

Unexpected phase assemblages in inclusions with ternary H₂O-salt fluids at low temperatures

Research Article

Ronald J. Bakker *, Miriam Baumgartner

*Resource Mineralogy, Department of Applied Geosciences and Geophysics
University of Leoben, Peter-Tunner-Str. 5, 8700, Leoben, Austria*

Received 27 October 2011; accepted 15 December 2011

Abstract: Phase assemblages and temperatures of phase changes provide important information about the bulk properties of fluid inclusions, and are typically obtained by microthermometry. Inclusions are synthesized in natural quartz containing an aqueous fluid with a composition in the ternary systems of H₂O-NaCl₂-CaCl₂, H₂O-NaCl-MgCl₂, and H₂O-CaCl₂-MgCl₂. This study reveals that these fluid inclusions may behave highly unpredictably at low temperatures due to the formation of metastable phase assemblages. Eutectic temperatures cannot be detected in most of the fluid inclusions containing these ternary systems. Nucleation of a variety of solid ice and salt-hydrate phases in single fluid inclusions is often partly inhibited. Raman spectroscopy at low temperatures provides an important tool for interpreting and understanding microthermometric experiments, and visualizing stable and metastable phase assemblages. Final dissolution temperatures of ice, salt-hydrates, and salt must be treated with care, as they can only be interpreted by purely empirical or thermodynamic models at stable conditions.

Keywords: fluid inclusions • phase equilibria • microthermometry • metastability • ternary fluid systems • H₂O-NaCl-CaCl₂ • H₂O-NaCl-MgCl₂ • H₂O-CaCl₂-MgCl₂ • Raman spectroscopy

© Versita Sp. z o.o.

1. Introduction

Natural fluid inclusions do not contain a single component fluid system. Dissolved salts, especially chlorides, including NaCl, CaCl₂, and MgCl₂, that reluctantly integrate into crystal lattices of host minerals, such as quartz and calcite, are major components in natural aqueous fluid systems, e.g. [1, 2]. These solutes have a significant influence on fluid properties; therefore, the identification of dissolved salts is a major objective in fluid inclusion research. Ion-chromatographic and microthermometric analyses of aqueous fluid inclusions are commonly used to

identify the type and amount of electrolytes dissolved. Identification using microthermometry is based on final dissolution temperatures of precipitated phases, such as ice and salt hydrates, in addition to first dissolution temperatures, i.e. eutectic conditions, e.g. [3].

Experimental data in the binary H₂O-NaCl, H₂O-CaCl₂, and H₂O-MgCl₂ systems have been described in a variety of publications [4, 5]. Stable phase assemblages are predicted with thermodynamic models of activity coefficients, e.g. [6, 7] and purely empirical best-fit equations, e.g. [8–10] in a wide range of compositions, temperatures, and pressures. Nevertheless, fluid inclusions studies are often discussed in terms of ternary or multiple component systems, because they are more relevant for natural systems, e.g. [11].

*E-mail: bakker@unileoben.ac.at

The behaviour and properties of a ternary H₂O–NaCl–CaCl₂ system in fluid inclusions in microthermometric experiments was modelled with activity coefficients of dissolved ions in aqueous solutions that were obtained from osmotic coefficients [6, 7, 12] at relative low salinities. In addition, this ternary is modelled with purely empirical equations [13–15] that cover only part of the compositional variation. The H₂O–NaCl–MgCl₂ system was only modelled for H₂O-rich compositions [6, 10] at temperatures below 25°C. Reliable purely-empirical modelling of the ternary system H₂O–CaCl₂–MgCl₂ is not possible due to the lack of experimental data [16, 17]. A thermodynamic model of activity coefficients [6] provides only limited information about this ternary system below 25°C.

Many of the previous studies illustrate that multi-component salt systems in fluid inclusions show various complex phase assemblages at low temperatures consisting of liquid, ice, and salt-hydrates independent of their composition [18–21]. Not all systems achieve stable phase assemblages upon cooling, more often metastable coexistence of phases is assumed based on observations of unexpected phase transition temperatures. The nature of a phase assemblage in fluid inclusions is difficult to identify by optical means; assemblages may represent both stable and metastable conditions. Furthermore, the presence of a specific phase, whether stable or metastable, can often not be determined by optical microscope observations [9, 22]. In this study, phases (liquid, ice, and salt hydrates) in fluid inclusions are identified by a combination of microthermometry and Raman spectroscopy according to the method described by Bakker [22]. In addition, phase changes are accurately characterized by changes in Raman spectra at low temperatures, see also [9, 22, 23]. Fluid inclusions with varying compositions are synthesized in natural quartz in the ternary systems H₂O–NaCl–CaCl₂, H₂O–NaCl–MgCl₂, and H₂O–CaCl₂–MgCl₂, to study the formation of stable and metastable phase assemblages during microthermometric experiments.

2. Methods

Fluid inclusions were synthesized in natural quartz using a crack healing process [24] at about 600°C at pressures ranging from 123 and 269 MPa, depending on the salinity and composition of the fluid (Table 1). The experimental conditions are selected in the fluid one-phase field, in order to synthesize a homogeneous assemblage of fluid inclusions.

Microthermometry was performed with a LINKAM MDS 600 heating-freezing stage attached to an optical microscope. The sample chamber was

cooled to –190°C using liquid nitrogen. The stage was calibrated with synthetic fluid inclusions of CO₂ (melting at –56.6°C) and H₂O (melting at 0.0°C and critical homogenisation at 374.0°C). The analytical precision of the measurements is about 0.2°C. All observations were made with an Olympus 100x long-working-distance objective (LMPlanFI, 0.80 numerical aperture).

Raman spectroscopy was used to identify the nature of phases, which were subjectively optically characterized. Furthermore, the temperature of phase transitions (i.e. eutectic and melting points) was determined by changes in Raman spectra in a microthermometric heating experiment [9, 22]. A LINKAM THMSG 600 stage was combined with the Raman spectrometer to perform heating and freezing experiments. Identification of fluid and solid species was performed with a LABRAM (ISA Jobin Yvon) instrument using a frequency-doubled 120 mW Nd-YAG laser with an excitation wavelength of 532.2 nm. Raman spectroscopy was primarily applied to species yielding wavenumbers ranging from 2800 to 4000 cm^{–1}, where the variety of salt hydrates, ice, and aqueous liquid solutions can be characterized by specific spectra. The phases in this study were identified with standard Raman spectra as illustrated in Bakker [22], including water, brine, ice, hydrohalite, MgCl₂ hydrates, and metastable phases, such as super-cooled water and a glassy brine, and, and in Baumgartner and Bakker [25], including ice, hydrohalite, CaCl₂ hydrates, and MgCl₂ hydrates.

