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DIFFERENTIAL THERMAL STUDY OF Mg-BEARING CLAYS FROM SALINE LAKES OF SOUTHERN TUNISIA

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Abstract

Clays high in Mg content occur frequently in the high saline environment of salt lakes in southern Tunisia. The DTA curves of these clays show a striking endothermic-exothermic reaction in the temperature range of 800–820°C. A strong correlation is observed between the intensity of these coupled reactions and the Mg content of the initial clay sample. The initial endothermic reaction is interpreted as the melting/dehydroxylation of the Mg-bearing smectites. The subsequent exothermic peak is interpreted as caused by the crystallisation of the new Mg-silicate phase enstatite. Therefore, the DTA is considered as a suitable method for the identification and relative quantification of high Mg clay minerals (e.g. trioctahedral smectites). Variations of the Mg content of the studied samples were well detectable by means of DTA, disclosing a distinct distribution pattern of the salt lake clays. Clues to bulk chemical composition of the initial clay assemblage can also be found in the results of the X-ray analysis of the firing products.

Keywords: DTA-TG, endo/exothermic double peak, enstatite, saline lake sediments, trioctahedral smectites

Introduction

The DTA-TG method is commonly used for the characterisation of evaporites from modern saline lakes, e.g. Mg-sulfates or carbonates [1]. Frequently associated with these evaporites are the 'saline' clay minerals palygorskite, sepiolite and the trioctahedral smectites (saponite and stevensite). Due to the major interest in the evaporite minerals and to the extensive sample preparation for clay mineral analysis, however, clay samples from saline environments have been only sparsely studied by means of DTA-TG.

A dominant process of the clay mineral genesis in various alkaline evaporative shallow-water environments is the uptake of Mg from the brine through neo-

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formation of clay minerals and/or transformation of detrital clay minerals. The resulting saline clay assemblages are often marked by increased Mg contents and distinct clay phases [2]. Therefore, the Mg-content is considered as a valuable indicator for determing the range and stage of clay mineral genesis in many evaporative settings. It is difficult to make an exact identification of the clay mineral assemblage only by means of the standard method XRD-analysis, especially of the smectites, whether dioctahedral or trioctahedral. This can even be impossible due to the low degree of structural order in the crystal lattice and to complex mixtures. An easy and reliable identification of some saline clay minerals would seem to be possible by means of thermal analysis. In particular, variations in the Mg-content are expected to be well recordable by DTA. An obvious S-shaped endothermic-exothermic peak in the range of 700–900°C has been documented in earlier studies [3–5] for various Mg-rich clay minerals, e.g. trioctahedral smectites and sepiolite.

The aim of the present study is to reveal if the double peak mentioned above is directly controlled by the Mg content of the clay sample. If so, it can be taken as diagnostic for dividing different clay mineral assemblages. For this purpose we have analysed a total of thirteen natural clay samples from two saline lakes in southern Tunisia. Additionally, the nature of the double peak was examined by X-ray diffraction and thermogravimetric investigations.

Experimental

Materials

Thirteen sediment samples were collected from the Sebkha el Melah and the Sebkha el Menikra, two ephemeral saline lakes in southern Tunisia. The sampled section in the Sebkha el Melah consisted of nine sample points running from the lake rim to the center. At each of the nine sampling points a mixed sediment sample from the subsurfacial layers (down to 0.2 m depth) was taken, thus yielding a total of nine samples in this lake (for details see [6]). In the Sebkha el Menikra a sediment core, down to 1 m depth, was taken in the central part. From this core, four samples from different depth intervals were analysed.

To prepare the samples for clay mineral analyses, they were passed through a 63 μm sieve, and then treated with a 0.2 M EDTA solution (pH 11) for evaporite removal. Afterwards, the samples were washed with destilled water (pH 7) until the clay mineral suspensions were fully dispersed. The <2 μm size fraction of the desalted samples was separated by settlement in the gravity field (technique of Atterberg). Since the loss of interlayer water from the clays during heating is mainly influenced by the saturating cation present, the clay fraction was Ca-saturated by repeated treatment with a $CaCl_2$ solution. Finally, the samples were washed with demineralized water, and air-dried. Due to low contents of organic matter and iron oxides, their removal was skipped.

