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THERMAL STUDIES ON THENARDITE

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ABSTRACT

Two natural thenardite (Na_2SO_4) single crystals, e.g. from Wadi El-Natron and Searles Lake, and one synthetic thenardite were studied by combined thermal techniques (e.g. DTA, TG, TMA, TOA and MS) mainly with regard to the occurring phase transitions and in order to determine the reason for the observed differences in the transition behaviour of the studied samples. The synthetic thenardite which was chemically very pure (especially free of water) showed its phase transitions during heating and cooling for be much closer together and (1st heating) a little shifted to higher temperatures compared with the natural samples which contained remarkable amounts of water and carbon, respectively. Simultaneously with the phase transitions, both natural samples lost some weight, showed very sharp, clear changes in the TMA curves and released water and CO_2 during the first heating. The thermal transitions started at distinct spots within the single crystals, easily recognizable at different interference colours when using crossed nicols in the thermomicroscope. These spots were interpreted as domains with a certain crystal physical defect character which partly enables earlier phase transitions at the defect domains. The spots seem to include very small particles of mirabilite, $Na_2SO_4 \cdot 10\ H_2O$, or carbon flakes which are the reason for the defect domains and the observed release of water and CO_2.

INTRODUCTION

Sodium sulphate forms two naturally occurring minerals, mirabilite ($Na_2SO_4 \cdot 10\ H_2O$) and thenardite (the low-temperature form of Na_2SO_4). Both are in thermodynamic equilibrium at 32°C which may be lowered to 18°C in the presence of foreign ions [1]: mirabilite crystallizes from aqueous solutions below this temperature and thenardite above, the solutions being poor in chlorine. Due to their environment of formation, four different types of natural thenardites may be distinguished:

(a) evaporitic thenardite crystallizing in terrestric salt flats (arid environments, e.g. Searles Lake, California, or Wadi El-Natrun, Egypt *);

(b) minerals formed by processes of weathering, as a product of efflorescence or by dehydration of mirabilite (arid and semi-arid environments);

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* Ref. 2: "The Wadi Natrun and another locality are mentioned as sources of salt mixtures as Na_2CO_3, $NaHCO_3$, Na_2SO_4 and NaCl."

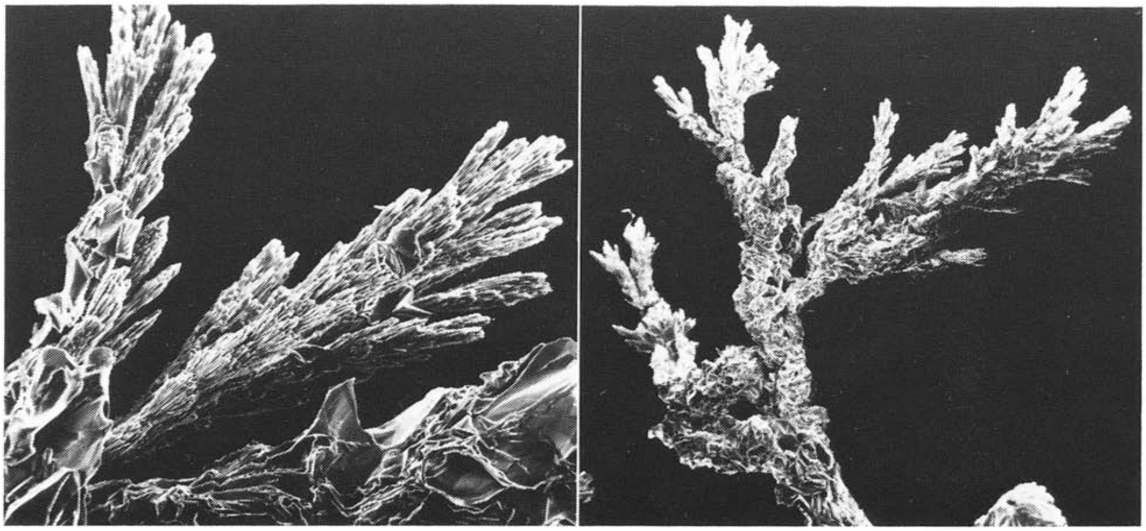

Fig. 1. Crystal tree of thenardite.

(c) thenardite formed by volcanic exhalations (e.g. Vesuvius, Italy); and

(d) crystals formed diagenetically or low-grade metamorphically in marine salinar deposits (e.g. Stassfurt or Berchtesgaden, Germany).

Sodium sulphate, though very simple in chemical composition and common in nature, has been the subject of various applications and investigations. The peasants of old Egypt collected it from the salt flats of the country (as in Wadi El-Natron *), transported it to the markets of ancient towns or transformed it by special preparation techniques to dendritic crystal trees (Fig. 1), and finally used it for salt mixtures taken for the preservation of mummies [4] and for medical treatment [5]. Today, it is used for the production of glasses and paints and for thermal energy storage techniques [6]. Besides these applications, thenardite has been the topic of numerous scientific investigations.

