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Reversible folding in sepiolite: study by thermal and textural analysis

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Abstract

The structural changes of sepiolite under thermal treatment, and their reversibility, have been examined by thermogravimetry. These changes have been related to the textural changes, determined by N_2 adsorption under similar conditions. The folding of this material starts at 390°C, from this temperature the microporosity of the material disappears. This folding is reversible, becoming permanent at 570°C. From 390 to 570°C the surface area remains stable, corresponding to the external surface area of the mineral.

Keywords: Sepiolite; Structure folding; Textural changes; Thermal analysis

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1. Introduction

Sepiolite is a fibrous silicate, ideal formula $[Si_{12}Mg_8O_{30}(OH)_4](H_2O)_4 \cdot 8H_2O$ according to the model of Brauner–Preisinger [1], whose structure is composed of two bands of silica tetrahedrons linked by magnesium ions in octahedral coordination. Due to the alternating position of the apical oxygens which are not shared in the tetrahedrons, there are channels between the bands (37×106 nm^2), oriented longitudinally with the fibers. There is very little replacement of either magnesium or silicon ions. In the unit cell water molecules are bound to octahedral cations and there is also water bound to exchange cations as zeolitic water.

When the sepiolite is heated, it undergoes structural changes bound to the dehydration process which takes place during the heating. Three steps can be distinguished in the dehydration process [2]:

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(1) the loss of surface-adsorbed and zeolitic water;

(2) loss of the first molecules of water coordinated to the octahedral sheet, which produces the folding of the structure; and

(3) loss of the rest of the coordinated water, and dehydroxylation of the tetrahedral sheet.

In the heating process, when a certain temperature is reached, the folding which started at the second step becomes permanent, causing the formation of a new structure.

Folding of palygorskite (a silicate with a similar structure) has been identified and studied by us using the TG technique combined with N_2 adsorption [3]. The folding of the sepiolite and palygorskite has been studied by several authors by IR [2, 4, 5], microcalorimetry [6], N_2 adsorption [7–9] and electron microscopy [10].

The aim of this research is to study, by the techniques TG and adsorption isotherms of N_2, respectively, the structural and textural changes caused by thermal treatment of the sepiolite.

In order to prove such changes the following procedure was applied:

(1) first, the temperatures at which there is mass loss were verified;

(2) after verifying these temperatures two sample sets, A and B, were taken.

The samples in set A were rehydrated after being treated thermally.

The samples in set B were not rehydrated after the heating process.

Thermal analysis and N_2 adsorption isotherms of every sample were carried out in order to study the changes mentioned above and their relationship to the processes of reversibility or irreversibility.

2. Experimental

2.1. Starting material

The work was performed on Sepiolita Burrus, provided by Tolsa S.A. The mineralogical composition obtained by X-ray diffraction showed a sepiolite content higher than 80%, and quartz, calcite, brucite and feldspar as main impurities. The chemical composition in mass%, (water and carbon dioxide from calcite present as impurity are excluded) is shown in Table 1.

Table 1
Chemical composition of sepiolite in mass%

Component	Amount	Component	Amount
SiO_2	51.97	CaO	5.8
MgO	9.63	Na_2O	1.38
Al_2O_3	4.82	K_2O	2.26
Fe_2O_3	1.16	TiO_2	0.35

2.2. Apparatus and methods

The thermal analysis was performed on a Setaram TG–DSC-111 apparatus. The heating rate was 5°C min^{-1} under a dynamic air-flow.

Thermal analysis of the starting material was carried out to determine the temperatures at which the losses of water corresponding to the three dehydration stages occur.

The thermal treatments to which the two sets of samples were submitted are as follows:

Set A: three samples were oven-heated at 210, 390 and 570°C respectively for 2 h. They were then kept in a water-saturated atmosphere for two weeks, to enable their rehydration. These samples were called A-210, A-390 and A-570, the number corresponding to the temperature of heating.