Methods

DTA-TG runs were carried out with a Netzsch STA 409 apparatus on 80 mg of the treated clays. Range of heating was from 20 to 1000°C, heating rate was 10 K min^{-1}. In order to suppress the oxidation of organic matter, the analyses were carried out under nitrogen atmosphere in the furnace [7], nitrogen flow rate was 80 ml min^{-1}. For means of standardization of the relative humidity, the treated samples were stored in a desiccator over a saturated $Mg(NO_3)_2 \cdot 6H_2O$ solution for at least one week. Only when the relative humidity is standardized are the results concerning the amount of interlayer water really comparable between different samples.

Chemical analyses was performed with a Philips X-ray fluorescence spectrometer (PW 1400) on the treated and oven-dried (105°C) clay samples. XRD powder analysis was carried out on one Mg-rich and one Mg-poor sample after the thermal treatment. For determination of bulk clay composition, XRD analysis on oriented aggregates of the clays was carried out on one untreated, one ethyleneglycol solvated, and one heat-treated (550°C for 2 h) specimen. The relative abundance of clay minerals was estimated from XRD peak intensities. A Siemens D 500 X-ray diffractometer with a CuK_α tube operating at 45 kV and 25 mA was used. Scanning speed was 1° per min. Evaluation of the diffractograms was done in accordance to the data handbook issued by the International Center for Diffraction Data (JCPDS, 1994).

Results

X-ray diffraction and chemical analysis

X-ray analysis of the treated samples revealed distinct variations in the mineralogical composition of the clays from both saline lakes (Table 1). The two endmembers of this system can be characterized as follows: Type 1 is dominated by an interstratified illite-smectite (i-s mixed layer) with minor amounts of palygorskite (pal), kaolinite (kaol) and illite (ill); Type 2 is marked by an enrichment of palygorskite, kaolinite and illite over the illite-smectite. These mineralogical variations correspond closely to the chemical composition revealed by XRF analysis. A clear systematic modification of content was observed for the major constituents: Mg, Al and Fe. Type 1 shows high Mg-concentrations, up to 26 wt.%, whereas the concentrations of Type 2 are much lower, down to 11 wt.%. The distribution pattern of Al and Fe show an inverse correlation to Mg. Al and Fe are mainly related to the occurrence of kaolinite, palygorskite and illite. The strong positive correlation of smectite and Mg content proves that the smectite is of trioctahedral nature. The distribution pattern is clearly zonal for both the Sebkha el Melah and the Sebkha el Menikra samples. Type 1 clay composition was found in the rim samples from Sebkha el Melah and in the samples from the

Table 1 Characterization of sample locality, clay mineral composition and Mg-content

SEBKHA EL MELAH				SEBKHA EL MENIKRA			
Sample	Sample location	Characteristic clay mineral(s)	Mg/%	Sample	Depth/cm	Characteristic clay mineral(s)	Mg/%
Mel 1	Sebkharim	i–s mixed layer	23.6	Men 1	6–18	pal, kaol, ill	14.2
Mel 2	Sebkharim	i–s mixed layer	24.9	Men 2	18–48	pal, kaol, ill	15.0
Mel 3	Sebkharim	i–s mixed layer	26.1	Men 3	48–65	i–s mixed layer	17.9
Mel 4	Sebkharim	i–s mixed layer	25.6	Men 4	65–85	i–s mixed layer	20.8
Mel 5	Sebkacenter	pal, kaol, ill	16.1				
Mel 6	Sebkacenter	pal, kaol, ill	14.5				
Mel 7	Sebkacenter	pal, kaol, ill	13.8				
Mel 8	Sebkacenter	pal, kaol, ill	11.3				
Mel 9	Sebkacenter	pal, kaol, ill	10.8				

Samples Mel 1–4 and Men 3+4 are referred to as Type 1 samples
Samples Mel 5–9 and Men 1+2 are referred to as Type 2 samples