PREVIOUS STUDIES

The structure of thenardite (orthorhombic) and its crystal chemistry are well known and are described in detail by Mehrotra et al. [7] and Miyake et al. [8]. Crystal physics, especially the thermal behaviour of thenardite which is controlled by several structural transitions, still include some problems which have not yet been satisfactorily solved. Thenardite belongs to a crystallographic system of four (or five?) polymorphs (Na_2SO_4-I to Na_2SO_4-V), being rather complicated due to different transition kinetics and structural relationships of the polymorphs [7,9]. Therefore, publications on thenardites include a lot of contradictory information and results. Table 1 contains some of the published data on the thermal transitions of thenardites, and shows the discrepancies in transition temperatures and the vari-

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* Cited from ref. 3: "The Tale of the Eloquent Peasant."

TABLE 1

Selected data on the structural transitions of Na_2SO_4 (mainly heating values)

Ref.	Method of study	Thermal transitions observed (°C)					
19	Cooling curves						234
9	DTA	160—180	185				241
11	DTA			(227)			243
20	DTA						270 (!)
21	DTA						240
22	DTA			(227)			243
23	DTA		180	220	230	235—255	
24	DTA			220	230	235—255	
15	DTA	147 [a]		215			245
25	DTA						245
8	DTA + optics			222	230	235—254	
16	DTA	125 [a]		215			245
26	DTA						245
10	DTA + X-ray			212	236	242—250	
12	TOA		190	221			250
7	DTA			200	230		238

[a] Not reversible.

ations from "normal" transition behaviour. Due to hysteresis effects and kinetic barriers, the transitions occur at different temperatures during heating and cooling and the occurring phases are also different. The most agreeable transition scheme seems to be that shown in Fig. 2 which is based on the data of Mehrotra et al. [7] and Wiedemann et al. [21]. But the transition steps and their interpretation seem to be more complicated than previously believed, leading to a detailed rediscussion of the results of Kracek [9], Mackenzie [11], Heide [20] and others. Heide [22] confirmed the opinion of Mügge [23] (cited by Heide [22]), concluding that thenardite as the low-temperature modification of Na_2SO_4 was seemingly stabilized by small contents of water. This is corroborated by Mehrotra et al. [7] who found that this "Na_2SO_4—V" (= thenardite) could not be obtained again when cooled to room temperature from 230°C (compare with Fig. 6).

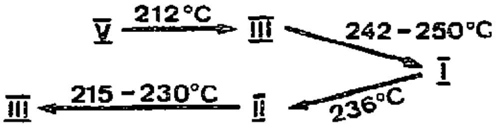


Fig. 2. Scheme of Na_2SO_4 phase transitions (after Mehrotra et al., [7]).

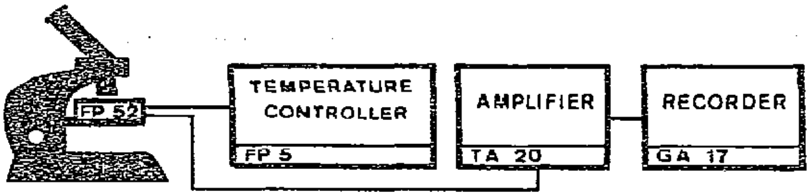
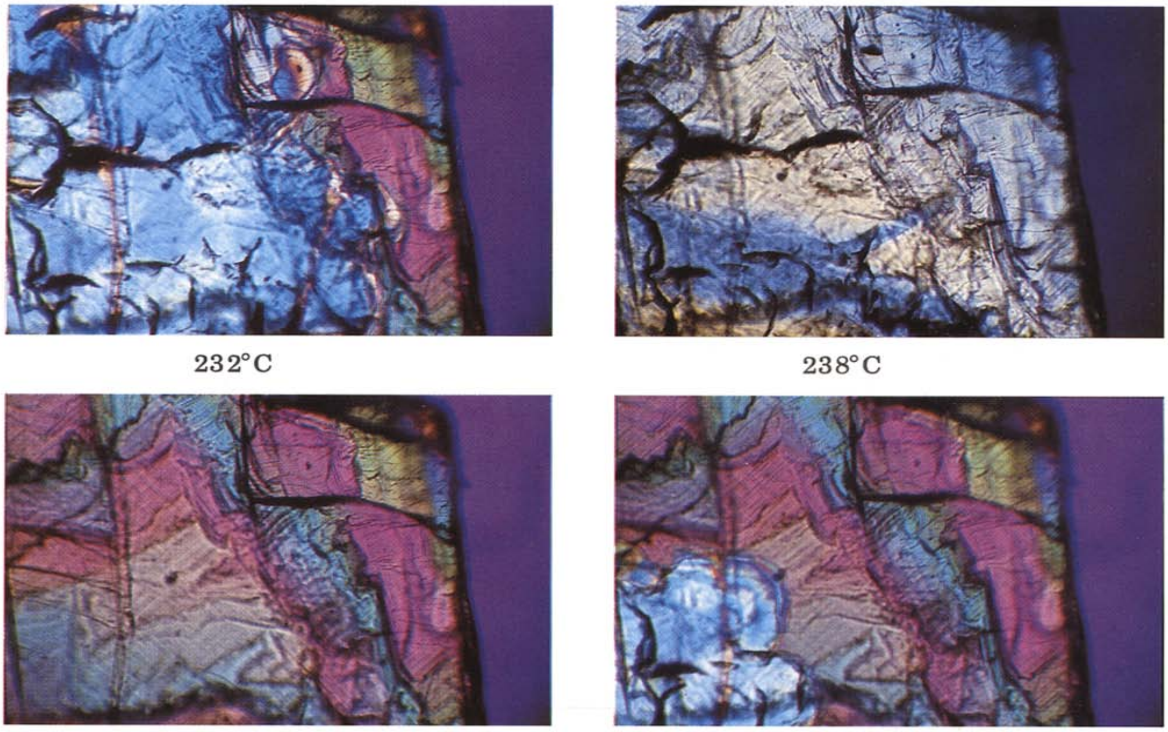


Fig. 3. Scheme of simultaneous DTA/thermomicroscopic analysis.



