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Fluid Inclusions in Zechstein Evaporite Minerals from the Asse Salt Anticline (NW-German Basin): A Preliminary Report of MT, LRM, FTIR and SEM Results

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ABSTRACT

Microthermometric and microspectroscopic investigations were carried out on Zechstein evaporite minerals from the Asse salt mine, SE of Braunschweig (NW German Basin) in order to examine the diagenetic development and migration processes of fluid systems in salt diapirs.

Extracting and measuring the ion content of the solutions is only possible for inclusions > 250 μm. Therefore different analytical methods have been used to study the composition of single inclusions in the range 5–200 μm. Microthermometry (MT), laser Raman microspectroscopy (LRM) and infrared microspectroscopy (FTIR) are used to characterize and analyze the liquid, gas and solid phases in fluid inclusions.

Monophase inclusions (liquid or vapor), two-phase inclusions (liquid + vapor or liquid + daughter crystal) and multiphase inclusions (liquid + daughter crystals ± vapor) are observed. For primary multiphase inclusions in chevron structures the estimated salinities are > 40%, whereas the salinities of mono- or two phase secondary inclusions range from 26 to 33 wt.% $NaCl_{eq}$. They all belong to the Ca-Mg-(K) system, saturated with respect to NaCl. SEM analyses of the precipitates from decrepitated inclusions confirm the presence of these elements. Variations in fluid composition indicate mixing of fluid solutions with lower salinity formation or diagenetic waters.

Homogenization temperatures of 40–60°C may indicate the halite crystallization temperature. Daughter crystals of anhydrite, kieserite, carnallite and polyhalite were identified by Raman spectroscopy. Additionally, equimolar mixtures of CH_4 and N_2 have been detected in fluid inclusions in anhydrite and halite by LRM. FTIR spectra of primary and secondary inclusions show different absorption bands for the bending and stretching frequency of the water molecule, reflecting differences in anion content.

INTRODUCTION

A number of destructive techniques have been applied to study the composition of fluid inclusions in salt minerals, extraction by dissolution (e.g. Roedder, 1958; Kramer, 1965; Petrichenko, 1973), heating/decrepitation in vacuum (e.g. Knauth and Kumar, 1981) and extraction of single inclusions (e.g. Holser, 1963; Lazar and Holland, 1988; Herrmann et al., 1991).

Non-destructive analysis such as microthermometry (MT) (e.g. Roedder, 1984a; Stein, 1985; Lowenstein and Spencer, 1990), laser Raman spectroscopy (LRM) (Rosasco and Roedder, 1979; Dubessy et al., 1982, 1983; Higgins and Stein, 1986; Grishina, 1987; Mernagh and Wilde, 1989) and infrared spectroscopy (FTIR) (Götzinger, 1990; Pironon and Barres, 1990; Wopenka et al., 1991) were also used for qualitative and semiquantitative analyses of gas and liquid phases in inclusions in halite.

A knowledge of the solution content of single inclusions provides valuable information on the genesis of evaporites, the chemical transport mechanisms and possible pathways for fluids.

The composition of solutions in caverns and fissures of evaporites is known from earlier studies, whereas the content of single fluid inclusions, ranging in size from 1 to larger than 500 μm occurring in evaporite minerals, are more difficult to examine. In order to analyze individual fluid inclusions, several destructive and non-destructive methods have been applied. Destructive methods are essentially restricted to inclusions larger than 250 μm. Therefore, these data provide only information on one particular group of inclusions, and are not representative of the overall fluid content. In most cases several inclu-

sion types (primary, secondary) occur in evaporite minerals. Most fluid inclusions are smaller than 250 μm and MT, LRM and FTIR are the best methods to characterize and analyze these inclusions. These methods make possible the analysis of liquid, gas and solid phases.

GEOLOGICAL SETTING AND SAMPLE DESCRIPTION

The first investigations were carried out on samples from the Asse salt mine, SE of Braunschweig (NW-German Basin). The Asse mine is used as a testing site for the final disposal of radioactive waste in the Z2 "Staßfurt-Steinsalz" and is managed by GSF GmbH, München.

