Fluid inclusions in thenardite from northern Mali: experimental stretching and microthermometric investigations

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Abstract

Large thenardite crystals have been sampled at New Agorgott, in the Taoudenni area of northern Mali. They are still in equilibrium with a pressurized NaCl saturated brine capped by a halite layer. Clays located about 1 m above the thenardite occurrence have been dated at 6760 y.BP. The crystals contain numerous, large, brine and solid inclusions. Microcryscopic studies show that the fluids can be explained by the addition of $MgCl_2$ to the Na_2SO_4–NaCl–H_2O system (eutectic temperature: −31 to −35 °C; possible bloedite $Na_2Mg(SO_4)_2.4H_2O$ formed after freezing). The homogenization temperatures of primary fluid inclusions are in the range 28 to 50 °C. In order to understand the significance of the highest T_h values, overheating experiments under 1 bar pressure were performed at different heating rates up to 170 °C. The results are as follows:

(i) When the temperature of stretching (T_{Oh}) is higher than about 10 °C, overheating is recorded and fossilized (identical T_h after some hours, several days or 8 months storage at 5 °C).
(ii) The lowest T_h values (28 °C) are probably near the formation temperature of thenardite; the highest ones reflect stretching under present desert conditions.
(iii) With T_{Oh} lower than about 60 °C, a fair correlation is observed between T_h and T_{Oh}.

Finally, taking into account recent natural overheating, the fluid inclusion data are compatible with the formation of thenardite from underground brines later than the beginning of desert conditions in the Taoudenni area (i.e. about 3000 y.BP).

KEYWORDS: fluid inclusions, thenardite, microthermometry, stretching, Mali.

Introduction

RECENT continental evaporites have retained thermal information about Quaternary paleoclimates, as exemplified by studies of recent gypsum crystals from various climatic zones (Sabouraud, 1975). Among other Sabkha minerals, thenardite (Na_2SO_4) crystals often contain large fluid inclusions which are easily studied by microthermometry. Thenardite however is a very brittle solid, so it is debatable whether the initial densities of the inclusions have remained constant, or were modified by stretching after exposure to the sun. Stretching (Roedder, 1984; Bodnar and Bethke, 1984; Guilhaumou *et al.*, 1987) is an irreversible volume increase of fluid inclusions related to deformation induced by overpressures resulting from overheating. A number of investigations have been carried out on quartz, fluorite, baryte and carbonate minerals, but with the exception

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of halite (Roedder, 1984), little is known about the stretching of salt minerals.

Results of a microthermometric study of fluid inclusions in thenardite samples from northern Mali are presented. These data are interpreted in the light of an experimental investigation of stretching related to moderate overheating, intended to mimic natural exposure to sun under desert conditions.

Large thernardite crystals, forming rosettes 10 to 30 cm in diameter, were collected from pits and trenches at New Agorgott, Taoudenni area (Mali). When collected, they were still in equilibrium with a pressurized brine capped by a halite layer. Clays located about 1 m above the sampling site have been dated at 6760 ± 110 y.BP (Fabre and Petit-Maire, 1988).

Fluid inclusion studies

Description of fluid inclusions. Cleavage fragments and whole crystals of thenardite, polished very mildly, have been studied. The samples contain abundant, large, solid and fluid inclusions. Most of the solids remain undetermined; however thenardite and halite have been identified from their optical characteristics, and glauberite [$NaCa(SO_4)_2$] from Raman microprobe data (courtesy C. Beny).

From the shape, number of phases, filling coefficient and size, three main types of fluid inclusion may be distinguished:

(i) Irregular, large (~0.4 mm) two-phase inclusions with elevated vapour/total volume ratios. Presumably such inclusions have lost a part of their original liquid content.
(ii) Elongated, smaller (50 to 30 μm), two-phase inclusions with a minute vapour bubble. Most of the thermometric investigations have been carried out on such inclusions.
(iii) Multiphase inclusions of variable size and filling coefficient, with trapped and/or daughter salts (e.g. halite).