232°C

238°C

219°C

228°C

Fig. 12. Thermooptical characteristics of the phase transition V → III of thenardite (single crystal from Wadi El-Natrun); crossed nicols; magnification: 100X. Heating rate 2°C min^{-1}.

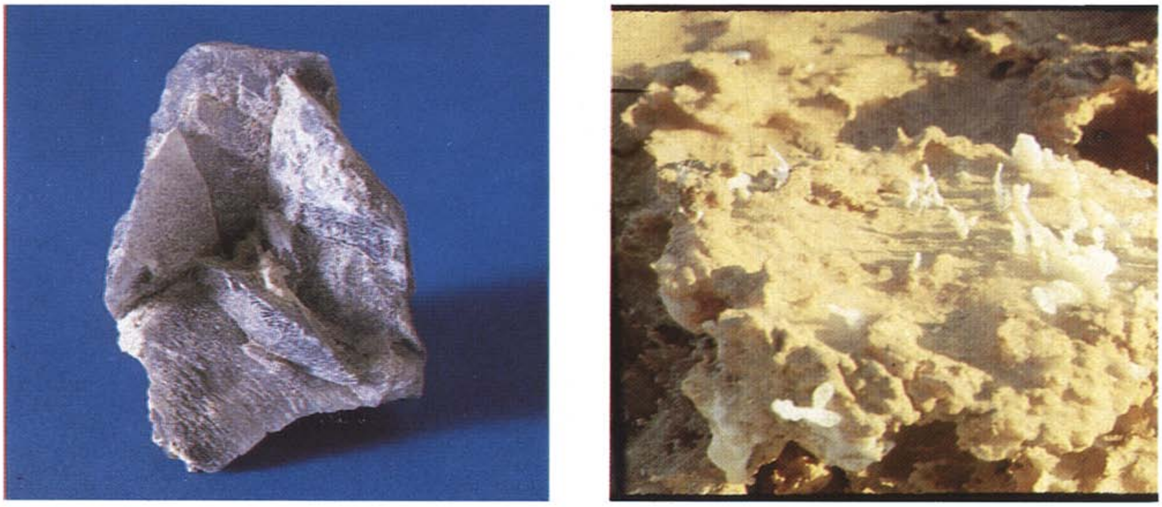


Fig. 4. (a) Thenardite single crystal from Wadi El-Natrun, Egypt; long edge 5 cm. (b) Salt cover with halite and thenardite, Sebcha of Zouila, Fezzan, Libya.

Mügge [23] and Heide [22] pointed out that thenardites crystallized from aqueous solutions showed some characteristics different to those which had formed from sodium sulphate melts. Heide [22] thought the small water content in thenardites formed from aqueous solutions to be responsible for the observed differences. Water was also found in some natural thenardites by Wiedemann et al. [21], but the nature of this water in thenardites is not yet clear.

METHODS AND SAMPLES

Answers to questions concerning the state of the water present in some thenardites and what happens when Na_2SO_4 transforms are attempted by means of combined thermal techniques, e.g. by the correlation of the five different methods thermo-optical, thermomechanical, thermogravimetric, differential thermal and mass spectrometric analysis. The instruments used were: a Mettler thermoanalyzer TA-1, Mettler TA-2000 C, combined with Balzers quadrupole mass spectrometer QMG-1, and a Mettler DTA/thermomicroscope. This simultaneous measurement (see Fig. 3) is based on a commerical microscope and the Mettler FP hot-stage (FP-5 control unit, modified FP-52 hot stage). For the thermomechanical measurements the new Mettler TA-3000 (TC10, TA processor, TMA 40 measuring cell) was used. The detailed conditions of analysis are included in the figures.

Two natural samples (from Searles Lake in California and Wadi El-Natron in Egypt) and one synthetic thenardite (grown from aqueous solutions of Na_2SO_4 suprapure from Merck) were studied. While the natural single crystal from Wadi El-Natron (Fig. 4) was clear and colourless, the crystals from Searles Lake were transparent but pale yellow, as described earlier by Pemberton [24]. Both samples from salt flats were evidently pure: the amount of trace elements (mainly Ca, Mg, and K) did not exceed 1000 ppm [21].

RESULTS

The influence of grinding on the transition behaviour of the clear crystals from Wadi El-Natron can be seen by comparing the DTA curves of a single crystal with those of the same material but ground in an agate mortar to a grain size <150 mesh (Fig. 5). The single crystal shows sharp, reproducible transition peaks. The powdered unheated thenardite exhibits a completely different transition behaviour: the phase transitions are shifted to somewhat higher temperatures and show a kind of "smear-over" effect, appearing over a temperature range much larger than in the case of the single crystal, but ΔT decreased considerably. Seemingly, the powdered material recrystallizes partly during the first heating as can be seen in the increase of the III → I phase transition peak (and its ΔT) of the second run (Fig. 5).