The lithological facies of the evaporite series in the Asse generally differs from that of the North German Zechstein Basin, namely by an increase in polyhalite content in the upper part of the "Staßfurt" layer and the local sedimentation of the "Tonlinien-salz". The Zechstein 3 is characterized by a loss of potash seams. The salt anticline consists of layered salts in the lower part (>2000 m) and of diapiric salt in the main salt dome. The samples were taken from the Zechstein layers Z1–Z3.

FLUID INCLUSIONS

Three types of fluid inclusions can be distinguished, namely monophase inclusions (liquid or vapor), two-phase inclusions (liquid + vapor or liquid + daughter crystal) and multiphase inclusions (liquid + daughter crystals ± vapor). The sizes range from <1 μm to >200 μm, whereas most inclusions are in the range 5–35 μm. Primary, multiphase inclusions are normally arranged in chevron structures, as shown in Figs. 1a and 1b. Secondary inclusions are in general flat, mono- or two-phase inclusions, on healed grain boundaries (inclusion films or chains). In some cases multiphase inclusions filled with anhydrite crystals have textures similar to secondary.

ANALYTICAL METHODS AND PRELIMINARY RESULTS

Microthermometry

The most common study method applied to fluid inclusions is microthermometry. This technique allows the measurement of phase transitions temperatures in inclusions. In this study a LINKHAM TH 600 heating/cooling stage was used for microthermometric analysis in the temperature range of –185°C to +400°C.

Interpretations of fluid inclusion phase equilibria

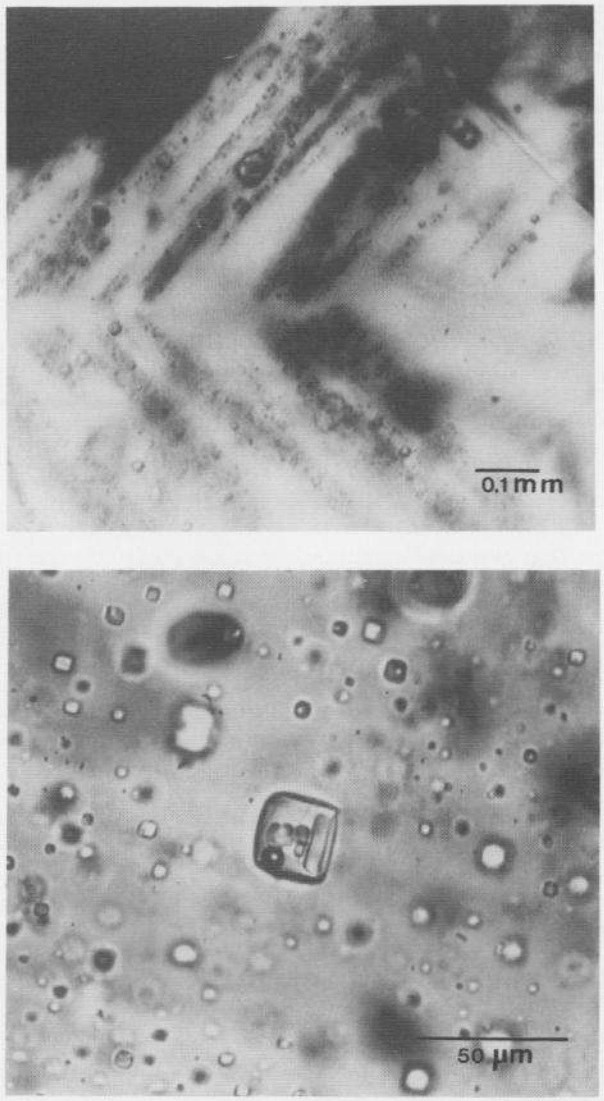

Fig. 1. Top: (a) Chevron structure in halite with inclusion-rich (dark) and inclusion-poor (light) growth bands. Bottom: (b) Primary multiphase inclusion containing anhydrite (prismatic crystal) and kieserite daughter crystals, gas phase consists of CH_4.

are based on experimental data of salt-water systems. For example inclusions containing $CaCl_2$ are generally characterized by low initial melting temperatures (Te). For the system $CaCl_2$-NaCl-H_2O the ternary eutectic temperature is –55°C, whereas fluid inclusions containing NaCl±KCl±$MgCl_2$ have eutectic temperatures between –21 and –35°C. Table 1 summarizes the phase data for salt-water systems most relevant to aqueous fluid inclusions (Shepherd et al., 1985).