3. Ternary aqueous systems with two types of salt

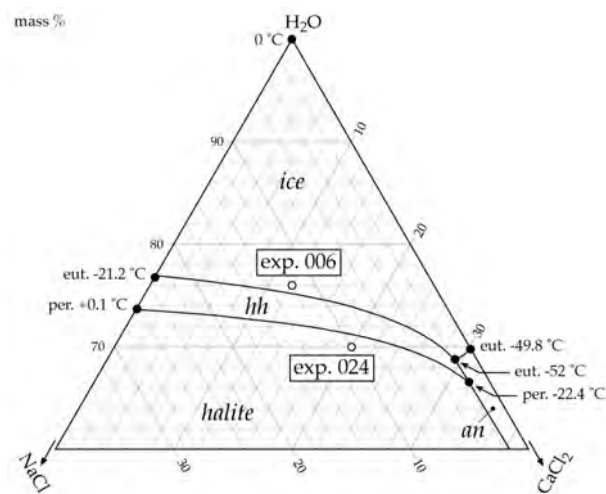
3.1. H₂O–NaCl–CaCl₂ system

The H₂O–NaCl–CaCl₂ fluid system was modelled with purely empirical best-fit equations [13–15] and with activity coefficients [6, 7]. Isotherms below room temperature in the ternary composition diagram of this system that can be constructed with these models are divided into several fields: (1) ice; (2). hydrohalite; (3) halite; and (4) antarcticite (Figure 1). The solid phase indicated in the fieldname is the last phase that dissolved in the aqueous liquid solution upon heating a fluid inclusion. Metastable dissolution processes are not illustrated in Figure 1. These can only be modelled by extrapolation of the individual fields into adjacent fields. The purely empirical best-fits are partly not suitable for these extrapolations, e.g. [13, 15], whereas others display reasonable extensions into metastability, e.g. [14].

Two syntheses were performed in the ternary system of NaCl–CaCl₂–H₂O: *Exp 006* with an initial fluid compo-

Table 1. Experimental conditions of synthesis of fluid inclusions within ternary H₂O-salt systems. FI No. are the number of fluid inclusions that are analyzed with microthermometry and Raman spectroscopy.

Ternary System	Exp. No.	mass % NaCl	mass % CaCl ₂	mass % MgCl ₂	Exp. Pres. / MPa	Exp. Temp. / °C	FI No.
H ₂ O-NaCl-CaCl ₂	006	12	12	-	227.4 ± 0.8	600.2 ± 1.3	20
	024	10	20	-	268.8 ± 1.7	600.5 ± 0.7	20
H ₂ O-NaCl-MgCl ₂	033	10	-	13	156.8 ± 0.5	600.1 ± 0.1	20
	035	2	-	24	123.4 ± 0.1	600.1 ± 0.1	20
	038	10	-	13	200.3 ± 0.4	600.8 ± 0.2	27
H ₂ O-CaCl ₂ -MgCl ₂	050	-	10	10	164.1 ± 0.4	600.8 ± 0.9	20
	051	-	10	20	164.1 ± 0.4	599.5 ± 0.5	20

**Figure 1.** Ternary phase diagram of the H₂O-NaCl-CaCl₂ system with eutectic and peritectic temperatures (*eut.* and *per.*). Cotectic and peritectic lines divide the fields of ice, hydrohalite (*hh*), antarticite (*an*) and halite. The experimental conditions are illustrated for *Exp 006* and *Exp 024*.

sition of 12 mass % NaCl and 12 mass % CaCl₂ and *Exp 024* with an initial composition of 10 mass % NaCl and 20 mass % CaCl₂ (see Table 1 and Figure 1). In accordance with theoretical thermodynamic considerations, inclusions from *Exp 006* and *Exp 024* should freeze to a stable phase assemblage of hydrohalite (NaCl·2H₂O), antarticite (CaCl₂·6H₂O), and ice below the ternary eutectic temperature of -52°C. The composition of the first liquid phase during heating is highly depleted in NaCl and enriched in CaCl₂: 1.8 mass % NaCl and 29.4 mass % CaCl₂ (Figure 2) with antarticite completely dissolving in both experiments. During further heating, the composition of the aqueous liquid solution follows the cotectic line, as long as both ice and hydrohalite are present. Inclusions from *Exp 006* display a final dissolution of hydrohalite at -25.4°C with a brine of 12.4 mass % NaCl and

an equal amounts of CaCl₂ (Figure 2A), calculated with purely empirical equations [15]. The remaining ice crystal will eventually dissolve at -24.3°C, defining the final composition of the brine. Inclusions from *Exp 024* show final ice dissolution at -32.9°C at cotectic conditions in the presence of a 5.4 mass % NaCl and 21.8 mass % CaCl₂ brine (Figure 2B). At about -10.3°C, the remaining hydrohalite crystal begins to transform to halite by releasing H₂O. This transformation is completed at the peritectic line at -10.0°C. The final dissolution of halite took place at about +60°C, marking the final composition of the brine.

3.2. H₂O-NaCl-MgCl₂ system

The part of the H₂O-NaCl-MgCl₂ system with relatively low salinities can be modelled with purely empirical equations [10] and activity coefficients [6, 7]; the ice field, hydrohalite field and MgCl₂·12H₂O field (Figure 3). The halite field is only characterized by a limited amount of experimental data. This ternary system has a eutectic temperature of about -35°C [5] or -35.2°C [6].