Freezing data. Low-temperature phase transitions may be understood from a study of the system Na_2SO_4–NaCl–H_2O (Pascal, 1966). The eutectic point (−31.5 to −35 °C) is significantly lower than the lowest invariant point of the system (with hydrohalite + ice + mirabilite at −21.7 °C), indicating significant amounts of other cations. This result was confirmed by a preliminary qualitative energy-dispersive microprobe analysis of frozen inclusions (courtesy C. Ayora), indicating the presence of Na, Cl, S and Mg. Accordingly, Mg^{2+} is probably the extra cation.

Solids formed on freezing include: (*a*) hydrohalite (metastable melting to +12 °C); (*b*) probable mirabilite (dissolution at +17 °C, very near the mirabilite–thenardite transition at 17.9 °C in halite-saturated brines), and (*c*) possible bloedite, $Na_2Mg(SO_4)_2.4H_2O$ (dissolution in the range +24 to +41 °C). In conclusion, the trapped brines belong to the Na_2SO_4–NaCl–$MgCl_2$–H_2O system and were near halite saturation at the time of entrapment.

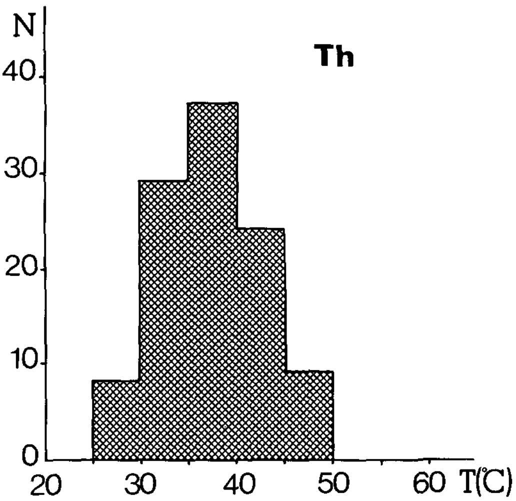

FIG. 1. Histogram of the homogenization temperatures of primary brine inclusions in thenardite from New Agorgott.

Heating data. About 110 determinations of homogenization temperature (T_h) have been obtained. As fluid inclusions in thenardite are abundant, most of the samples used for freezing were later discarded. When an inclusion was subjected to both heating and freezing, heating was carried out first. Accordingly, no damage resulting from 'freeze-stretching' may be invoked. The results (Fig. 1) range from 28.3 °C to 50.5 °C, with a mean value of 37.5 °C. Fig. 2 shows T_h values for one sample in which there is a large gradient, from 29.5 °C at the top to 43.9 °C at the bottom. We suggest that this T_h distribution reflects a differential sun exposure at the time of sampling. Unfortunately, the effect of sun irradiation had not been suspected when the thenardite samples were collected and we were unable to investigate fluid inclusions in unexposed crystals.

A microthermometric investigation of fluid inclusions in thenardite from the Grizim Sebkha, Erg Chech, Sahara (Sabouraud, 1975) led to essentially similar results, with T_h from 30 to 55 °C, and most of the data in the range 38 to

44 °C. Referring to the variation of the thenardite solubility with temperature, Sabouraud suggested that, on slow natural cooling, Na_2SO_4 formed on the inclusions walls; during rapid heating runs, a range of T_h values would then arise if re-equilibration had not been attained.

However, if the median values of the T_h histogram (in the Grizim case 38 to 44 °C) are supposed to correspond to the mean trapping temperatures, the former hypothesis cannot explain temperatures in the interval 44 to 55 °C, and another explanation is required. For these reasons, an experimental investigation of stretching, corresponding to possible overheating after exposure to the sun, was carried out. Furthermore, in order to check the 'lack of re-equilibration' hypothesis, thenardite chips in which T_h had been measured were stored for about 8 months at +5 °C. Further T_h measurements repeated on the same inclusions gave values only about 1 °C lower than the earlier determinations.