Phase changes in the negative temperature range are sometimes difficult to determine, and in some cases no freezing could be observed. Most inclusions show only phase changes after several freezing runs.

TABLE 1

Eutectic temperatures of salt systems

Salt system	Eutectic temperature (°C)
H_2O-NaCl	–21.2
H_2O-NaCl-KCl	–23.5
H_2O-NaCl-$MgCl_2$	–35
H_2O-$MgCl_2$-$CaCl_2$	–52.2
H_2O-NaCl-$CaCl_2$	–55

All these inclusions seemed to be syrupy and highly viscose at room temperature. Roedder (1984b) found that this metastable behaviour is typical for solutions saturated with the chlorides of Na, K, Mg and Ca.

All primary inclusions containing daughter crystals are genetically linked to a higher evaporation state, like kieserite or carnallite. Therefore their salinity should be higher than for mono- or two-phase secondary inclusions which contain none of the daughter crystals mentioned. Based on the extremely low Te-values the fluid inclusion are interpreted in terms of the system $CaCl_2$/$MgCl_2$-NaCl-H_2O. By using the $CaCl_2$-$MgCl_2$-H_2O diagram after Yanatieva (1946) the melting temperatures of hydrated phases, determined as $CaCl_2$ and $MgCl_2$-hydrates indicate a Ca/Mg ratio of approximately 1:1, with a total salinity of the inclusion fluids greater than 40% (NaCl+$MgCl_2$+$CaCl_2$).

During cryometric investigations in secondary mono- and two-phase inclusions the eutectic temperature, the melting of ice and hydrohalite could be observed. Te and Tm ice values ranges from –87 to –38°C and –37 to –21°C, respectively. Hydrohalite melting is observed in the range of –5 to +1°C. Eutectic temperatures <–75°C indicate the presence of divalent cations such as Ca and Mg. Experimental investigations on the systems $CaCl_2$-NaCl-H_2O and $MgCl_2$-NaCl-H_2O (Davis et al., 1990) reveal that these low eutectics may be due to the melting of metastable salt hydrates.

The variation of the Ca/Na ratios for secondary inclusions indicate a Ca–Na interchange whereas the equilibration of younger secondary inclusions tends to lower Ca/Na ratios. Dilution with water of lower salinity, like formation or diagenetic water (dehydration water from the transition of gypsum to anhydrite), may be responsible for this effect. Secondary inclusions with daughter crystals of anhydrite indicate dissolution of easily soluble salts remaining in NaCl solutions and low soluble anhydrite. The calculated salinities for secondary inclusions are 26–33 wt.% $NaCl_{eq}$. Figure 2 shows the microthermometric data of secondary inclusions plotted in the $CaCl_2$-NaCl-H_2O diagram. Tie-lines show the limits of cation ratios.

In some inclusions the salinity was determined by the melting temperatures of halite daughter crystals in the range of +9 to +56°C and indicate salinities greater 26 Gew.% $NaCl_{eq}$.

Assuming that the volume of an inclusion remains constant and the inclusion remains isolated, cooling of the inclusion will result in the shrinkage of the fluid. This results in the formation of a two-phase (liquid/vapor) inclusion. By measuring the disappearance of the vapor bubble (homogenization temperature Th) it is possible to determine the minimum trapping temperature of fluid inclusions, if no stretching or leakage affect the original PVT-conditions.