Two compositions were selected to synthesize fluid inclusions: (1) 10 mass % NaCl and 13 mass % MgCl₂ (*Exp 033* and *038*) and (2) 2 mass % NaCl and 24 mass % MgCl₂ (*Exp 035*), close to the composition of the ternary peritectic point at -22.1°C (Table 1 and Figure 3). Cooling inclusions well below the eutectic temperature should initiate the precipitation of ice, hydrohalite, and MgCl₂·12H₂O. The first brine that appears on heating these fluid inclusions has an approximate composition of 4.7 to 5 mass % NaCl and 18 to 18.2 mass % MgCl₂ (eutectic brine). Consequently, this brine is depleted in NaCl for *Exp 033* and *Exp 038*, whereas it is diluted in both NaCl and MgCl₂ in *Exp 035* (Figure 4A and 4B). The MgCl₂·12H₂O phase is completely dissolved in *Exp 033* and *038* at eutectic conditions (Figure 4A), whereas the hydrohalite crystals dissolve completely in *Exp 035* (Figure 4B). During further heating, the composition of the brine in *Exp 033* and *038* moves along the ice-hydrohalite cotectic line, until

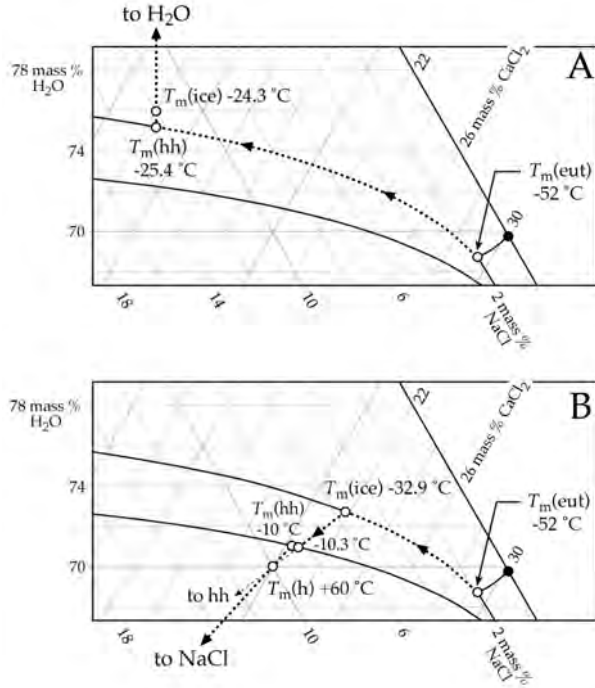


Figure 2. Theoretical compositional path (dashed lines) of the aqueous liquid solution in fluid inclusions from a heating experiment with Exp 006 (A) and Exp 024 (B). $T_m(\text{eut})$ is the eutectic temperature of the ternary system at -52°C . $T_m(\text{ice})$, $T_m(\text{hh})$ and $T_m(\text{h})$ are the final ice, hydrohalite, and halite dissolution temperatures, respectively.

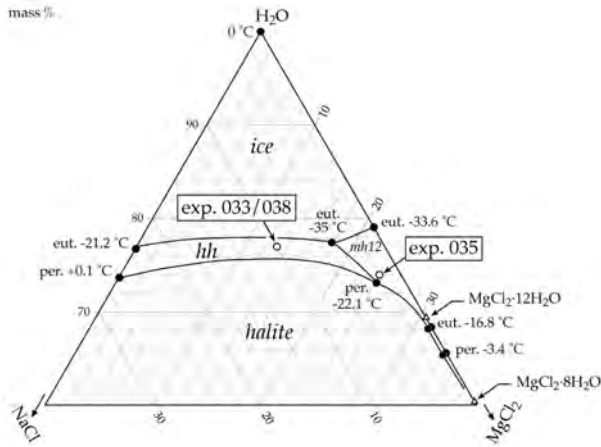


Figure 3. Ternary phase diagram of the H₂O-NaCl-MgCl₂ system with eutectic and peritectic temperatures (*eut.* and *per.*) Cotectic and peritectic lines divide the fields of ice, hydrohalite (*hh*), halite, and MgCl₂·12H₂O (*mh12*). The experimental conditions are illustrated for Exp 033, Exp 035, and Exp 038.

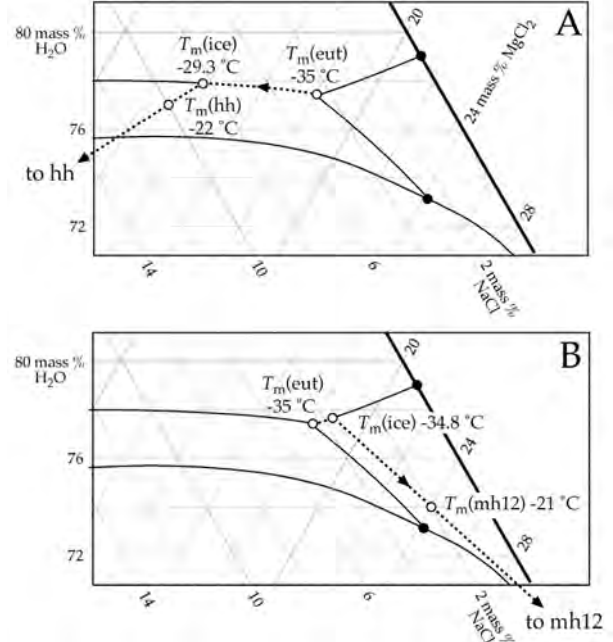


Figure 4. Theoretical compositional path (dashed lines) of the aqueous liquid solution in fluid inclusions from a heating experiment with Exp 033, Exp 038 (A) and Exp 024 (B). $T_m(\text{eut})$ is the eutectic temperature of the ternary system at -35°C . $T_m(\text{ice})$, $T_m(\text{hh})$ and $T_m(\text{mh12})$ are the final ice, hydrohalite and MgCl₂·12H₂O dissolution temperatures, respectively.

ice is completely dissolved at about -29.3°C (Figure 4A), where the brine has a composition of 8.2 mass % NaCl and 14.1 mass % MgCl₂. Isotherms in the hydrohalite field can only be estimated with thermodynamical modelling [6], and are used to calculate the final dissolution temperature of hydrohalite at about -22°C . The composition of the brine in fluid inclusions from Exp 035 moves along the ice-MgCl₂·12H₂O cotectic line upon further heating (Figure 4B). The ice will be completely dissolved at -34.8°C , corresponding to a brine composition of 3.7 mass % NaCl and 18.7 mass % MgCl₂. The remaining MgCl₂·12H₂O finally dissolves at about -21°C .

