

*Dedicated to Professor Lisa Heller-Kallai on the occasion of her 65<sup>th</sup> birthday*

## **DETERMINATION OF IMPURITY IN SEPIOLITE BY THERMAL ANALYSIS**

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### **Abstract**

The aim of this work was to demonstrate, by means of thermoanalytical methods (DTA, TG and DTG), that sepiolite from Vallecas (Spain) is mixed with another mineral which is difficult to determine by X-ray diffraction and chemical analysis in routine mineralogical studies.

The low temperature endothermic effect and weight loss shown by this material can be separated into two effects: one from sepiolite and the other from an accompanying mineral—identified as a magnesium smectite. The concentration of this latter mineral in the mixture attained up to 15%.

**Keywords:** DTA-TG-DTG, magnesium smectite, mineralogical characterization, sepiolite, X-ray

### **Introduction**

Sepiolite from Vallecas is a silicate used in many basic studies and technical applications [1,2]. Its use is based on its specific physico-chemical properties and high purity in this deposit. When a mineral previously considered highly pure is demonstrated to be mixed with another (although of similar nature), unclear behaviour may become explicable; or reconsideration can be given to an earlier hypothesis in which the lack of purity of the mineral had not been taken into account.

Mineralogical characterization can be performed using thermoanalytical techniques that depend basically on weight changes (TG and DTG) or energy changes (DTA and DSC) [3]. Sepiolite has been studied by these experimental techniques for some years [4, 5]. In the differential thermal analysis curves of sepiolite there is a low temperature endothermic effect around 150°C, which sometimes breaks down into two compounds in some samples. Less often, there

is a shoulder around 200°C. The TG curve shows a weight loss coinciding with these effects. According to Martín Vivaldi and Fenoll [4] this first effect is due to loss of free water adsorbed on the surface and from the channels of the mineral (zeolitic water). At intermediate temperature there are two endothermic effects around 300 and 500°C that correspond to two weight losses in the TG curve, representing 6.3% of the total sample. These two effects have been attributed to loss of the water bonded to the edge of the crystal [6].

At high temperature, there is an endothermic effect around 825°C, followed by an exothermic one at 850°C. The first represents dehydroxylation of the structure and a change in entropy due to structure collapse, and the second enstatite formation.

The aim of this work is to use thermoanalytical technique (DTA, TG and DSC) to demonstrate that the sepiolite from Vallecas is mixed with another mineral, whose nature is difficult to determine by other experimental techniques used in mineralogical studies, mainly XRD.

## Experimental

### *Material*

A natural sample of sepiolite from Vallecas (Spain) and a natural sample of magnesium-smectite, both supplied by Tolsa, S.A. (Sapin), were used.

### *Methods*

#### X-ray diffraction

X-ray powder diffraction patterns were obtained using a Siemens Kristalloflex D-500 diffractometer with Ni-filtered  $\text{CuK}\alpha$  radiation and a goniometer speed of  $1^\circ 2\Theta/\text{min}$ .

#### Scanning electron microscope

Fractured samples were coated with Au or C to make them conducting, and examined under a scanning electron microscope (ISI model SS-40).

#### Chemical analyses

Total chemical analysis were performed two ways: a) treating the sample with HF in a Teflon-lined pressure vessel and b) with an acid mixture containing  $\text{HNO}_3$ ,  $\text{HClO}_4$  and HF at atmospheric pressure, evaporating to dryness and

digesting with diluted HCl [7]. The concentration of the elements was determined using atomic absorption spectrometry. Na and K were determined by means of flame photometry. The cation exchange capacity was determined with ammonium acetate. Chemical analysis were also made by X-ray energy dispersive equipment (Kevex, model 8000) fitted to the scanning electron microscope.

### Thermal analyses

Differential thermal analysis (DTA) and thermogravimetric analysis (TG) were obtained simultaneously in static air with a thermal analyzer (Model PTC-10A Thermoflex, Rigaku Co., Tokyo, Japan) at various heating rates (from 5 to 12 deg·min<sup>-1</sup>). The natural material (as received) was crushed, lightly ground and sieved to 100 mesh before further study.

One part of the sample was kept in a desiccator at a relative humidity of 50%. Another part was left in equilibrium with the ambient conditions of the laboratory.

Samples were gently packed each time in a platinum holder. The amounts of sample used varied from 10 to 42 mg. When small samples were used, these were diluted with calcined alumina. Calcined alumina was used as reference material.