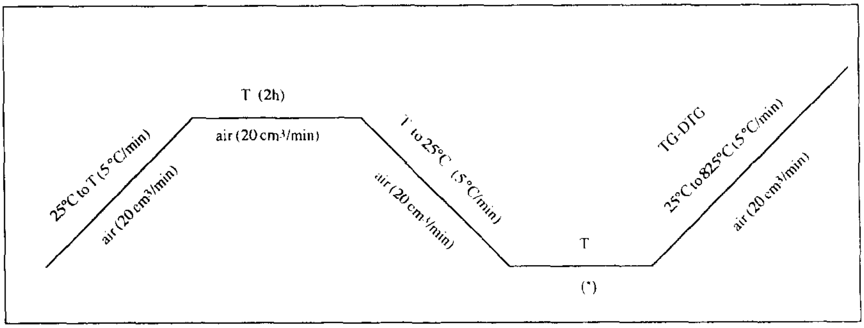
Set B: three samples were heated in the thermobalance at the three mentioned temperatures, 210, 390 and 570°C, respectively, and maintained in situ at every temperature for 2 h. They were then left to cool under a flow of dry air and the thermal analysis was performed without rehydration of the samples. They were called B-210, B-390 and B-570. Fig. 1 shows the scheme of this treatment.

The textural characteristics were studied by means of N_2 adsorption isotherms at 77 K. A Micromeritics ASAP 2000 apparatus was used. The two sets of samples, A and B, were degasified at 125°C, prior to the performance of the isotherms. Specific surface area was determined by applying the BET equation to the isotherm [11]. Micropore volume (V_m) and external surface area (S_t) were deduced by Boer's t-plot method [12].

3. Results and discussion

The mass losses corresponding to the three dehydration steps, Fig. 2, are assigned as follows:

Up to 210°C the loss of surface water and the water bound to the exchange cations of the silicate, 8.06%, takes place.



T=210 or 390 or 570°C
(*)=Samples A are rehydrated; samples B are not rehydrated

Fig. 1. The different steps to which samples were submitted.

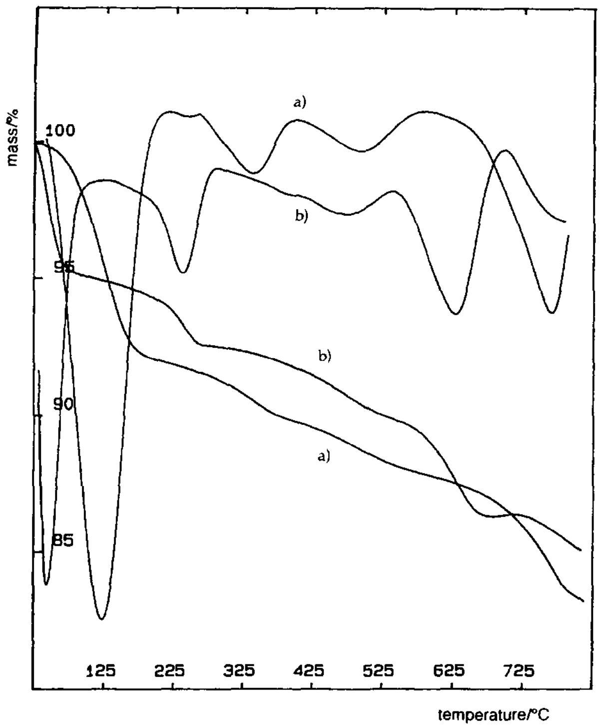


Fig. 2. TG and DTG curves of sepiolite: (a) in air; (b) under vacuum.

The second step, up to 390°C, 2.22%, corresponds to the first two water molecules coordinated to the octahedral sheet.

The loss of the rest of the coordinated water molecules, 2.11%, takes place at 570°C, overlapping with the dehydroxylation of the tetrahedral sheet.

A fourth step can be recognised at 750°C; this is attributed to calcite impurities, as was confirmed by acid treatment with HCl, after which this step disappeared. These impurities do not affect the results, because the changes in the sepiolite, which are examined here, take place at lower temperatures.

The above mentioned losses of water are related to the changes produced in the structure of the clay. The loss of the first two coordinated water molecules in the second step is accompanied by a reversible structural folding (Fig. 3); whereas in the next step, as the remaining coordinated water is lost, there is an irreversible folding.