The homogenization temperatures show two frequency maxima at 50 and 110°C. Th data in the range 20–60°C may indicate halite crystallization temperatures and trapping temperatures of the inclusions. This is in a good agreement with the melting temperatures of halite daughter crystals, which may indicate original trapping temperatures.

Higher temperatures are due to re-equilibration effects or originate from stretching during heating and freezing runs. Another possibility is that the higher Th values originate from the subsidence stage of the evaporites.

Laser Raman spectroscopy

In order to identify the daughter crystals, gas species and dissolved sulphates in fluid inclusions LRM investigations were carried out. All investiga-

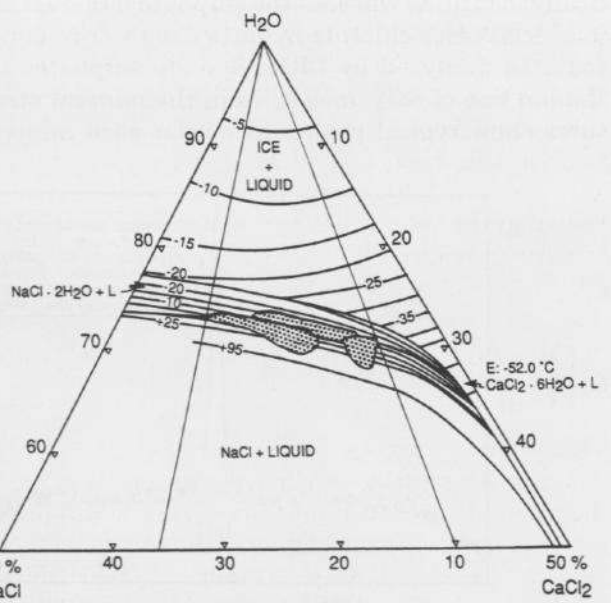

Fig. 2. The ternary system $CaCl_2$-NaCl-H_2O with plotted data for secondary inclusions. Tie-lines mark the limits of Ca/Na ratios in the fluid inclusions.

tions were done with the RAMANOR U 1000 laser Raman microprobe supplied with a multi-channel detector. An Olympus microscope with magnification of 50x to 150x enables the analysis of single inclusions of less than 5 μm. The excitation line of the laser is 514.4 nm with a laser power of 500 mW. Normally the duration for single measurements is 10–200 s. Semi-quantitative analysis, especially for gas mixtures, is achieved from relative Raman cross scattering sections and peak areas.

Raman analysis of dissolved phases

Dissolved sulphate (SO_4^{2-}) could be determined by the Raman line at 982 cm^{-1}. The ratio between intensities of the Raman lines of the H_2O- and the SO_4^{2-} molecule were used for the semi-quantitative analysis of the dissolved sulphate in fluid inclusions as shown by Higgins and Stein (1986). Preliminary calibrations were carried out on standard solutions but were insufficient to be discussed here.

Under cryometric conditions it is possible to analyze the frozen hydrates of the dissolved solutions (Dubessy et al., 1982). First examinations in the temperature range of –120 to 0°C have shown that Ca-hydrates exist in solutions of secondary inclusions. This is in good agreement with the observed microthermometric data.

Daughter crystals

The multiphase (primary) inclusions, normally arranged in chevron structures, contain one to three different daughter crystals. NaCl and KCl were optically identified whereas the sulphate minerals and in special cases chloride-hydrate daughter minerals could be analyzed by LRM. For the sulphates the Raman line of SO_4^{2-} molecules in the mineral structures show typical peak maxima for each mineral.

TABLE 2

Raman peak positions of analyzed daughter minerals in fluid inclusions in halite

Identified mineral	Raman peak position (cm^{-1})
Anhydrite ($CaSO_4$)	1017
Kieserite ($MgSO_4\,H_2O$)	1043
Carnallite ($KMgCl_3\,6H_2O$)	1643/3430
Glauberite ($Na_2Ca(SO_4)_2$)	1000
Polyhalite ($K_2MgCa_2(SO_4)_4\,2H_2O$)	988/1012

Figures 3a and 3b show Raman spectra of anhydrite and kieserite daughter crystals in a primary fluid inclusion. Chloride-hydrate minerals such as carnallite could be identified by analyzing the shift of the stretching frequency (ν1 + ν3) at 3400 cm^{-1} and the bending frequency (ν2) at 1640 cm^{-1} of the H_2O molecule. Wave numbers were calibrated by detection of silicon and diamond standards. Minerals in fluid inclusions identified by LRM are summarized in Table 2. To identify the daughter crystals in inclusions, 20 common evaporite minerals were analyzed by LRM.