The apparatus was fitted with a data processing system for differential thermal analysis (model DPS-1, Rigaku Co., Tokyo, Japan). The processor was connected to an X-Y plotter.

### Specific surface areas (BET)

Specific surface areas were obtained with an automatic system (Model 2200 A Micromeritics, Norcross, GA, USA) using nitrogen gas as adsorbate at liquid nitrogen temperature.

## Results and discussion

The chemical composition of Vallecas sepiolite is listed in Table 1. It shows a high proportion of SiO<sub>2</sub> and MgO. The Al content is 1.70% and apparently is not part of the sepiolite fibres as deduced by energy dispersive X-ray. Other chemical components are in low concentrations. The cation-exchange capacity of this sample is 10 meq/100 g; the exchangeable cations are Mg<sup>2+</sup> and Ca<sup>2+</sup>. The N<sub>2</sub> surface area (BET method) is 290 m<sup>2</sup>/mg. These data indicate a nearly pure mineral.

The XRD results are shown in Fig. 1. The sepiolite contains few impurities and appears very crystalline – the diffraction pattern contains many clearly re-

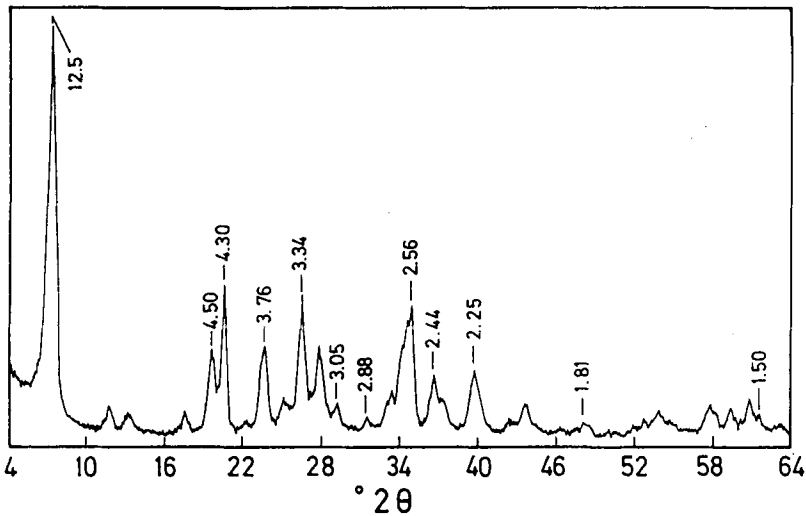


Fig. 1. XRD diagram of sepiolite from Vallecas (the numbers at the top of each peak are given in Angstrom)

solved peaks compared with other sepiolites studied. The diffraction patterns are very similar to those reported by other authors [8].

The X-ray diffractogram shows an intense reflection at 12,5 Å and others of medium intensity corresponding to 2.56, 3.34 and 4.30 Å reflections of sepiolite. These are followed by other characteristic reflections of the same mineral at 4.50, 3.76, 2.44, 2.25 Å, etc. Calcite (3.05 Å), dolomite (2.88 Å) and quartz (3.32, 1.81 and 1.50 Å) were also detected in low amounts. The 4.30 Å diffraction of sepiolite masks the 4.24 Å of quartz, whose presence has been confirmed by scanning electron microscopy and chemical analysis by X-ray energy dispersive techniques.

Table 1 Chemical analysis of Vallecas sepiolite

SiO <sub>2</sub>	62.05
Al <sub>2</sub> O <sub>3</sub>	1.70
Fe <sub>2</sub> O <sub>3</sub>	0.45
TiO <sub>2</sub>	0.09
CaO	0.49
MgO	23.80
Na <sub>2</sub> O	0.32
K <sub>2</sub> O	0.61
H <sub>2</sub> O <sup>+</sup>	10.90
Total	100.42

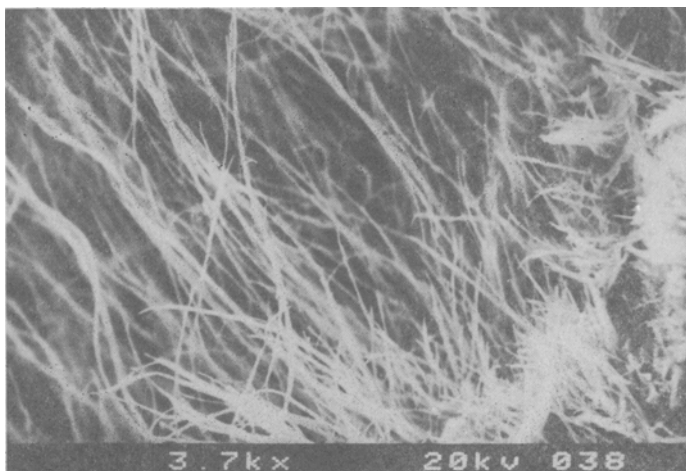


Fig. 2 SEM micrograph of sepiolite from Vallecas

Scanning electron microscopy (Fig. 2) shows that the Vallecas sepiolite fibres are usually curved.