Reheating of Na_2SO_4 samples leads to two significant changes in the thermal behaviour (Fig. 6). From the investigations of Mehrotra et al. [7] it

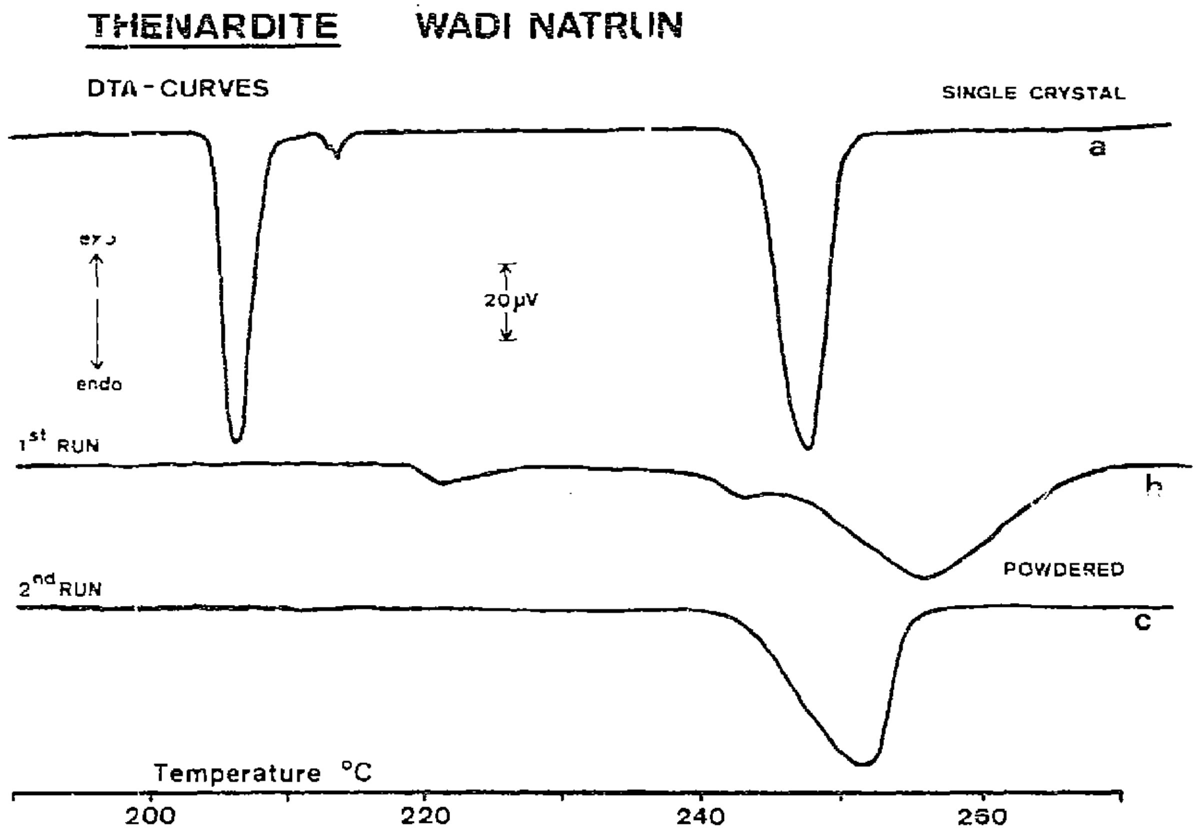


Fig. 5. DTA curves of thenardite from Wadi El-Natron in dependence on grinding: (a) single crystal; (b) same material but cautiously ground in an agate mortar; (c) as (b), second heating.

is known that the modification V (= thenardite) cannot be obtained by cooling (and this, of course, is the explanation for the mentioned differences between thenardites grown from aqueous solutions and Na_2SO_4 crystallized from sodium sulphate melts!). But phase II occurs (only!) in cooling runs, and the small effect which is partly overlapped by the larger I → III transition appears more and more separately with increasing number of runs. This effect was observed by Heide [22].

Figure 7 shows the simultaneously measured TG/DTA curves of both natural thenardites studied. The endothermal effect around 890°C represents melting of the sodium sulphate. The thenardite from Searles Lake surprisingly exhibits a strong weight loss of nearly 4% (0.6 from 16.14 mg) which is evidently related to the strong exothermic DTA peak occurring in the same temperature range. The fact that the weight loss started simultaneously with the first phase transition (V → III) is clearly to be seen in Fig. 8(a) and (b), and there is a good correlation between the weight loss and temperature of the two phase transitions occurring during first heating. The TG curves of the second run (Fig. 8a,b) show only the normal buoyancy effect. Obviously the synthetic material is free of weight-loss producing substances (Fig. 9). Both phase transitions appear close together in the case of synthetic thenardite.