Gas phases in fluid inclusions

In the anhydrite-layer of Z1 (Werra-anhydrite) gas-inclusions of equimolar mixtures of N_2-CH_4 were observed. The inclusions are monophase at room temperature with an average size of 10 μm. Raman lines at 2331 cm^{-1} and 2917 cm^{-1} reveal equimolar mixtures of N_2 and CH_4. Critical homogenization takes place between –108 to –100°C and indicates low densities (~0.3 g/cm^3).

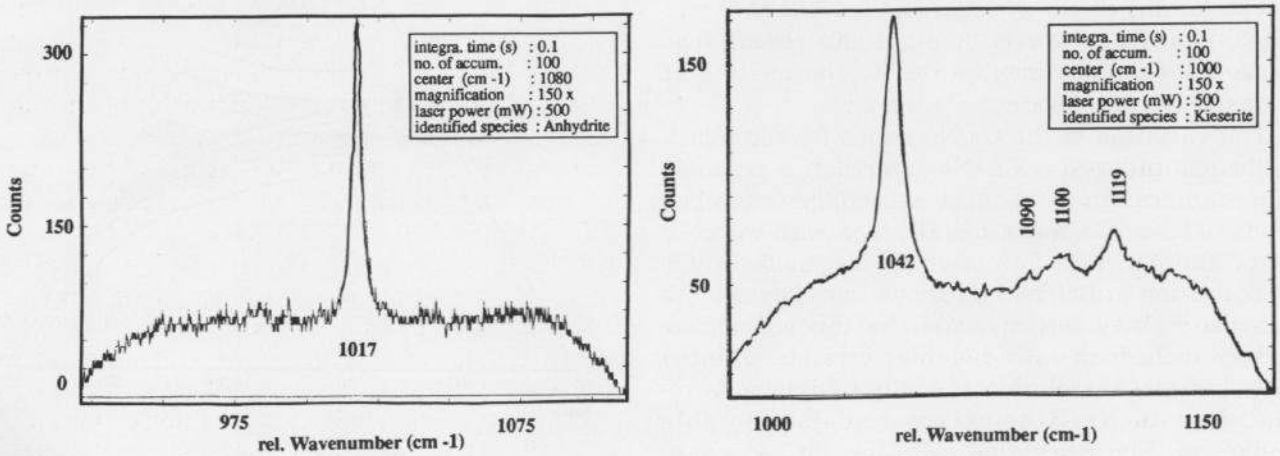

Fig. 3. Left: (a) Raman spectrum of an anhydrite daughter crystal in a primary inclusion. Right: (b) Raman spectrum of a kieserite daughter crystal in a primary inclusion.