Previous studies [9] have shown that the purity of Vallecas sepiolite ranges from 65 to 98%. The most important impurities detected by X-ray diffraction, IR spectroscopy, electron microscopy and chemical analysis are magnesium smectite, illite, calcite, quartz, cristobalite, feldspars, goethite, chlorite palygorskite and dolomite. The magnesium smectite is probably stevensite, according to Martínez de Vidales et al. [10] who have studied the occurrence of stevensite in similar nearby deposits in the Madrid Basin. For our study, a natural sample of high purity was chosen; only the X-ray study detected traces of calcite, dolomite and quartz.

Figure 3 shows differential thermal and thermogravimetric analysis curves obtained with a 42 mg sample of the sepiolite studied in this work, under ambient laboratory conditions. These curves have been chosen because the DTA curve shows only one effect at low temperature – probably one is being masked by another – and is similar to most DTA curves reported in the bibliography for this mineral. There is an endothermic effect at 118°C, with a weight loss of 14.60%. This effect is due to the loss of water adsorbed on the outer surfaces and from the channels. The form of the endothermic effect, the energy consumed (80.000  $\mu\text{v}\cdot\text{min}/\text{g}$ ) and the weight loss are variable, depending on the ambient conditions of the laboratory and the other factors such as those discussed later in this work. It must also be taken into account that although the sample is kept under equilibrium conditions before the study, even the most careful manipulation in making the thermal analysis may have an influence on

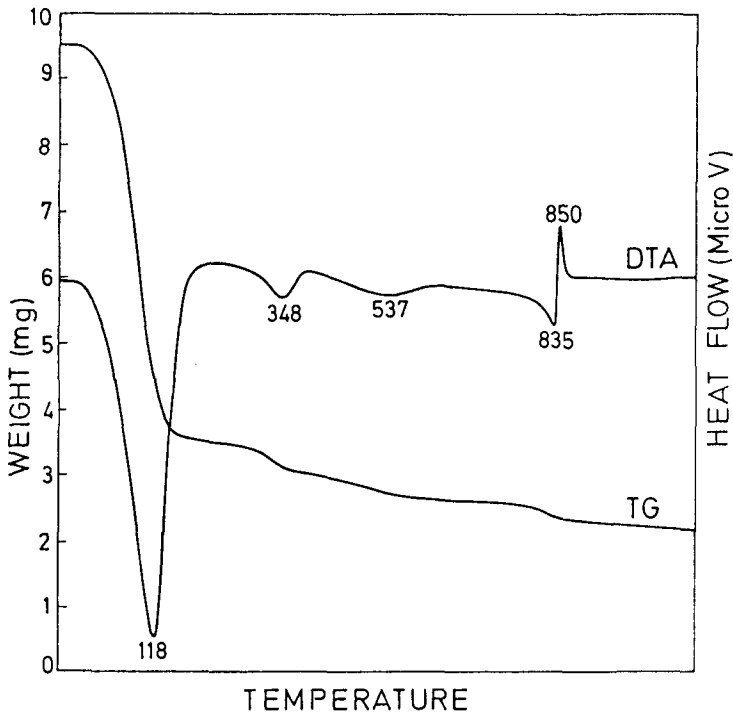


Fig. 3 DTA and TG of sepiolite from Vallecas

this effect. There are two endothermic effects at 348 and 537°C, [6] with weight losses of 3.30% and 2.92% respectively. That at 348°C is sharper and more intense, and is attributed to the loss of all the water coordinated to the outer edges of the crystal and half the water coordinated to the inner edges, producing structural transformations and breakdowns in the mineral. The other half of the water molecules coordinated to the inner edges is in collapsed channels, hindering its escape from the crystal [6].

In the high temperature zones, there is a very marked endothermic effect at 835°C, with a weight loss of 2.70%, due to the loss of octahedral OH and probably the loss of OH of some edge SiOH [11]. This effect is followed by a sharp, intense exothermic one at 850°C due to the formation of enstatite.