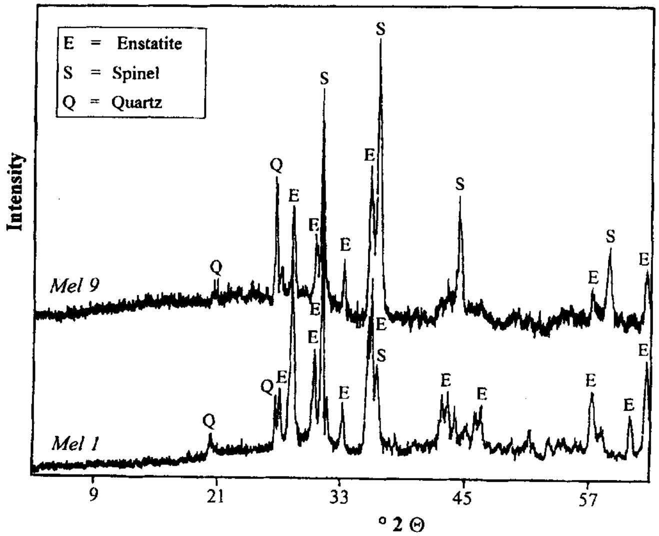

Fig. 1 X-ray diffractograms of Type 1 and Type 2 samples after thermal treatment

deeper layers of Sebkha el Menikra. On the other hand, Type 2 clay mineral composition prevails in the samples from the central parts of Sebkha el Melah and in the uppermost samples from Sebkha el Menikra.

Striking differences in the mineralogical composition were also encountered when X-ray analysis was applied to the firing products of Type 1 and Type 2 samples (Fig. 1). Thermal treatment of the Type 1 samples resulted in the formation of a Mg-silicate enstatite with minor amounts of quartz. The Type 2 sample consisted after heating mainly of a Fe-Al-silicate spinel with subordinate enstatite and quartz. The mineralogical composition of the firing products was rather simple when compared to the initial clay assemblages.

Thermal analysis

The compiled DTA curves of the samples from Sebkha el Melah and Sebkha el Menikra are shown in Figs 2 and 3, respectively. A characterization of the major endo- and exothermic peaks is given in Table 2. The most striking feature of all DTA curves is a large and broad endothermic peak at about 160°C. This low-temperature peak reflects the release of interlayer water. The loss of interlayer water was quantified for all samples by means of TG, which is indicated in Table 3 as mass loss at <160°C. The TG measurements are in good accordance with the results gained by X-ray analyses. Samples rich in smectite (Type 1) show the highest amounts of interlayer water. This water mainly originates from the interlayer regions of the clay minerals, particularly from the smectites.

The next strong deflection is a rather broad endothermic peak occurring at 525°C (Figs 2 and 3). This peak was originated by the nonisothermal release of