When the TG is performed under vacuum conditions the signals corresponding to reversible steps are shifted to lower temperatures, while those of irreversible changes are not shifted (Fig. 2).

TG–DTG curves (Fig. 4) show the disappearance of the first step (surface and zeolitic water) in sample B-210, while in A-210, the rehydrated sample, this step has been recovered. The curve is then like that of the natural sepiolite.

Fig. 5 corresponds to samples A-390 and B-390. In the curve for B-390, only the third step is present. At this temperature the structure undergoes the folding caused by the

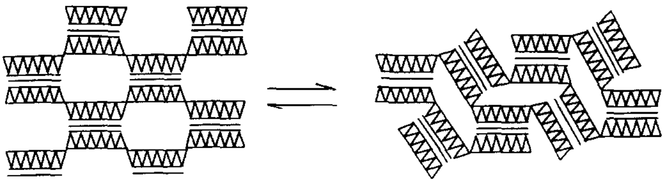


Fig. 3. Scheme showing the reversible structural folding of sepiolite.

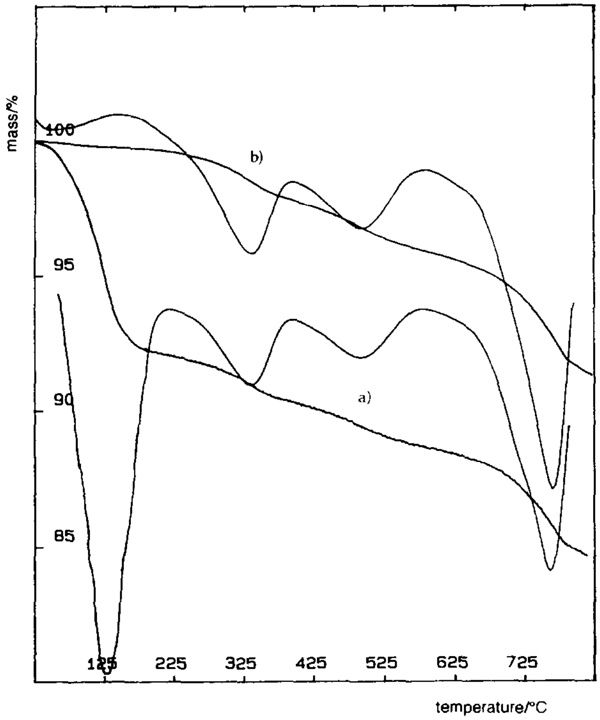


Fig. 4. TG and DTG curves of sepiolite treated at 210°C: (a) A-210; (b) B-210.

loss of the first two coordinated water molecules. In contrast, A-390 recovered steps one and two after being exposed to water-saturated atmospheric conditions. This means that the folding at this stage is reversible.

The TG–DTG curves corresponding to samples B-570 and A-570 are represented in Fig. 6. In B-570 curves none of the first three steps is present, which implies the complete dehydration and dehydroxylation of the sample after treatment at 570°C. Sample A-570 only shows a first step, corresponding to water adsorbed on the surface. This implies that the folding at 570°C is irreversible.

The textural changes in the sepiolite as a result of the thermal treatments are associated with variations in the micropore system and the surface area.