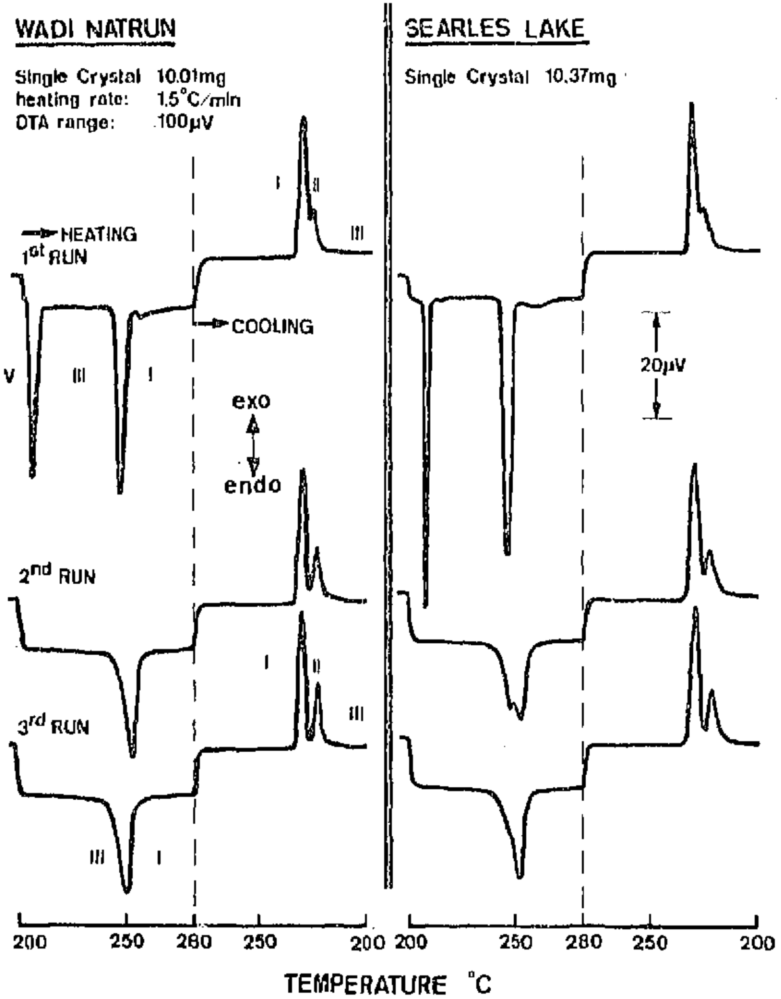


Fig. 6. DTA curves of the natural thenardites from Wadi El-Natrun and Searles Lake; three repeated runs (heating to 280°C and cooling to room temperature).

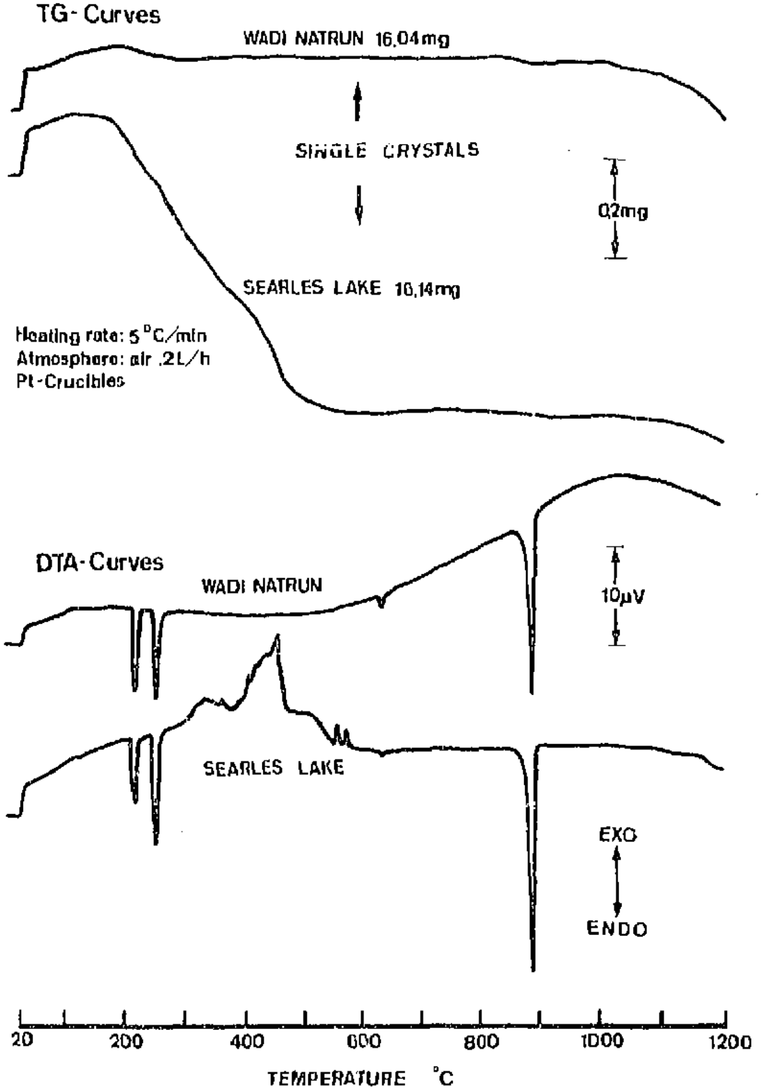


Fig. 7. Simultaneous TG and DTA curves of the natural thenardite samples; heating to 1200°C.