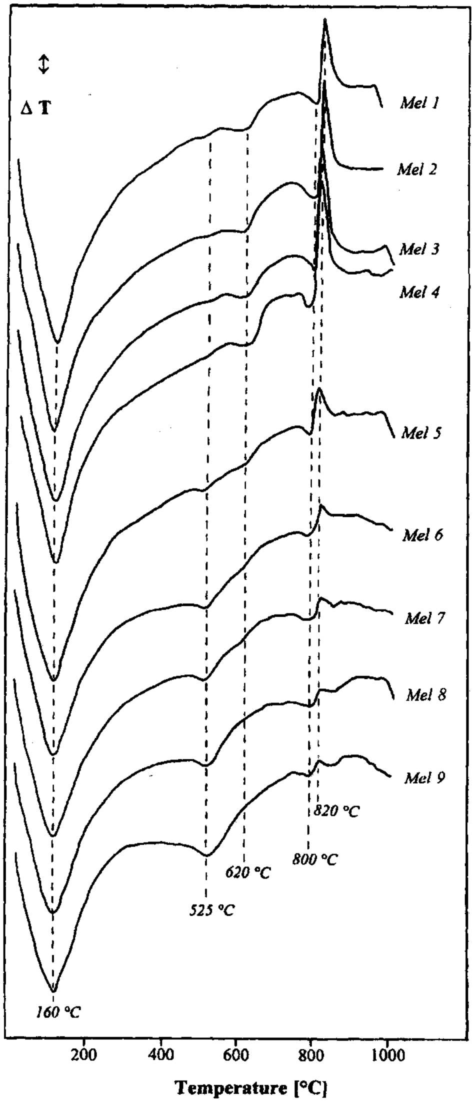

Fig. 2 Compiled DTA curves of samples from Sebkha el Melah

OH from kaolinite, palygorskite and illite. The relatively low dehydroxylation temperature indicates an extremely disordered kaolinite. An elevated intensity of the 525°C peak can be observed for all Type 2 samples.

The following endothermic reaction at 620°C demonstrates the dehydroxylation of smectite and is therefore most pronounced in the Type 1 samples. The 525°C and the 620°C endothermic peaks show clear inverse trends, and both are accompanied by an enforced mass loss.

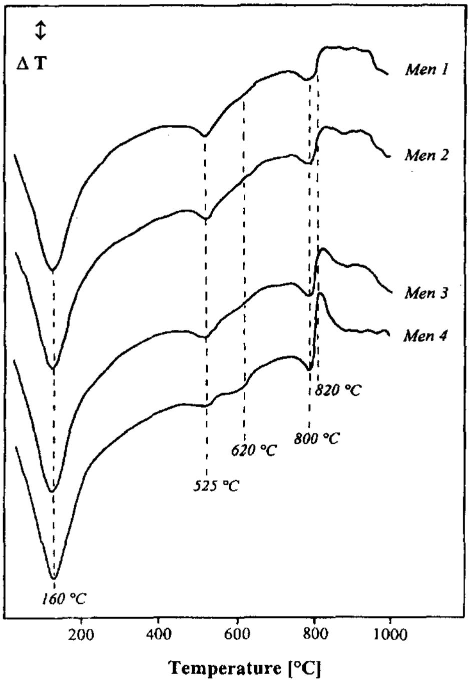

Fig. 3 Compiled DTA curves of samples from Sebkha el Menikra

The endothermic deflection at 800°C can be explained by different dehydroxylation reactions of the primary clay minerals. This peak was closely followed by a very sharp exothermic peak at 820°C. The variations in peak size and shape showed the genetic link of these two closely located peaks. The two peaks share an absolutely identical trend throughout all samples. The strongest deflections were observed in Type 1 samples. As the samples became poorer in Mg, the diminution was clear to see.

The TG curves show small but significant differences. The total mass loss resulting from the decomposition of the initial clays, is generally accomplished in four steps (Fig. 4 and Table 3). First there is a rapid loss due to the release of interlayer water. The amount of released water varies between 5.4 and 8.7 wt.%, and strongly depends on the smectite content (see above). Between 160 and 450°C only slight mass loss was observed. From 450–650°C an enhanced mass loss again takes place, most probably generated by a raised release of OH from the structure of various clay minerals. In step three, from 650–800°C, the mass loss is clearly reduced, but is still higher in Type 1 samples, pointing to an increased dehydroxylation of the smectites. The final mass loss, above 800°C, is only small or even negligible (<0.1 wt.%), but is unequivocally higher in Type 1 samples. This high temperature mass loss is primarily attributed to the final de-

Table 2 Summarized DTA data

Sample	Endothermic/°C				Exothermic/°C
	160	525	620	800	820
Mel 1	XXX	—	X	XX	XXX
Mel 2	XXX	—	X	XX	XXX
Mel 3	XXX	—	X	XX	XXX
Mel 4	XXX	—	XX	XX	XXX
Mel 5	XXX	—	X	XX	XX
Mel 6	XXX	X	—	X	XX
Mel 7	XXX	XX	—	X	X
Mel 8	XXX	X	—	X	X
Mel 9	XXX	XX	—	X	X
Men 1	XXX	XX	—	X	X
Men 2	XXX	X	—	X	X
Men 3	XXX	X	—	XX	XX
Men 4	XXX	X	X	XX	XXX

XXX=high intensity, XX=medium intensity, X=low intensity, — =not recorded
Samples Mel 1–4 and Men 3+4 are referred to as Type 1 samples
Samples Mel 5–9 and Men 1+2 are referred to as Type 2 samples

hydroxylation of the smectites. Altogether, the mass loss ranges from 15.8–18.5 wt.%, the higher values being found solely in Type 1 samples.