As mentioned above, some authors have found in the differential thermal analysis of sepiolite that the first endothermic effect sometimes appears broken down into two. A detailed study of more than fifty DTA and TG curves of different samples and different experimental conditions permitting the separation of very close effects, indicates the presence of a breakdown in all the curves, with the two peaks more or less differentiated. Figure 4 shows various curves

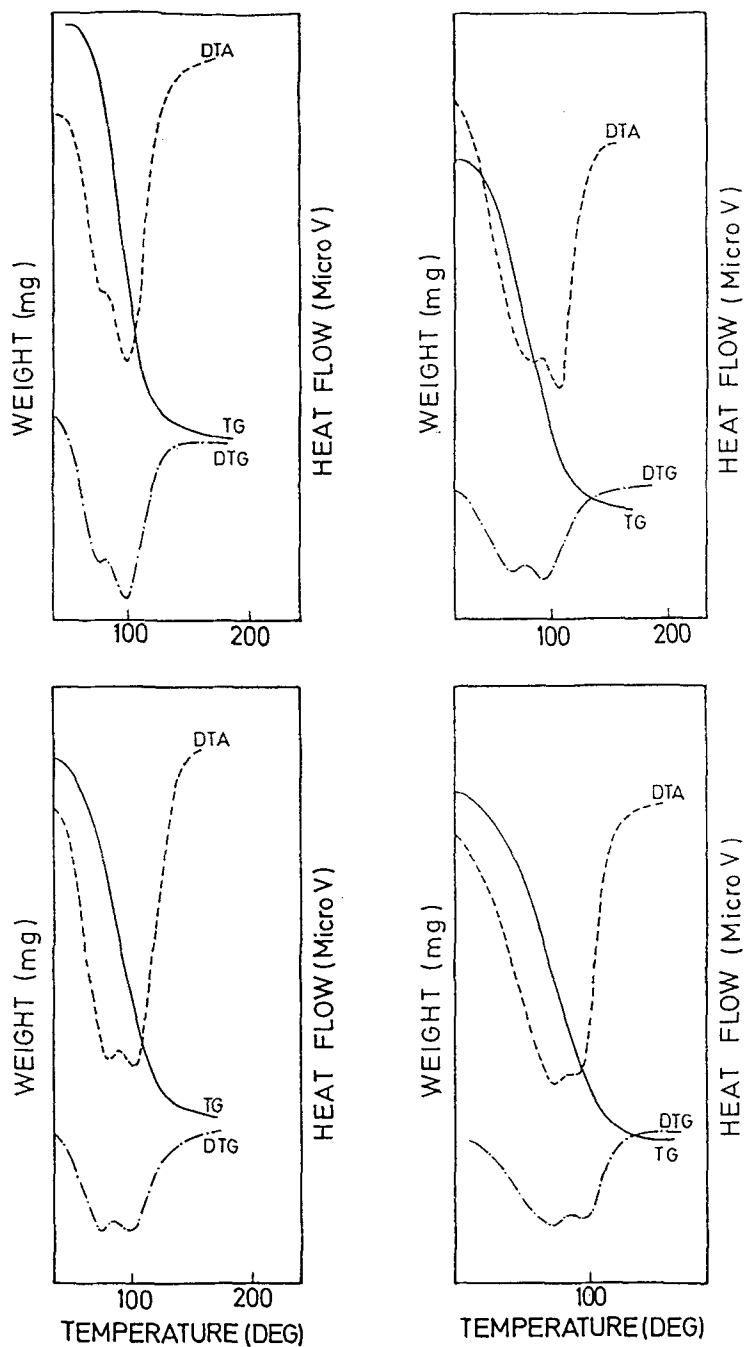


Fig. 4. DTA, TG and DTG between 25 and 300°C of different samples of sepiolite from Vallecas (weight and heat flow scales are in arbitrary units)

for this sepiolite in which the two endothermic effects can be seen clearly, one at 87°C and the other at 118°C. The curves are very affected by the different fragments of sample used, and especially by ambient laboratory conditions.

The TG curve presents only one weight loss, but the DTG curve shows two effects that coincide with those of the differential thermal analysis. These two effects correspond to two weight losses, suggesting the presence of two different forms of bonded water. Both of these could be in the sepiolite, or they could be contributed by two minerals. In the latter case, the non-sepiolite mineral could be a magnesium smectite (which is present, as will be demonstrated).