3.3. H₂O-CaCl₂-MgCl₂ system

Purely empirical equations are not available for the ternary H₂O-CaCl₂-MgCl₂ system. Isotherms in the ternary compositional phase diagram can only be constructed by interpolating scarce experimental data [4, 5, 16, 17] and modelling activity coefficients [6, 7] at temperatures below 25°C (Figure 5). This diagram contains 5 different fields at relative H₂O-rich compositions: (1) ice; (2) MgCl₂·12H₂O; (3) antarcticite; (4) MgCl₂·8H₂O; and

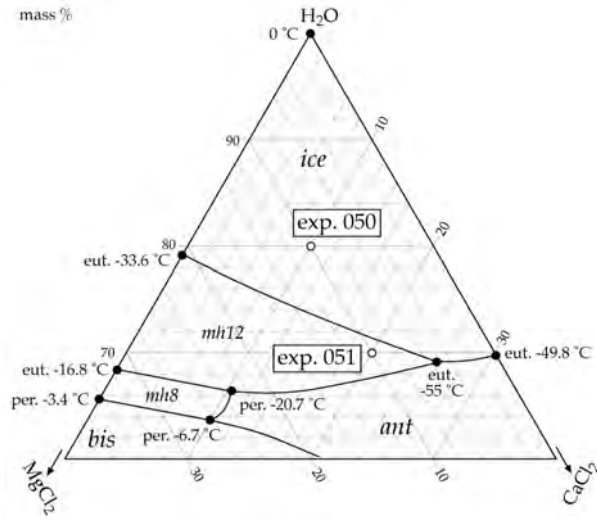


Figure 5. Ternary phase diagram of the H_2O - CaCl_2 - MgCl_2 system with eutectic and peritectic temperatures (*eut.* and *per.*) Cotectic and peritectic lines divide the fields of ice, $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ (*mh12*), antarctite (*ant*), $\text{MgCl}_2 \cdot 8\text{H}_2\text{O}$ (*mh8*), and bischofite (*bis*). The experimental conditions are illustrated for Exp 050 and Exp 051.

(5) bischofite, each separated by a variety of cotectic and peritectic lines.

Fluid inclusions are synthesized with a composition of 10 mass % CaCl_2 and 10 mass % MgCl_2 in Exp 050 and a composition of 10 mass % CaCl_2 and 20 mass % MgCl_2 in Exp 051 (Table 1 and Figure 5). The ternary eutectic temperature of this system is -55°C [17] with a brine composition of 26 mass % CaCl_2 and 5 mass % MgCl_2 . Equilibrium thermodynamics calculated with activity coefficient models [6] results in eutectic conditions of -52.2°C , and a brine of 27 mass % CaCl_2 and 3.5 mass % MgCl_2 . Fluid inclusions from both experiments contain ice, antarctite, and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ below the eutectic temperature. At this temperature antarctite completely dissolves and the first brine appears in the system (Figure 6A and B). Upon further heating, the composition of the aqueous solution moves along the ice- $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ cotectic line. The salinities at this cotectic line can be modelled according to purely empirical equations between -55 and -33.6°C (Eq. 1)

$$w(\text{MgCl}_2) = 5.0 + 0.43622 \cdot T_D + 0.0072008 \cdot T_D^2 + 0.00034223 \cdot T_D^3 \quad (1a)$$

$$w(\text{CaCl}_2) = 26.0 - 1.02 \cdot T_D + 0.029328 \cdot T_D^2 - 0.0017945 \cdot T_D^3 \quad (1b)$$

$$T_D = T - T_{eut} \quad (1c)$$

where w is the mass % of either CaCl_2 (Eq. 1a) or MgCl_2 (Eq. 1b), T is temperature in $^\circ\text{C}$, and T_{eut} is the eutectic

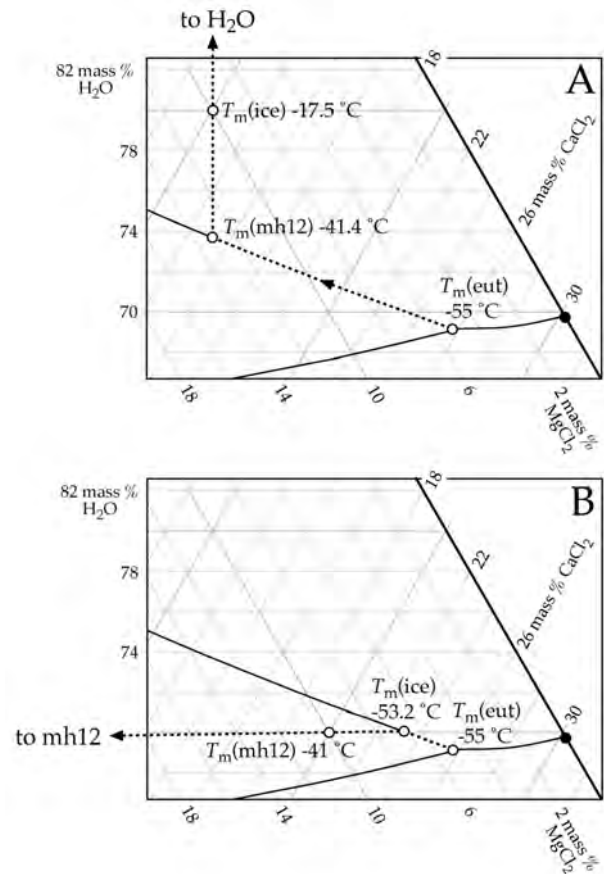


Figure 6. Theoretical compositional path (dashed lines) of the aqueous liquid solution in fluid inclusions from a heating experiment with Exp 050 (A) and Exp 051 (B). $T_m(\text{eut})$ is the eutectic temperature of the ternary system at -55°C . $T_m(\text{ice})$ and $T_m(\text{mh12})$ are the final ice, and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ dissolution temperatures, respectively.

temperature of this ternary system (-55°C). $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ dissolves at -41.4°C according to Equation 1 in Exp 050 (Figure 6A). The final ice melting temperature is calculated at -17.5°C [6]. In Exp 051, ice is the first phase to dissolve completely at the cotectic line at -53.2°C (Eq. 1), resulting in a final dissolution temperature of $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ of about -42°C (Figure 6B). This temperature is only an estimate based on linear interpolation of experimental data [4, 5].

4. Observations in fluid inclusions

4.1. H_2O - NaCl - CaCl_2 fluid inclusions

Experiment 006

The fluid system in inclusions from Exp 006 may react to form two different phase assemblages during cooling, both

are metastable. In addition to a vapour phase, the phase assemblage at -100°C may consist of: (1) ice, hydrohalite, and a brine (Figure 7A); (2) ice and a brine (Figure 7B). Note that the initial freezing of both types of inclusions are optically similar (compare images at -70°C in Figure 7A and B) and in-situ Raman spectroscopic analyses of the phase assemblages are necessary to identify the phases. The phases in these assemblages coexist at lower temperatures, down to -190°C , the approximate lower limit of the freezing stage. The nucleation of ice or a mixture of ice and hydrohalite cannot be stimulated by heating and cooling cycles, and it occurs randomly, occasionally in the same fluid inclusion, in repeated microthermometric experiments. Antarcticite, or any other hydrate of CaCl_2 , was not observed in fluid inclusions at low temperatures.