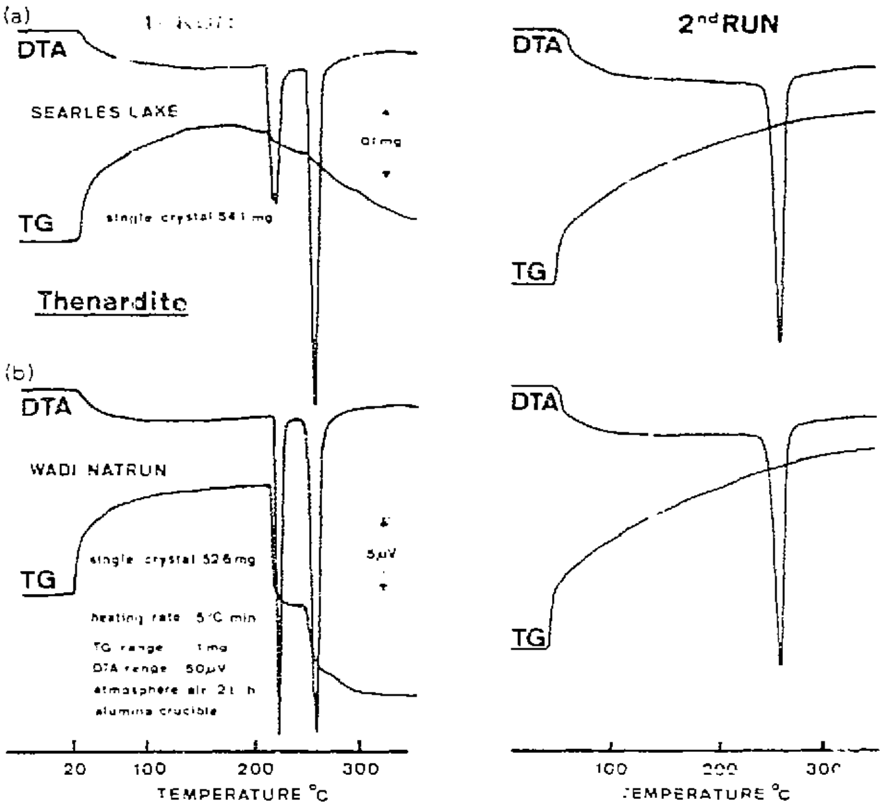


Fig. 8 (a) + (b). Simultaneous TG and DTA curves of natural thenardites; first and second heating up to 300°C.

There is also good correlation between phase transitions and thermomechanical changes on heating and cooling (Fig. 10). Small changes in the extension behaviour at lower temperatures (<200°C) observed by Heide [22] may be due to dehydration effects. Some authors report small endothermic DTA effects between 100 and 180°C possibly due to the presence of water [9,17,19]. Both natural thenardites studied contain small amounts of water (cf. Fig. 11) and CO_2. The crystals from Searles Lake release remarkable amounts of CO_2 and smaller amounts of CO and water (as observed in simultaneous mass spectrometric and TG runs). The MS runs are made in vacuum which depresses the intensity of degassing reactions compared with reaction intensity in air.

Table 2 contains the heats of transitions of the three samples studied. The values are comparable, though those of the natural crystals from Searles Lake show heats of transition which seem to be a little low.

DISCUSSION

Compared with both natural thenardite single crystals studied, the phase transitions of synthetic crystals occur somewhat delayed and closer together