To test this possibility, mixtures of the sepiolite studied in this work were prepared with different proportions of magnesium smectite from the same zone as the sepiolite deposit. Figure 5 shows the DTA and TG curves of sepiolite, magnesium smectite and mixtures of both. Smectite presents a low temperature endothermic effect at 85°C, coinciding with one of the two presented by sepiolite – the other being at 118°C. As smectite is added to the mixture, the effect at 85°C increases and that at 118°C decreases.

It should be noted that the low temperature weight loss is greater for magnesium smectite than for sepiolite, so that as the amount of the former in the mixture increases, the weight loss of the mixture increases faster. Table 2 shows the weight losses for the different mixtures and the difference from the weight loss of the sepiolite before mixing. Plotting these differences versus the percentage of sepiolite present in the mixture, a straight line is obtained with the following values:  $r = -0.9954$ , negative correlation at significance level  $P < 0.001$ , slope =  $-27.90$  and ordinate at the origin =  $114.46$ . Plotting the differences vs. the energy released in the endothermic effect from DTA gives very similar values. From these data, it can be deduced that the sepiolite used in this work is accompanied by magnesium smectite in a proportion of approximately 14.46%.

The data are affected by the purity of the magnesium smectite. Given that the magnesium smectite used in this work contains some sepiolite, the real percentage of magnesium smectite could be somewhat different.

**Table 2** Weight loss of mixtures of sepiolite and magnesium-smectite

Mixture / %	Weight loss	Difference Sep-Sep/Sm Mixture
100 Sep.	9.8	----
90 Sep/25 Mg-Smect.	10.6	0.80
75 Sep/25Mg-Smect.	11.4	1.60
50 Sep/50Mg-Smect.	12.0	2.20
25 Sep/75Mg-Smect.	13.0	3.20
10 Sep/90Mg-Smect.	13.55	3.75