The brine in inclusions that nucleate ice and hydrohalite exists at the metastable extension of the cotectic line at temperatures below the eutectic point (Figure 7A). First dissolution processes, the first appearance of a liquid phase, cannot be observed in these inclusions because a supersaturated brine remains present in the phase assemblage down to -190°C . Upon heating, the inclusions indicate a final ice dissolution temperature of $-27.6 \pm 0.4^{\circ}\text{C}$ at the stable part of this cotectic line, with a brine composition of 9.1 mass % NaCl and 16.2 mass % CaCl_2 [14]. The compositional trajectory of the brine during further heating crosses the hydrohalite-halite peritectic line at about -10°C and moves into the halite-field during further dissolution of hydrohalite (Figure 7A). The inhibition of recrystallization of hydrohalite to halite enlarges the hydrohalite field. Final dissolution of hydrohalite occurs in a temperature range of -4.6 to -0.1°C , representing a metastable process. The range of temperatures may indicate that irregular spontaneous nucleation plays an important role at metastable conditions. Salinities in this metastable hydrohalite field can only be calculated with purely empirical equations from Naden [14], yielding values of 14.0 ± 0.2 mass % NaCl and 14.0 ± 0.2 mass % CaCl_2 . This composition is significantly different from the initial experimental composition (see Table 1) due to experimental difficulties (see paragraph 5: Discussion).

Inclusions that nucleate only ice upon cooling reveal a final ice melting temperature of $-34.2 \pm 1.1^{\circ}\text{C}$ (Figure 7B). According to the thermodynamic stability of phase assemblages, an aqueous solution with a NaCl/ CaCl_2 mass ratio of 1/1 (c.f. initial composition in Table 1) should have a minimum ice dissolution temperature of -26.9°C at the ice-hydrohalite cotectic line (Figure 8). The metastable absence of hydrohalite enlarges the ice field in a ternary phase diagram to lower temperatures and lower H_2O concentrations. The purely empirical equation of the ice field according to Naden [14] can be extrapolated to lower tem-

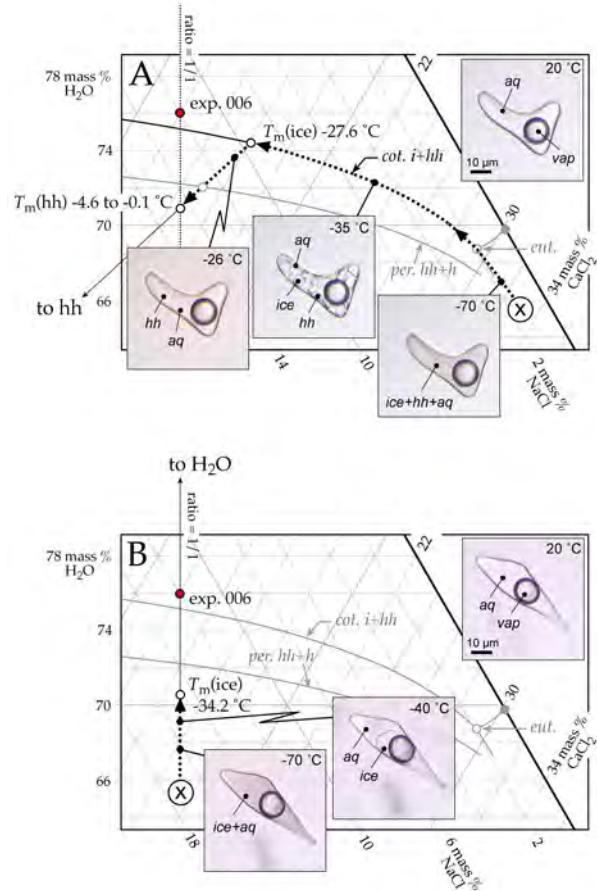


Figure 7. Trace of the brine composition (thick dashed lines) in fluid inclusions in the ternary H_2O -NaCl- CaCl_2 system (Exp 006) during a heating experiment. The symbol x indicates the approximate composition at about -190°C . Absent stable phase boundaries are illustrated in grey lines. $T_m(\text{ice})$ and $T_m(\text{hh})$ are the final ice, and hydrohalite dissolution temperatures, respectively. The phase assemblages are illustrated in photomicrographs at selected temperatures for fluid inclusions that nucleate only ice (A) and ice + hydrohalite (B) on cooling. Abbreviations: aq = aqueous liquid solution (brine), hh = hydrohalite, vap = vapour, cot. i+hh = the cotectic line of ice and hydrohalite, per. hh+h = peritectic line of hydrohalite and halite. Equal masses of NaCl and CaCl_2 is illustrated with the short-dashed line ratio 1/1.

peratures for the metastable dissolution conditions of ice, resulting in a calculated salinity of 14.7 ± 0.3 mass % NaCl and 14.7 ± 0.3 mass % CaCl_2 . This salinity is consistent with the previously obtained salinity from metastable dissolution temperatures of hydrohalite.

Experiment 024

A variety of cooling and heating sequences may result in three different metastable phase assemblage at low temperatures in fluid inclusions from Exp 024: (1) unfreezable brine; (2) hydrohalite and a brine (Figure 9A); (3) hydro-