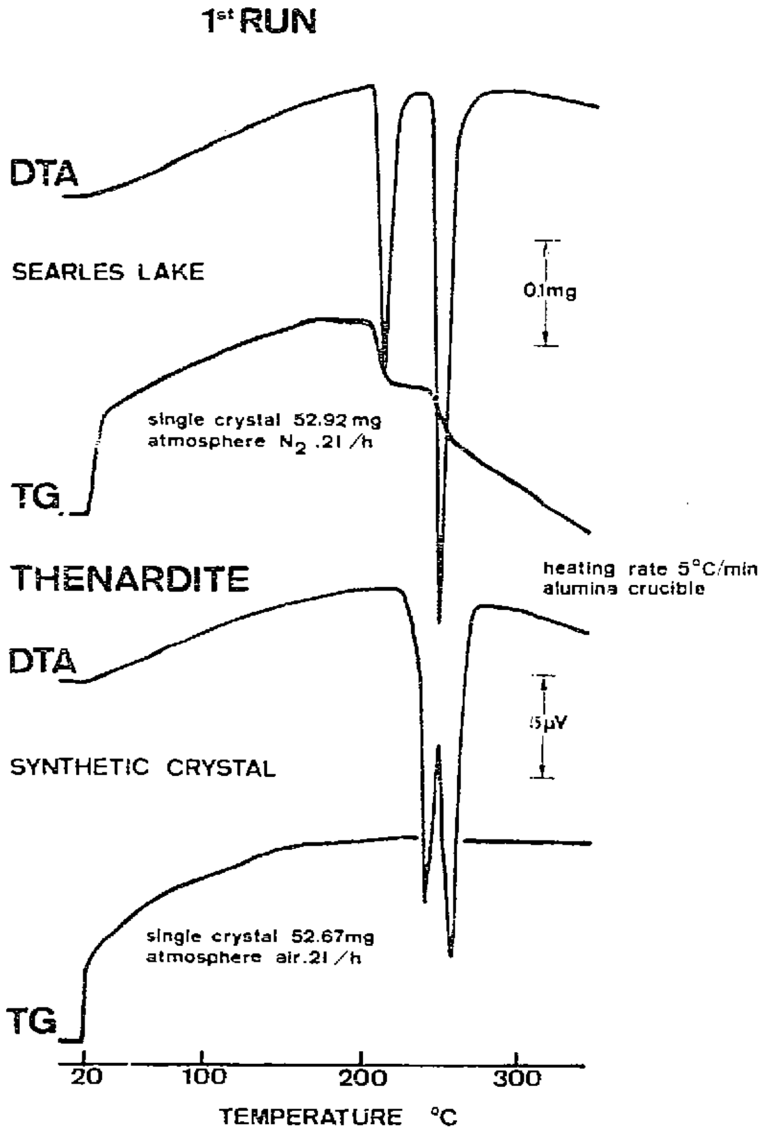


Fig. 9. Simultaneous TG and DTA curves up to 300°C; single crystal from Searles Lake and synthetic crystal.

(Figs. 8 and 9). From the TG curves of Fig. 8 and also from mass spectrometric and chemical analysis, it emerges that this synthetic material ("Na_2SO_4 suprapure" from Merck) is free of water or CO_2. Obviously a correlation between the detected amounts of water (or CO_2) and the temperatures of the phase transitions exists. A correspondence between defect character and phase transition temperatures was also found in former phase transition studies, e.g., for the high—low inversion of quartz or cristobalite crystals [25,26]. It seems that the required transition energy is lowered by increasing crystal chemical or physical defects.

This may be emphasized by watching the transition mechanism in the thermomicroscope (Fig. 12a—d). The transition starts from certain spots (Fig. 12a) somewhere in the centre or at the rim of the crystal. In photo-

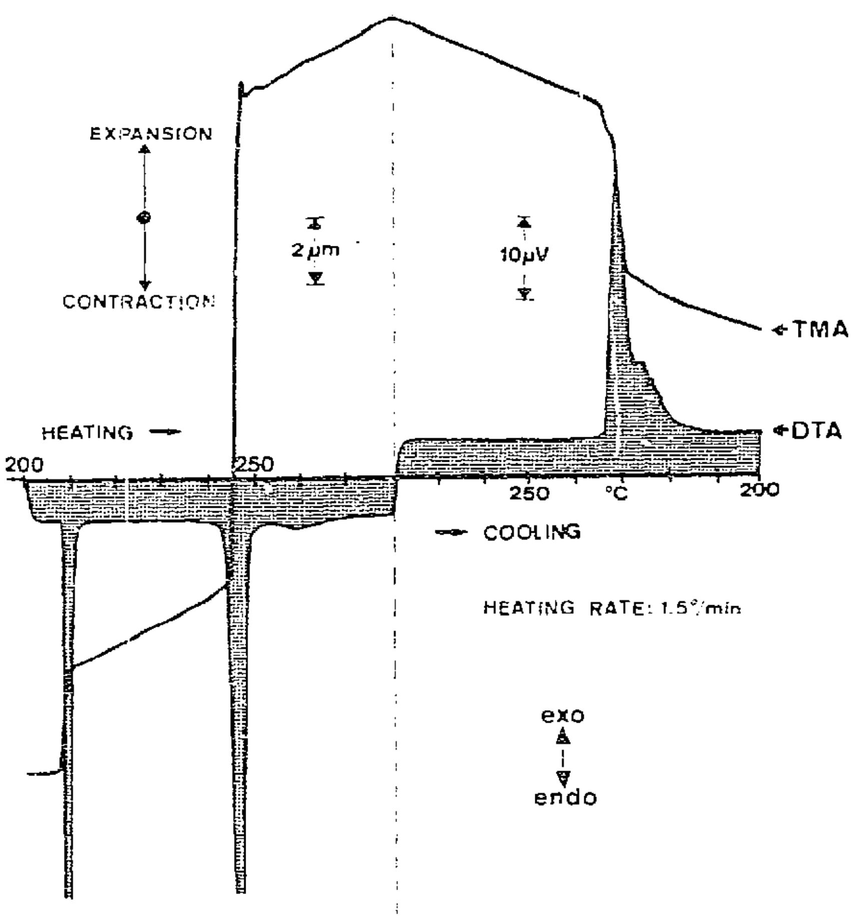


Fig. 10. Superimposed DTA and TMA curves; single crystal from Wadi El-Natron.