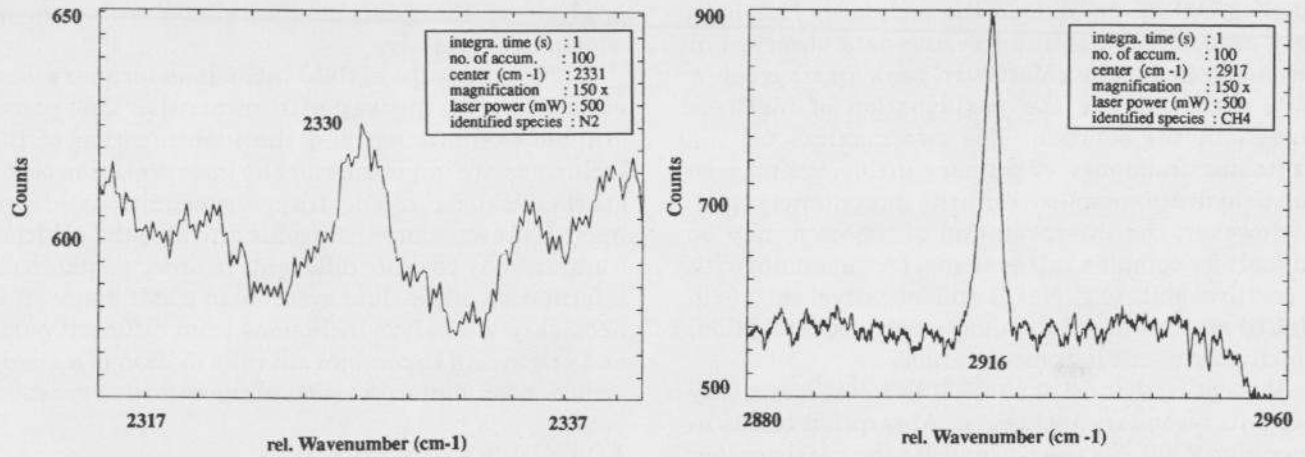

Fig. 4. Left: (a) Raman spectrum of CH_4 in an inclusion in halite (see text for explanation). Right: (b) Raman spectrum of N_2 in an inclusion in halite (see text for explanation).

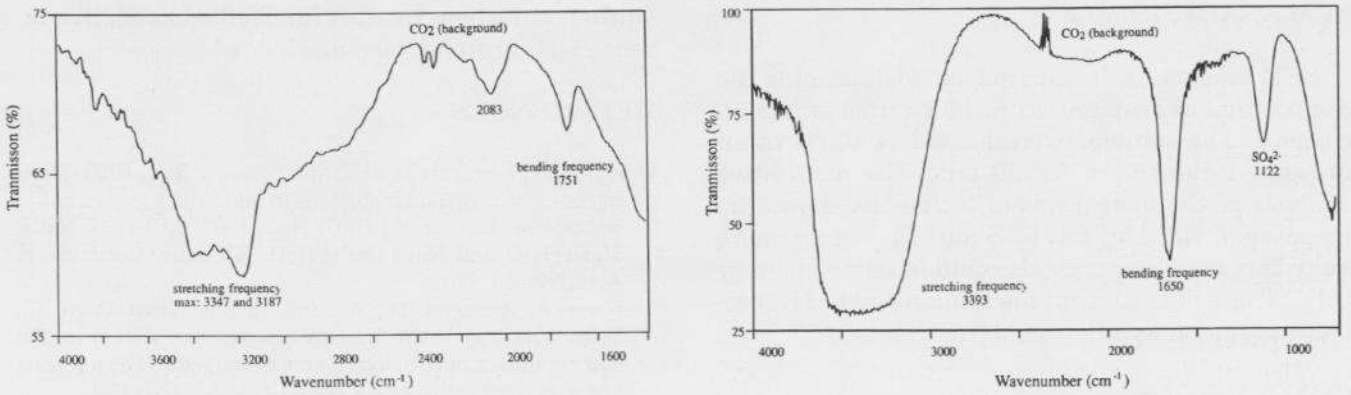

Fig. 5. Left: (a) IR-spectrum of a primary multiphase inclusion (22 x 20 μm) (see text for explanation). Right: (b) IR-spectrum of a secondary monophase inclusion (18 x 20 μm) (see text for explanation).

Preliminary results on the vapor phase in inclusions in halite chevron structures indicate similar compositions for two-phase inclusions (liquid + vapor) with vapor/liquid ratios greater than 50%. Multiphase inclusions have lower vapor/liquid ratios (5–10%) and the vapor phase consists of CH_4 only. Figures 4a and 4b show Raman spectra of CH_4 and N_2 in two-phase inclusions in halite.

Infrared microspectroscopy (FTIR)

The measurements were done using a Perkin Elmer 1760x FTIR spectrometer in the mid-IR range of 4000–700 cm^{-1}.