Discussion

The results presented above suggest, that the double peak at 800–820°C can be used as an indicator for the Mg-content of clays, which is mainly controlled in the present study by the occurrence of trioctahedral smectites. A similar peak was mentioned by several authors [8–10] for various Mg-rich clay minerals, e.g. serpentine, chlorite, vermiculite, sepiolite and trioctahedral smectites. After heating these clay minerals, numerous recrystallized minerals were found, e.g. enstatite, spinel, mullite, sillimanite, forsterite and olivine. The initial clay mineral determined which high-temperature phase was to be formed. Our investigation proves that enstatite forms from samples rich in trioctahedral smectite. Because of the broad diversity of the primary and newly formed minerals, it is obvious that the double peak can only be used for the quantitative estimation of the Mg-content between samples with similar initial-phase composition. Taking into account this restriction, many Mg-rich clay minerals can probably be accurately

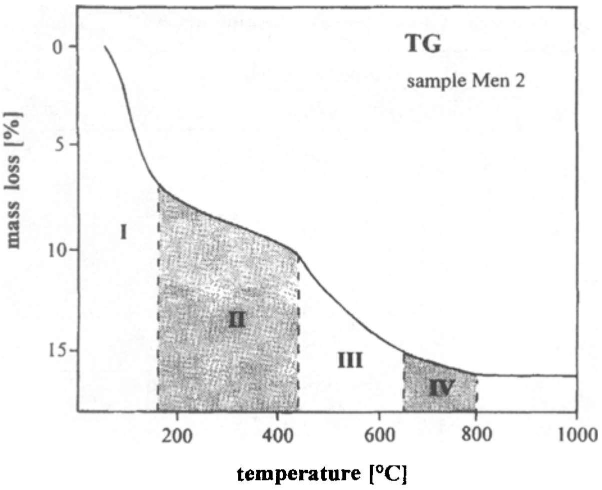

Fig. 4 Exemplary TG curve, indicating typical steps of mass loss

estimated from the intensity of the double peak, as shown here for trioctahedral smectites. Not all Mg-bearing clay minerals show, however, this striking double peak. The Mg-clay mineral palygorskite, for example, does not [11], due to its lower Mg content compared to trioctahedral smectites. Samples rich in palygorskite (Type 2) with Mg-concentrations as high as approximately 10 wt.% show only minor reflections. Therefore it must be emphasized that the significance of the double peak is restricted to samples very rich in Mg. A Mg concentration of 10 wt.% seems to be the minimum required to be expressed as a double peak. The TG measurements provide further information on the mineralogical composition of the initial clay samples. The higher loss of interlayer water in Type 1 samples is attributed to the higher smectite content in these samples, thus matching the results of XRD and DTA. Furthermore, the nature of the endo/exothermic double peak is established from the TG data. Mass loss at 800°C supports the interpretation that the endothermic peak is partly caused by the dehydroxylation of the sample, though the mass loss by itself would seem to be too low to create the strong endothermic reflection. Therefore, a melting process is envisaged as the second driving force. The exothermic reflection is not accompanied by mass loss, and a crystallisation of a new phase seems to be its most likely cause. This matches the precede melt formation.