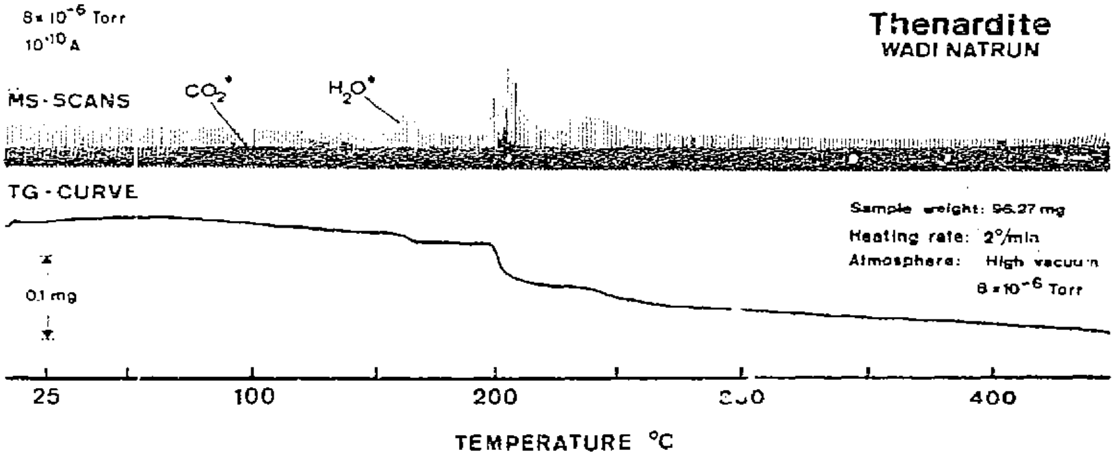


Fig. 11. Simultaneous TG curve/MS-scans; thenardite from Wadi El-Natrun.

TABLE 2

Heats of transitions (calculated from DTA curves)

Thenardite	Heat of transitions		(kJ mole^{-1})	
	Heating	1.5°C/min^{-1}	Cooling	1.5°C/min^{-1}
	V → III	III → I	III → II → I	
Wadi El-Natrun	2.96	5.82	4.87	
Searles Lake	2.98	5.76	4.53	
Synthetic	3.45	5.27	4.96	
			3.45	1.51

graphs taken with crossed nicols these spots are recognized by the development of different interference colours. From the spots the arising interference colour of the higher Na_2SO_4 phase is waving through the crystal mirroring the moving front of the phase transition (Fig. 12a—d).

It seems to be consequent when interpreting these spots of origin of the new phase as disturbed (defect) domains of the crystal. But what kind of "defects" do they represent? The answer may be easier when discussing first the nature of both the water and CO_2 found in the natural thenardites. Neither sample studied showed any crystalline phase other than thenardite, even in very sensitive X-ray Guinier runs. If the thenardite from Searles Lake (which in the MS/TG curve exhibits remarkable amounts of released CO_2 and small amounts of CO) included carbonate particles as the source of the CO_2, the corresponding DTA peak would have to be endothermic due to the decomposition of the carbonate. But the occurring DTA peak is exothermic (Fig. 7), reflecting an oxidation process of the primarily present C to CO_2 and CO. The pale yellow colour of the crystals from Searles Lake already described by Pemberton [24] underlines this interpretation: when growing from the salt brine of Searles Lake, the thenardite crystals may have included small flakes of organic matter being present in the brines; the pale yellow colour thus being caused by the very small inclusions of carbon.

The crystals from Wadi El-Natrun include water, proven by MS/TG and IR spectroscopic runs. IR measurements showed there to be only water and no OH detectable in all samples studied. The water is released from the thenardite crystals exactly when the phase transition starts (Figs. 8, 9 and 11). Evidently the water starts to vaporize at that moment when the thenardite phase starts to transform, and the phase transition temperatures are lowered by the presence of water.

It is hard to imagine that such water concentrations eventually present at accidental spots in the crystals are included as molecules of H_2O in the thenardite structure. But they may be easily explained as inclusions of small particles of mirabilite, $Na_2SO_4 \cdot 10\ H_2O$, too low in content to be detected by means of X-ray and too small to be seen under the microscope, but rich enough in water to cause the observed effects in TG, DTA or thermomicroscopic studies.

This means, that natural thenardites, having been formed from salt flat brines in arid environments (as was the case for the single crystals from Wadi El-Natrun and Searles Lake), may include small particles of mirabilite (and/or organic matter) when growing, thus preventing them from transforming to thenardite or CO_2 (in the case of carbon). The inclusions produce defects in their host crystals. The phase transitions start at the defect spots. Thus the defects cause partly a lowering of the phase transition temperatures. The included mirabilite shows the same phase transitions (V → III → I on heating), but for the transitions it must be dehydrated, so the processes occur simultaneously: the dehydration of the mirabilite inclusions starts when the surrounding thenardite domains (which are rich in defects) transform. The dehydration of the mirabilite is immediately followed by the transition of the mirabilite particles (but this effect is very close to the transition temperature of the host thenardite so that both effects overlap in thermal curves).

The observed effect of grinding on the transition behaviour seems to be contradictory to this interpretation but, in fact, it is not. Tests with small crystals of mirabilite showed that they quickly transform to thenardite when cautiously ground in an agate mortar. Of course, the grinding may also create defects, but the material loses its water by this mechanical process and this loss may be more than needed for compensation of the defects originated by grinding. The recrystallization effect which is only seen in this clear way in DTA curves (powdered/2nd run) of the ground sample (Fig. 5) may corroborate the present interpretation.

Remember the opinion of Heide [22] that "the low-temperature modification of Na_2SO_4, thenardite, seemingly is stabilized by small contents of water". As discussed before, the contrary seems to be the case, meaning that small contents of water (or carbon) present in natural thenardites lower the stability of this mineral, as may be seen by comparison with synthetic thenardites which are free of water or other impurities.

ACKNOWLEDGEMENTS

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