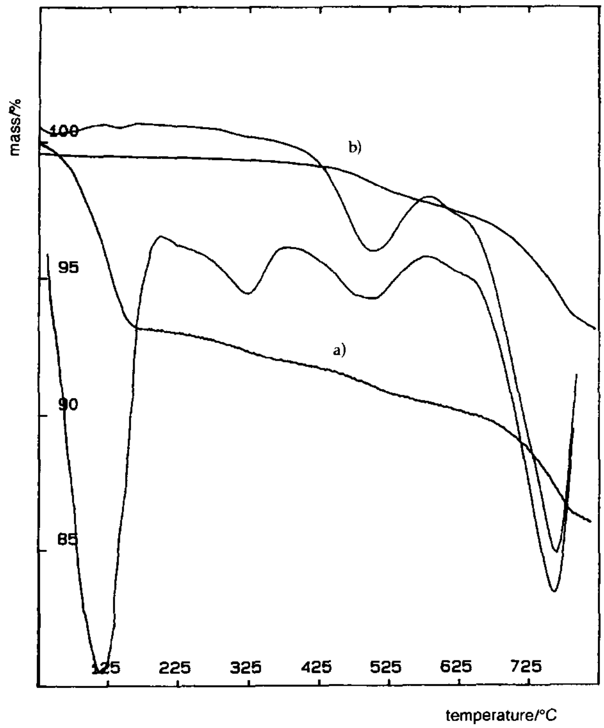


Fig. 5. TG and DTG curves of sepiolite treated at 390°C: (a) A-390; (b) B-390.

The specific surface area and micropore volume values after heating the samples at 210, 390 and 570°C are shown in Table 2. These changes can be explained by considering the structural modifications after several thermal treatments.

When the folding of the sepiolite structure has taken place, the surface area, (S_t), is only external surface, because the micropore system of the material has become inaccessible to the N_2 (Fig. 3). The data in Table 2 are very significant for corroboration of the results obtained through thermal analysis.

The samples treated up to 210°C, both non-rehydrated, B, and hydrated, A, show high values of S_{BET} and micropore volumes, V_m, because of the presence of the channels in the sepiolite structure. In the samples heated up to 390°C where, theoretically, the folding has taken place, the behaviour is different: in the non-rehydrated sample, B-390, the S_{BET} is notably reduced and the microporosity has disappeared, whereas in the rehydrated sample, A-390, similar values are maintained for the textural parameters as those at 210°C. This confirms that the folding at 390°C is reversible. Then by rehydration, the sample returns to its original structure. In both samples heated up to 570°C, the S_{BET} and V_m values are similar, which indicates that at this temperature the folding has become irreversible.

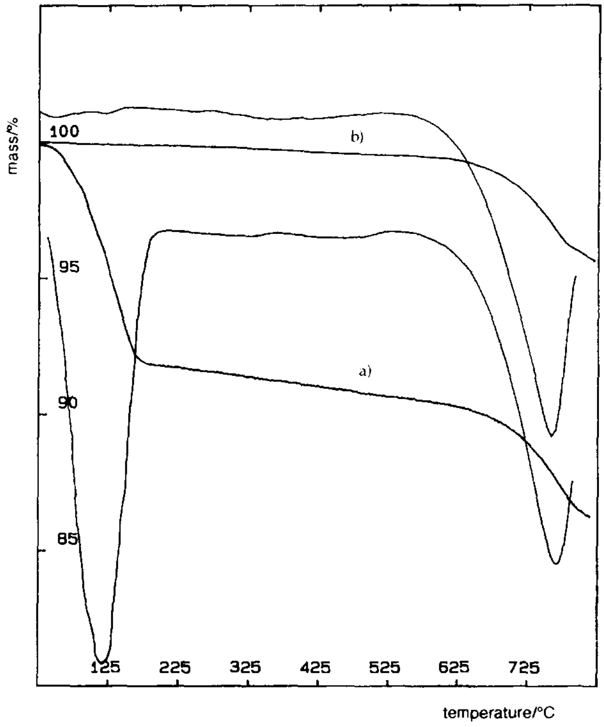


Fig. 6. TG and DTG curves of sepiolite treated at 570°C: (a) A-570; (b) B-570.

Table 2
Textural parameters of the samples

Samples	$S_{BET}/(m^2\,g^{-1})$	$S_t/(m^2\,g^{-1})$	$V_{micr}/(cm^3\,g^{-1})$
A-210	239	240	0.052
B-210	244	236	0.047
A-390	237	123	0.051
B-390	119	122	0.003
A-570	99	101	0.001
B-570	102	102	0.002

4. Conclusions

The TG–DTG analysis indicates that the folding of the sepiolite starts at 390°C under air flow, and at lower temperatures under vacuum. This folding is reversible. The folding becomes irreversible at 570°C.

The surface area of the samples decreases after thermal treatment which produce folding in the structure, because only external surface area can then be measured. The microporosity also disappeared because of the new structure. When the folding is reversible and the sample returns to the original structure, the textural parameters are also recovered.

Acknowledgement

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