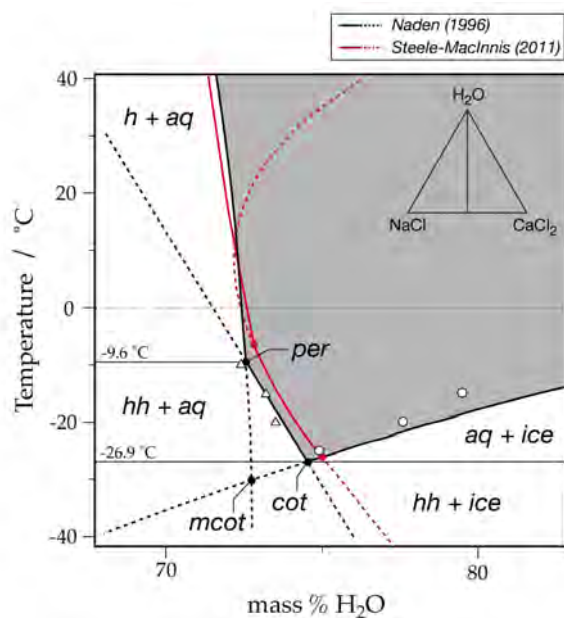


Figure 8. Section of the ternary H_2O - NaCl - CaCl_2 system with a $\text{NaCl}/\text{CaCl}_2$ mass ratio of 1/1. Stability limits for ice, hydrohalite and halite are calculated with purely empirical equations (black lines [14], red lines [15]). Experimental data [4, 5] are illustrated for ice (open circles) and hydrohalite (open triangles). The temperatures of the peritectic (*per.*) and cotectic point (*cot.*) are -9.6°C and -26.9°C , respectively. The metastable extensions of purely empirical equations are illustrated with dashed lines. *mcot* is the metastable cotectic point of halite and ice.

halite, ice, a brine (Figure 9B), and a vapour phase. The absence of antarcticite at low temperatures illustrates the metastability in all fluid inclusions.

Nucleation of solid phases in the aqueous fluid inclusions can be completely inhibited, resulting in the presence of a super-cooled brine at -190°C . Consequently, these unfreezable inclusions cannot be used to estimate salinities.

Fluid inclusions that nucleate only hydrohalite in cooling experiments recrystallize hydrohalite into halite during heating at temperatures between -12 to $+6^\circ\text{C}$ (Figure 9A). The range and the absolute values of this temperature illustrate that hydrohalite is metastably present within the halite field and not at the hydrohalite-halite peritectic line. The phase transition of hydrohalite to halite is irreversible, subsequently, cooling only results in a slight growth of the halite crystal. These fluid inclusions dissolve halite at 140 to 170°C with a salinity of 12.5 ± 0.5 mass % NaCl and 25 ± 1 mass % CaCl_2 [14] and at a $\text{NaCl}/\text{CaCl}_2$ mass ratio of 1/2 according to the initial experimental composition (c.f. Table 1). The salinity is significantly higher than indicated in Table 1, which suggests experimental difficulties (see paragraph 5 *Discus-*

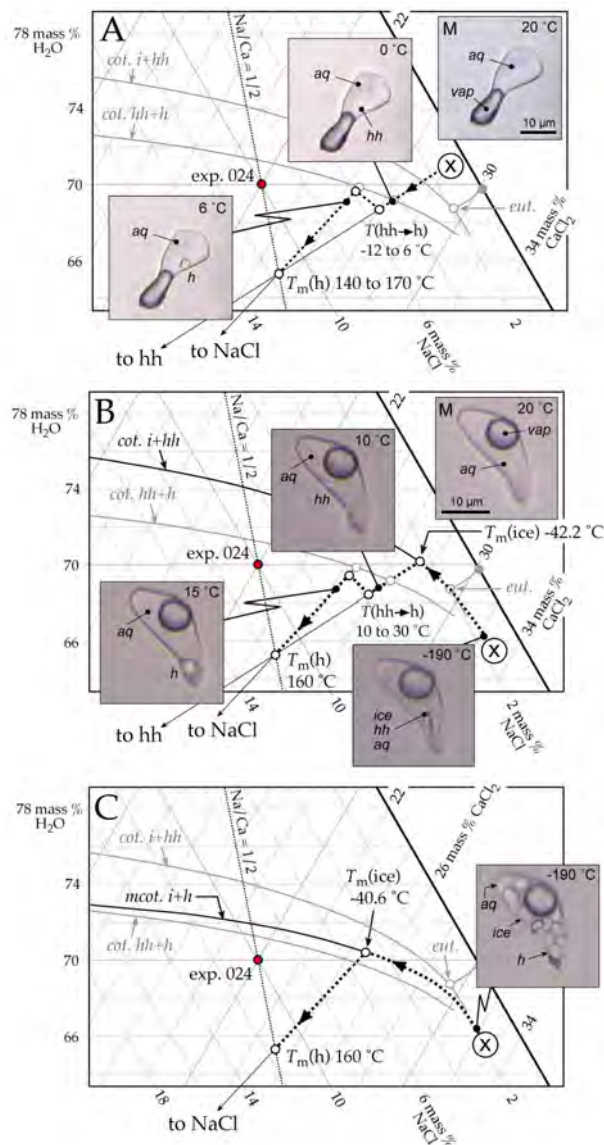


Figure 9. Trace of the brine composition (thick dashed lines) in fluid inclusions in the ternary H_2O - NaCl - CaCl_2 system (Exp 024) during a heating experiment. The symbol x indicates the approximate composition at about -190°C . The phase assemblages are illustrated at selected temperatures for fluid inclusions that nucleate only hydrohalite (A), ice + hydrohalite (B), and ice + halite (C) on cooling. The symbol M in the fluid inclusion images indicates a metastability at room temperatures (20°C). See text and Figure 7 for further details.

sion). Halite does not precipitate in the inclusions upon cooling after its final dissolution, and fluid inclusions reveal a metastable phase assemblage (supersaturated brine and vapour) at room temperatures.

Fluid inclusions in this sample may also nucleate hydrohalite and ice at lower temperatures, in the presence

of a brine and vapour (Figure 9B). Brine forms at the metastable extension of the ice-hydrohalite cotectic line, down to -190°C . The brine composition in the inclusion shifts into stable conditions along the cotectic line when heated to temperatures above -52°C (i.e. the eutectic temperature) without changing the phase assemblage. The final ice dissolution temperature is $-42.2 \pm 0.3^{\circ}\text{C}$ in the presence of a brine consisting of 2.7 mass % NaCl and 26.9 mass % CaCl₂. Subsequently, the brine composition shifts away from the cotectic line in the direction of hydrohalite as it continues to dissolve. Hydrohalite transforms to halite at temperatures ranging from $+10$ to $+30^{\circ}\text{C}$, where hydrohalite is metastable and not at the peritectic line. According to equilibrium thermodynamics, hydrohalite should transform at peritectic conditions between -15.4 and -13.4°C in these inclusions. Halite dissolves at 160 to 180°C , similar to the temperature range measured in inclusions that nucleate only hydrohalite. The calculated final salinity at these temperatures is 12 ± 1 mass % NaCl and 23 ± 1 mass % CaCl₂ [15], consistent with the initial experimental NaCl/CaCl₂ mass ratio of 1/2. Although a variety of metastable phase assemblages occur during a heating experiment, both the dissolution temperatures of ice and halite represent stable transformation conditions and can be used to calculate the salinity in the ternary H₂O-NaCl-CaCl₂ system. However, the presence of CaCl₂ in these fluid inclusions cannot be directly proven. This is due to the fact that the eutectic temperature of the fluid system cannot be observed due to metastabilities, and Raman spectroscopy does not illustrate the presence of any CaCl₂ hydrate at low temperatures.