Stretching experiments

Overheating experiments at different heating rates were carried out after total homogenization (at Th_1) on a Chaix-Meca heating stage. Overheating (T_{Oh}), i.e. the difference between the highest temperature reached by the sample and Th_1, varied from 5 to 170 °C. Later determinations of homogenization temperatures were performed after several hours, days or months (maximum duration 8 months) of storage at about +5 °C.

A plot of $Th_2 - Th_1$, the difference between homogenization temperatures after and before experimental overheating is given in Fig. 3.

Three main conclusions may be drawn:

(i) Overheating in the range 20 to 60 °C is strongly correlated with $Th_2 - Th_1$. The correlation line intersects the horizontal axis at about 10 °C.
(ii) Minor overheating (less than about 10 °C) is not recorded.
(iii) High overheating leads to significant scattering of the former linear correlation.

These data may be easily explained by transition at increasing T_{Oh} (and hence at increasing internal pressure), from elastic, to semi-plastic, then plastic deformation.

We note that no control of the stretching process by the size of inclusions has been observed. This result is in contrast with other experiments concerning smaller inclusions in fluorite (Bodnar and Bethke, 1984; Guilhaumou *et al.*, 1987). In thenardite, large inclusions (50 to 300 μm) have been studied; we suggest that above some (unknown) upper limit, stretching of inclusions in this brittle salt is no longer size-dependent. A reason for this could be that, above this limit, the number of defects where plastic deformation may initiate per unit area becomes constant.

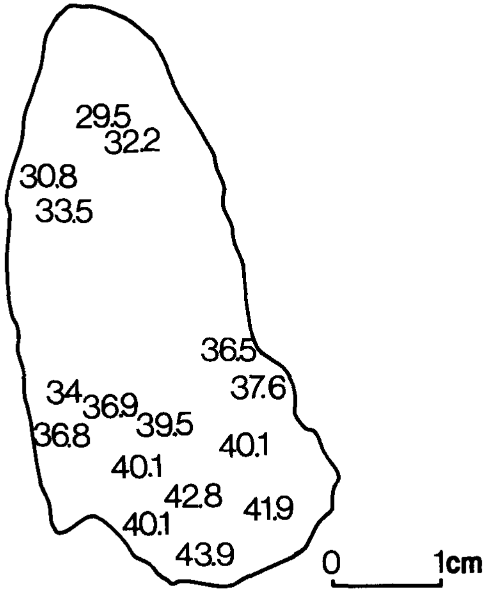

FIG. 2. Variations of Th within a thenardite monocrystal. Notice the large gradient from the bottom (supposed to be exposed to sun irradiation) to the top (supposed to be hidden).

Interpretation and conclusions

Most homogenization temperatures of primary fluid inclusions in thenardite from New Agorgott are in the range between +30 and +50 °C (mean value 37.5 °C). An experimental investigation of stretching after overheating suggests that such values probably result from variable sun exposure under desert conditions. In this respect, with an hypothetical initial Th_1 value of +28 °C and homogenization at $Th_2 = +50$ °C, one has: $Th_2 - Th_1 = 22$ °C. From Fig. 3, we deduce that $T_{Oh} = 40$ °C and hence thenardite temperatures of 28 °C + 40 °C (i.e. about 70 °C) occurred during exposure to the sun, in agreement with present desert surface conditions.

Accordingly, the histogram in Fig. 1 is assumed to be representative of the present climate, but only the lowest T_h (30 °C or less) is possibly indicative of palaeoclimatic conditions. The age and formation temperature of the studied crystals are theoretically correlated, because of the recent