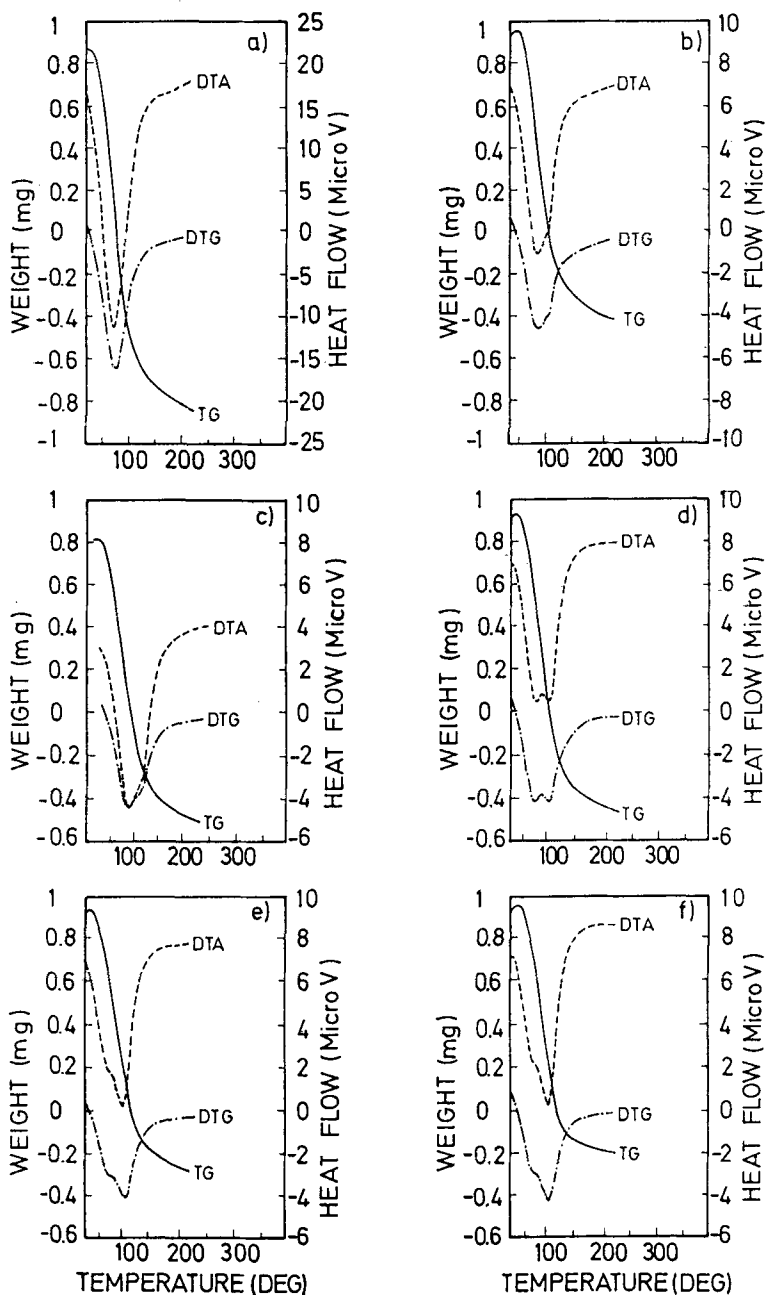


Fig. 5 DTA, TG and DTG of mixtures of Mg-Smectite and sepiolite; a) Mg-Smectite, b) 25% Sepiolite, 75% Mg-Smectite, c) 50% Mg-Smectite, 50% Sepiolite, d) 25% Mg-Smectite, 75% Sepiolite, e) 10% Mg-Smectite, 90% Sepiolite, f) Sepiolite

A detailed study of the sepiolite sample allowed the separation of fragments of material whose X-ray diagram is given in Fig. 6. A diffraction peak is observed around  $14\text{\AA}$  which swells with glycerol, and corresponds to a smectite. EDRX analysis shows the presence of Si and Mg.

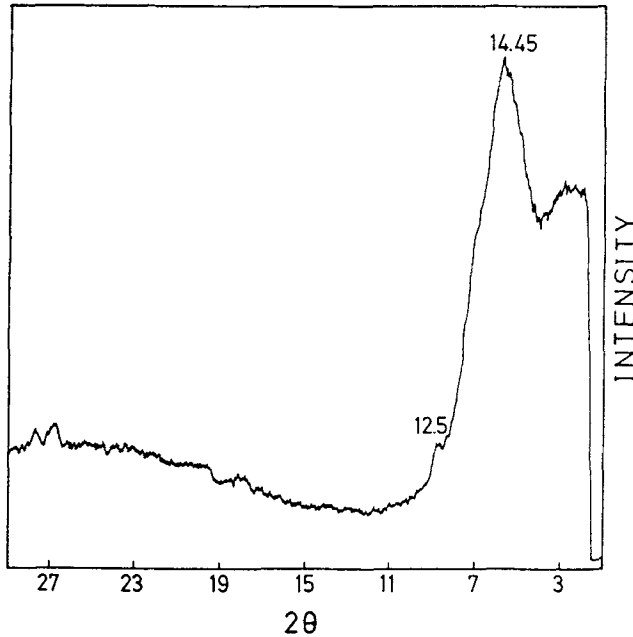


Fig. 6 XRD of separate sample of sepiolite from Vallecas

The diagram also shows that the mineral is poorly crystallized, so that when this material is mixed with the sepiolite, its characterization is difficult. Fukushima and Okamoto [12] give an X-ray diffraction diagram of a sample of sepiolite from Vallecas with a diffraction at  $14\text{\AA}$ , which they attribute to the presence of a small amount of magnesium smectite.

In conclusion, differential thermal and thermogravimetric analyses demonstrate that the low temperature endothermic effect, which is broken down into two, is not due to two forms of water adsorbed on the sepiolite – as indicated by other authors – but to two effects. One is attributed to the sepiolite and the other to the presence of another mineral, magnesium smectite. In the sample studied in this work, the percentage of smectite can reach 15%. The presence of this mineral may be responsible, at least partially, for the cation exchange capacity attributed to the sepiolite from Vallecas, since, from a structural point of view the latter has no possibility of cation exchange capacity. Bailey [13] mentioned minor substitution of Si in tetrahedral layer and also the total of the octahedral

cations usually ranges from 7.0 to 8.0. This may also be responsible for cation exchange capacity in this mineral.

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**Zusammenfassung** — Mit vorliegender Untersuchung sollte mittels DTA, TG und DTG gezeigt werden, daß Sepiolith aus Vallecas (Spanien) mit einem anderen, in mineralogischen Routineuntersuchungen durch Röntgendiffraktion und chemische Analyse schwer bestimmbar Mineral vermischt ist.

Der durch diese Substanz bei niedrigerer Temperatur gezeigte endotherme Effekt und Gewichtsverlust kann in zwei Teileffekte untergliedert werden: der eine von Sepiolith herführend, der andere von dem Begleitmineral, was als Magnesium-Smektit identifiziert wurde. Die Konzentration letzteren Mineralstoffes erreicht im Gemisch bis zu 15%.