Cooling of the stable phase assemblage consisting of halite, brine, and vapour from room temperatures results in the nucleation of ice around -100°C with the other three phases remaining present. The composition of the brine is at the halite-ice cotectic line, where it is metastable at all conditions (Figure 9C) and occurs at temperatures lower than the stable ice-hydrohalite cotectic line. The salinity of this metastable cotectic line can be obtained from the intersection of the extrapolated halite and ice field [14] (see also Figure 8). The inclusions reveal final ice dissolution temperatures at $-40.6 \pm 0.5^{\circ}\text{C}$, higher temperatures than in the presence of hydrohalite. Subsequently, final dissolution temperatures of halite are equal to the previously mentioned values. Although these fluid inclusions also reveal ice and halite dissolution temperatures, the ice dissolution temperature occurs at metastable conditions, i.e. in the absence of hydrohalite, in contrast to the previously described example. The value of mass % NaCl will be overestimated, whereas the mass % CaCl₂ is un-

derestimated if the salinity is calculated according to the example illustrated in Figure 9B.

4.2. H₂O-NaCl-MgCl₂ fluid inclusions

Experiment 033

Fluid inclusions synthesized in *Exp 033* may contain a phase assemblage of hydrohalite, ice, brine, and vapour at temperatures below the eutectic point (-35°C) in the ternary H₂O-NaCl-MgCl₂ system. The metastability is implied by the absence of an MgCl₂ hydrate phase and the presence of a brine at -190°C (Figure 10A). The coexistence of ice and hydrohalite defines the composition of the brine at the metastable extension of the cotectic line. Upon heating, the hydrohalite completely dissolves at $-25.4 \pm 0.4^{\circ}\text{C}$ at the cotectic line. The composition of the brine at this stable cotectic can be obtained from thermodynamic modelling of the activity coefficients [6]: 12.8 ± 0.7 mass % NaCl and 9.1 ± 0.4 mass % MgCl₂. Dissolution of the remaining ice at $-20.5 \pm 0.1^{\circ}\text{C}$ defines the salinity of these inclusions at 11.6 ± 0.7 mass % NaCl and 8.2 ± 0.4 mass % MgCl₂ (Figure 10A). Both dissolution temperatures occur in stable phase assemblages and can be used to estimate bulk salinities in a ternary system. However, there is no direct evidence of the presence of MgCl₂, whereas the presence of NaCl is proven by the formation of hydrohalite at low temperatures. Furthermore, the eutectic temperature of this fluid cannot be determined due to the absence of MgCl₂ hydrates at lower temperatures.

Experiment 038

A variety of metastable phase assemblages are obtained in fluid inclusions that are synthesized in *Exp 038* (Figure 10B). Freezing experiments may result in the nucleation of only ice in the presence of a brine and vapour. In a second freezing experiment with the same inclusion, ice and hydrohalite may nucleate, which cannot be distinguished optically from the first nucleation process. The absence of MgCl₂ hydrates at -190°C illustrates the metastability of these fluid inclusions. The composition of the brine is defined at the metastable extension of the ice-hydrohalite cotectic line below -35°C (Figure 10B, path 1). At $-39.0 \pm 0.4^{\circ}\text{C}$, the ice is completely dissolved at metastable conditions. The remaining hydrohalite dissolves at $-33.2 \pm 0.8^{\circ}\text{C}$, also at metastable conditions. The salinity of these inclusions can only be roughly estimated, because equations of state are not available for metastable conditions, yielding an approximate composition of 3.5 mass % NaCl and 21 mass % MgCl₂. The dissolution behaviour of metastable phases is consistent with observations of inclusions that only nucleate ice (Figure 10B, path 2). These inclusions reveal complete dissolution temperatures of ice of $-39.9 \pm 0.4^{\circ}\text{C}$, lower than

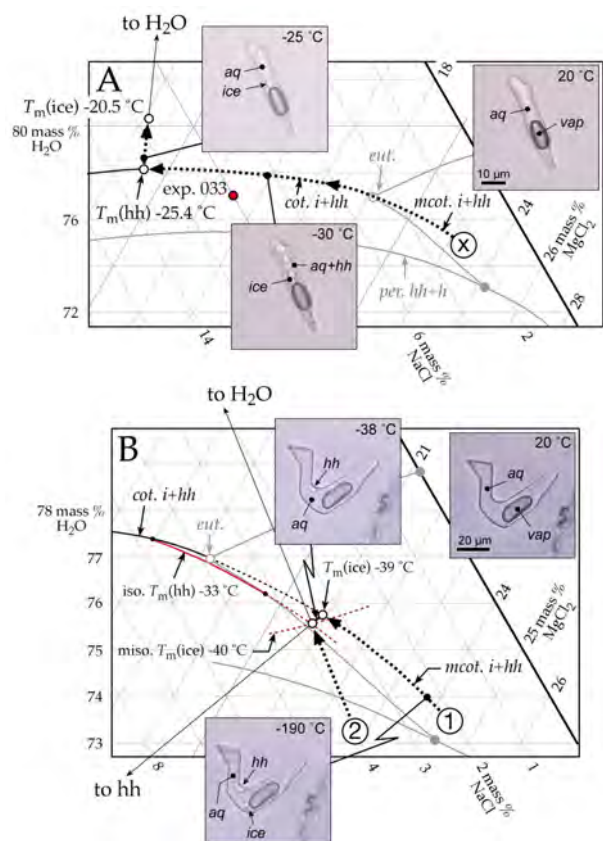


Figure 10. Trace of the brine composition (thick dashed lines) in fluid inclusions in the ternary H_2O - NaCl - MgCl_2 system (**A**, Exp 033, and **B**, Exp 038) during a heating experiment. The symbol x indicates the approximate composition at about -190°C . Path 1 and 2 (in **B**) illustrate fluid inclusions that nucleate ice + hydrohalite and only ice, respectively, at low temperatures. "mco. i+hh" is the metastable extension of the ice-hydrohalite cotectic line; "iso $T_m(\text{hh})$ -33°C " is the isotherm of hydrohalite dissolution at stable conditions (within the hydrohalite field); "miso $T_m(\text{ice})$ -40°C " is the isotherm of ice dissolution at metastable conditions (within the hydrohalite and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ field). See text and Figure 7 for further details.

in fluid inclusions that also nucleate hydrohalite because the remaining brine is slightly depleted in H_2O .