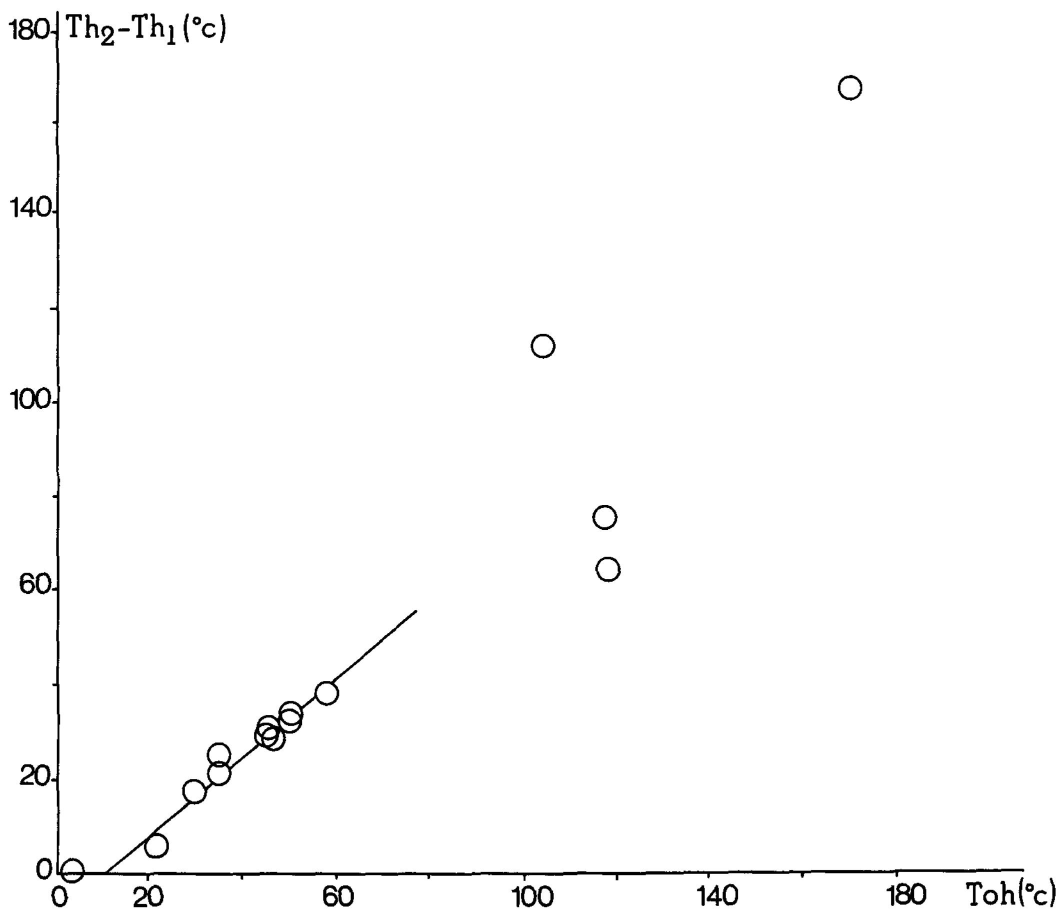

FIG. 3. Plot of overheating with the correlative *Th* rise ($Th_2 - Th_1$). See text.

climatic variations in the Taoudenni area (Fabre and Petit-Maire, 1988). There is no doubt that evaporitic thenardite formed about 7000 y.BP, at the onset of a climatic deterioration after a wet phase (disseminated Na_2SO_4 associated with glauberite, bloedite, halite, and magnesite in lake sediments). However, the size and shape of the studied crystals suggest that they formed after dissolution, probable migration, and recrystallization of former Na_2SO_4 during some unknown period. Two extreme hypotheses may be put forward:

(i) Early recrystallization, at about 7000 y.BP, under arid conditions.

(ii) Late recrystallization, after about 3000 y.BP, under desert conditions (the most probable hypothesis). In this respect the data displayed in Fig. 2 suggest that the T_h values at about 30 °C are 'unstretched' values, representative of desert conditions (Monod, 1938).

A re-sampling of thenardite, with storage in heat-insulated boxes, would be necessary for a definite conclusion. However, the data presented in this article strongly suggest that thenardite rosettes formed at New Agorgott under desert conditions, i.e. since 3000 y.BP.

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