a plateau up to 585°C.
Correlation of the DTA curve with the 'organic H$_2$O' (Fig. 5C) and CO$_2$ evolution curves reveals that the profile of the DTA curve is determined by the rate of combination of H and C with O from air. The locations of the two exothermic peaks at 390 and 590°C (Fig. 5A) represent the broad maxima in the CO$_2$ evolution curve at 390–585°C. The intensity of the 390°C peak relative to the 590°C peak (Fig. 5A) is due to the exothermic combination of the BA-hydrogen with O from air which shows a maximum at 290°C in the 'organic H$_2$O' evolution curve (Fig. 5C).

When the thermal analysis is carried out under N$_2$, the DTA curve shows two extremely broad peaks at 400–525°C and 525–725°C (Fig. 6A); these peaks are very weak and diffuse and it was not possible to define their maxima. The DTG curve shows a broad peak extending between 370 and 725°C.

EGA (Fig. 6B) shows the release of CH$_4$ (maximum at 570°C) and NH$_3$ (maxima at 530 and 610°C), indicating that small fractions of BA are degraded at this stage. The ion current signals are much weaker than those obtained for sepiolite (see legends to Fig. 6). IR spectra showed that as in sepiolite, a small fraction of the adsorbed BA is protonated and is
susceptible to degradation leading to the evolution of CO\textsubscript{2} and/or C\textsubscript{3}H\textsubscript{8}. Two very small peaks are observed in the M/Z = 44 evolution curve at 425 and 540°C. As with sepiolite, it is assumed that small amounts of BA undergo hydrolytic degradation. The evolution of H\textsubscript{2} (maxima at 480 and 650°C) and the intensity of the ion current signal indicates that as for sepiolite, condensation exceeds the degradation reactions. H\textsubscript{2}O was also evolved giving three peaks at 270 (very small), 440 and 540°C. It should be mentioned that the H\textsubscript{2}O evolution curve of the untreated palygorskite (Fig. 4B) shows only one peak at 475°C which represents the final stage of the bound water evolution together with the dehydroxylation of the clay. In the BA-treated palygorskite (Fig. 6B) this stage splits into two peaks (440 and 540°C). The dehydroxylation of the clay (Fig. 4) which occurs at 475°C in the absence of organic matter, is therefore shifted to higher temperatures in the BA-treated clay (Figs. 5B and 6B). Such a shift may be the consequence of the penetration of the organic molecules into the pores, preventing the free tilting of the mineral during the irreversible dehydration.

The evolved gases under helium flow were H\textsubscript{2}O (from the beginning of the thermal treatment), CO\textsubscript{2} (from 400°C), very small amounts of propane, propanol and ethanol, and traces of butene (from 500°C).

(c) The third region of the DTA curve. No water was evolved during the third stage when the thermal analysis was carried out either in air or N\textsubscript{2}, and only traces of CO\textsubscript{2} were detected in this region. This is in contrast to the considerable amounts of these two gases evolved during the third region of BA-treated sepiolite.

The evolution of H\textsubscript{2} at temperatures above 750°C is very intense indicating that thermal condensation of the residual organic matter is the principal reaction at this stage. The H\textsubscript{2} evolution curve shows a maximum at 820°C. The DTA curve recorded in N\textsubscript{2} shows a very small peak at 810°C, followed by a very small exothermic peak at 835°C, both peaks being associated with the recrystallization of the dehydroxylated meta-palygorskite. The peaks are at higher temperatures on the DTA curves of both the untreated palygorskite (Fig. 4A) and the BA-treated palygorskite recorded in air (Fig. 5A). It is therefore concluded that the residual char formed during the thermal analysis enhances the recrystallization reaction of the inorganic material.

**COMPARISON BETWEEN BA-TREATED SEPIOLITE AND PALYGORSKITE**

1. The profiles of the CO\textsubscript{2}- and the 'organic H\textsubscript{2}O'-evolution curves are useful for obtaining information on the oxidation reactions which occur during the thermal analysis of BA-treated clay in air. The CO\textsubscript{2} evolution curve shows a plateau between 360 and 720°C for sepiolite, and between 390 and 580°C for palygorskite, both treated with BA. The 'organic H\textsubscript{2}O' evolution curve shows one continuous stage of BA-hydrogen oxidation with a maximum rate at 355°C for sepiolite and 290°C for palygorskite. To conclude, H precedes C in combining with O from the air.

2. The profiles of the exothermic region on the DTA curves recorded in air are governed by the oxidation of both principal elements of the organic compounds—C and H. The temperatures of the most intense exothermic peaks on the DTA curves are determined by the rate of C oxidation, but the shape of the curves and temperatures of exothermic shoulders are determined by the rate of the interaction between H and O. This is not surprising if one takes into consideration the bonding energies of C–C, C–H, O–H and C=O which are 348, 416, 467, and 732 kJmole\textsuperscript{-1}, respectively.
3. The temperature of the principal exothermic peak is lower for sepiolite than for palygorskite. The fact that the peak temperatures are dependent on the mineral type may serve as evidence for the existence of interactions between BA and the clays.

4. TG and DTA curves show that the amounts of zeolitic and bound water become very small due to the penetration of the amine into the pores as a result of the adsorption of the organic molecules by both clays. Adsorbed molecules are held by the clays up to temperatures much above the boiling point of BA.

5. In the presence of BA, the dehydroxylation of both clays is shifted to higher temperatures compared to the untreated clays, possibly due to the presence of the organic molecule inside the pores. The penetration of BA molecules into the pores requires some flexibility of the silicate planes, and such flexibility in organo-montmorillonites was observed by Suito et al. (1969) using electron microscopy. A similar flexibility may occur in sepiolite and palygorskite. Rautureau & Mifsud (1977) and Rautureau et al. (1979) showed by electron microscopy that some of the pores in sepiolite and palygorskite have dimensions larger than previously reported; it is possible that similar pores are the location of the adsorbed BA molecules.

6. The evolution curves of NH$_3$ and CH$_4$ give information on the thermal pyrolysis of the amine in an inert atmosphere. NH$_3$ evolution maxima occur in both minerals simultaneously with the evolution of H$_2$O, the most intense peaks occurring together with the dehydroxylation of these minerals. Both minerals show intense NH$_3$ peaks at 530 and 610°C and a maximum CH$_4$ evolution at 570°C. Evolution of H$_2$ gives information on thermal condensation and charcoal formation. With sepiolite, considerable condensation occurs at 525°C together with the evolution of BA, and the principal evolution of H$_2$ occurs at 850°C. With palygorskite, condensation is observed at 480, 650 and 825°C, the condensation at high temperatures being associated with the recrystallization of the inorganic phase.

7. CO$_2$ and NH$_3$ formed during the thermal analysis of BA-treated sepiolite, either in air or under N$_2$, are trapped by the meta-phase and are evolved during the recrystallization. This is specific for sepiolite and is not observed for palygorskite.

REFERENCES

Thermal analysis of sepiolite and palygorskite treated with butylamine