Until now, clay samples from saline environments have been studied mainly by the standard methods of X-ray diffraction and chemical analyses. Considering the topics of saline clay mineralogy – formation of sepiolite, palygorskite, trioctahedral smectites and transformation of detrital clay minerals as kaolinite, illite, dioctahedral smectites, e.g. [12] – it is obvious that major clay characteristics are affected by the highly saline conditions. In the present study, an uptake of Mg from interstitial brine through the formation of Mg-smectites seems

Table 3 Percentage of mass loss in dependence on heating intervals (TG data)

Sample	Temperature range/°C					Total loss
	<160	160–450	450–650	650–800	>800	
Mel 1	7.5	3.7	4.6	1.7	0.5	18.0
Mel 2	7.5	3.5	5.7	1.3	0.5	18.5
Mel 3	7.5	3.7	5.3	1.8	0.5	18.8
Mel 4	7.5	3.6	4.9	1.5	0.5	18.0
Mel 5	5.9	3.9	4.4	1.2	0.4	15.8
Mel 6	6.5	4.9	5.1	1.3	0.5	18.3
Mel 7	5.4	4.5	5.2	1.0	0.4	16.5
Mel 8	6.0	4.5	4.9	1.0	0.2	16.6
Mel 9	5.8	4.7	5.2	1.0	0.2	16.9
Men 1	6.5	4.0	4.6	1.2	0.0	16.3
Men 2	6.8	3.4	4.8	1.2	0.0	16.2
Men 3	7.6	3.4	4.4	1.4	0.2	17.0
Men 4	8.7	4.0	3.9	1.6	0.3	18.5

Samples Mel 1–4 and Men 3+4 are referred to as Type 1 samples
Samples Mel 5–9 and Men 1+2 are referred to as Type 2 samples

probable, thus producing one clear zonal distribution pattern for the Mg-smectites and consequently for the total Mg-content of the clay fraction. Variations in the amount of interlayer water and in the uptake of Mg from the brine are especially convincing markers for the clay mineral genesis, and were recordable by means of DTA-TG. Differences in water content (adsorbed and/or intra-crystalline) were easily and reliably detected by TG-analyses. The other major feature, the incorporation of Mg in preexisting clay mineral structures or the neoformation of distinct Mg-clay minerals under evaporative conditions, can be easily disclosed by thermal analysis.

Starting with a complex assemblage of poorly ordered clay minerals, a small number of highly crystalline phases (enstatite, spinel and quartz) is produced by thermal treatment. A phase mentioned by some authors [13] is mullite. This phase is attributed to the transformation of trioctahedral smectites. The lack of mullite in the present study is probably due to relatively low Al-contents in the initial clay samples. The firing products are of major interest since they allow an easy estimation of the bulk chemical composition of the clays by X-ray diffraction analysis. This estimation can be made based on the finding that after thermal treatment the number of phases are fewer and are well ordered. However, the basically simple chemical composition of the firing products is commonly affected by isomorphous substitution. Yet even these variations are visible by X-ray analysis [14, 15]. A similar estimation cannot be done from X-ray investigation of the initial clays, due to their low degree of order and the extensive chemical variations, especially found in soil and weathering environments. Thermal analysis followed by X-ray analysis therefore provides access to an easy determination of the bulk chemical composition. Even small sample amounts can be very conveniently analysed in this way.

From the above considerations, it is obvious that thermal analysis can serve as an important link between the structural analysis (XRD) and the chemical analysis, as shown here in the case of saline clay mineral genesis.

Conclusions

1) Natural clay samples from saline environments underwent dehydroxylation and subsequent recrystallisation of enstatite in the temperature range of 800–820°C. This transformation of the initial clay minerals is documented in the DTA-curves as a striking S-shaped double peak.

2) The S-shaped double peak shows a strong positive correlation to the Mg and smectite content; hence, the double peak appears as well suitable for the quantitative determination of the trioctahedral (Mg) smectites and probably for other high-Mg clay minerals.

3) Based on careful sample preparation (cation saturation, standardization of relative humidity, use of an inert atmosphere) TG measurements can be applied to corroborate the XRD and DTA results.

4) X-ray diffraction analyses of the firing products offer clues to the bulk chemical composition of the initial sample. Thus, an X-ray analysis of the thermally treated samples should follow the thermal analysis of clays.

6) The clays in the salt lakes of southern Tunisia are affected by the uptake of Mg, crucial to the authigenesis of trioctahedral smectites, producing a zonal distribution pattern of the clays.

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