The analysis of fluid inclusions by means of FTIR, just as LRM, is easier in the present samples, because halite is not IR/LRM-active. In this case it is possible to analyze single inclusions by FTIR. The spectra reflect differences in anion content of the liquid solution and show absorption bands of daughter crystals in multiphase inclusions. Figures 5a and 5b show the different IR-spectra of primary and secondary inclusions in halite.

Primary inclusions found in the layered salt from the lower part of the Asse show two absorption maxima at 3150±5 cm^{-1} and 3390±5 cm^{-1} for the stretching frequency of the H_2O-molecule. The absorption maxima for the bending frequency are in the range 1745–1750 cm^{-1}. Secondary inclusions from the main diapir show different absorption bands for the stretching and bending frequency of the water molecule, with absorption maxima in the range between 3390 and 3450 cm^{-1} and mean values of 3420±10 cm^{-1} and 1678–1690 cm^{-1}.

The stretching frequency of distilled water is 3400 cm^{-1}. For a solution containing 26.6 g/100 ml NaCl the absorption maxima shifts to 3430 cm^{-1} (Rossmann, 1988). Götzinger (1990) reported a positive frequency shift of the stretching mode for saline solutions in fluid inclusions in fluorite with increasing NaCl concentration in solution. On the basis that only NaCl is responsible for the positive peak-shift, the absorption maxima for the mean value indicates

10–25 g/100 ml dry salt in the inclusion. This is in good agreement with the freezing data observed in secondary inclusions. Moreover, peak maxima below 3400 cm^{-1} indicate the participation of $MgCl_2$ ± $MgSO_4$ in the solution. The two maxima for the stretching frequency of primary inclusions may be due to hydrate complexes or little daughter crystals.

However, the interpretation of the data may be difficult for complex salt systems, because salts with a 'positive' shift (e.g. NaCl) and 'negative' shift (e.g. $MgCl_2$) are combined in equal molar concentration, which may result in compensation.

Absorption bands of SO_4^{2-} (1122 cm^{-1}) are only found in secondary inclusions. Absorption bands in the range 2900–3000 cm^{-1} indicate the participation of organic material (e.g. CH_4). A combination frequency for water was observed at 2130 cm^{-1}.

SEM ANALYSIS

SEM analyses were carried out to determine the composition of evaporation residues from single inclusions. The samples were heated to 400°C in an evacuated glass tube for 30 min. The qualitative analysis of the evaporates of inclusions shows the presence of Na, Mg, Ca, K, S and Cl. Furthermore anhydrite daughter crystals could be determined by SEM. These data confirm the Raman and FTIR spectroscopic and microthermometric results.

CONCLUSIONS

The methods that have been used are a useful tool for inclusion studies to obtain information about fluid genesis in evaporite minerals in a relative short time.

If the analytical method is restricted by the inclusion size, valuable information about the trapping conditions on smaller inclusions (<250 μm) could be lost. Larger inclusions (>250 μm) are genetically linked to recrystallization processes, and therefore represent only one of the last stages of a complex fluid evolution. Normally the trapped inclusions are smaller than 50 μm and therefore the analytical methods used here are helpful to characterize different inclusion groups.

Variation in cation content of inclusion fluids can be determined by MT and can be confirmed by SEM analysis of evaporation residues. Additionally FTIR analysis will show the differences in anion content of inclusion fluids. Daughter crystals can be detected by LRM as well as dissolved sulphate and gas phases. Furthermore, the combination of microthermometry and Raman spectroscopy are currently the most powerful methods for the semi-quantitative analysis of the gas phase of single inclusion, as shown in this study.

Different groups of fluid inclusions (primary, secondary) occur in evaporite minerals. The petrographic examination and the identification of the inclusions are important for the interpretation of the geochemical data. The trapping conditions of primary and secondary inclusions and also the solution contents may be quite different. In order to obtain all information of the fluid systems in a salt diapir, it is necessary to analyze inclusions from different parts and origin and to combine all information of a single inclusion for a interpretation of the inclusion genesis.

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