Experiment 035

Fluid inclusions synthesized in Exp 035 may reveal a stable phase assemblage of ice, hydrohalite, $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, and vapour at temperatures below the eutectic point of the ternary H_2O - NaCl - MgCl_2 (Figure 11A). It must be noted that this is the only example of nucleation of stable phase assemblages in fluid inclusions upon cooling to -190°C ; both hydrohalite and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ are detected with Raman spectroscopy. Upon heating, these inclusions reveal final dissolution temperatures of both hydrohalite and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ at $-35.6 \pm 0.3^\circ\text{C}$, close to the reported

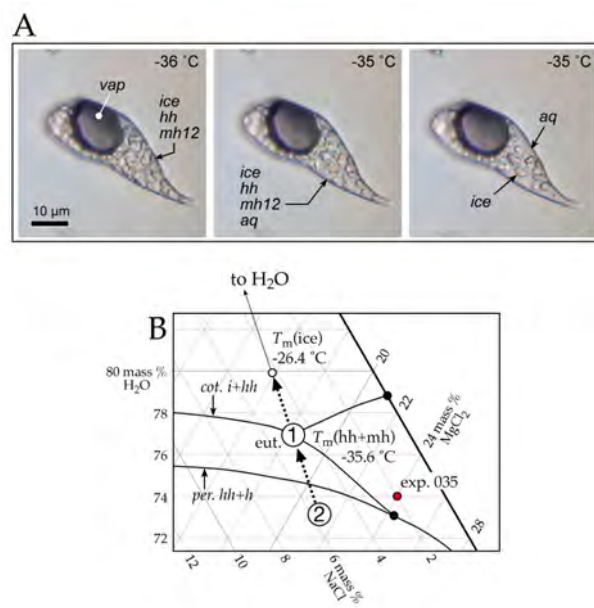


Figure 11. (**A**) Stable phase assemblages in a fluid inclusion from Exp 035 at eutectic conditions during a heating experiment from -36 to -35°C . Abbreviation: vap = vapour, hh = hydrohalite, mh12 = $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$, aq = aqueous liquid solution (brine). (**B**) Trace of the brine composition (thick dashed lines) in fluid inclusions in the ternary H_2O - NaCl - MgCl_2 system (Exp 035) during a heating experiment. The traces are illustrated for fluid inclusions that nucleate ice, hydrohalite and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ (path 1), and only ice (path 2). See text and Figure 7 for further details.

eutectic temperature of -35.2°C [6]. This temperature corresponds to the first appearance of a brine in the system. The remaining ice dissolves completely in the brine at -26.0°C , and indicates a salinity of 4.3 mass % NaCl and 15.8 mass % MgCl_2 [6] (Figure 11B, path 1). Within the same fluid inclusion, the nucleation of all salt-hydrate phases may be inhibited, with only ice crystal metastably present in a brine at low temperatures (Figure 11B, path 2). Optically, these two nucleation processes cannot be distinguished, and Raman spectroscopy is the only method to identify these phases.

4.3. H_2O - CaCl_2 - MgCl_2 fluid inclusions

Experiment 050

The hydrates of CaCl_2 (antarcticite) and MgCl_2 ($\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$) do not nucleate simultaneously in freezing experiments with fluid inclusions from Exp 050 in the ternary H_2O - CaCl_2 - MgCl_2 system. Three types of metastable phase assemblages can be generated within these inclusions at temperatures below -55°C (i.e. the eutectic point): (1) ice and brine; (2) ice, $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$,

and brine; and (3) ice, antarcticite, and brine in the presence of a vapour phase (Figure 12). The nucleation of only ice occurs at about -75°C and is observable as a greyish-brownish coloured microcrystalline mixture. Final dissolution of ice is the only measurable parameter from these inclusions and occurs in the stability field of ice at $-22.7 \pm 0.3^{\circ}\text{C}$. At temperatures below the eutectic point, the brine in fluid inclusions that nucleates ice and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ has appeared at the metastable extension of the cotectic line (Figure 12A), and is highly enriched in CaCl_2 . Upon heating, the composition of the brine shifts along the metastable extension of the cotectic line during dissolution of ice and $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$. Above the eutectic temperature of this system (-55°C), $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ dissolves completely at -35 to -40°C under stable conditions, and the remaining ice dissolves at about -22°C . The last two dissolution temperatures can be used to calculate the salinity of these inclusions yielding values of 11 ± 1 mass % CaCl_2 and 12 ± 1 mass % MgCl_2 using the activity coefficient model [6] and Eq. 1. There is no direct evidence for the presence of CaCl_2 .

The same fluid inclusions may reveal the nucleation of ice and antarcticite. The coexisting metastable brine at about -190°C is highly enriched in MgCl_2 (Figure 12B). The final dissolution temperature of antarcticite occurs at metastable conditions, whereas the final ice dissolution temperature take place in the stability field of ice at about -23°C . Although antarcticite was detected by Raman spectroscopy, there were no means to observe its final dissolution by optical methods.

Experiment 051

Fluid inclusions synthesized in *Exp 051* do not reveal any nucleation processes in cooling experiments. The unfreezable brine is highly metastable at temperatures down to -190°C .

5. Discussion

5.1. Natural fluid inclusions

Without any knowledge of the ionic composition of aqueous solutions in natural fluid inclusions, dissolution temperatures of ice, salt-hydrates, and salt were used to provide indirect information about the composition of this brine. This study has shows that only ice dissolution temperatures can be interpreted in both binary and ternary H₂O-salt systems (H_2O -NaCl- CaCl_2 , H_2O -NaCl- MgCl_2 , and H_2O - CaCl_2 - MgCl_2). The nucleation of salt-hydrates can be completely inhibited in these ternary systems, resulting in fluid inclusions that contain a metastable phase assemblage of ice and brine at temperatures below eutectic conditions. This assemblage cannot be distinguished

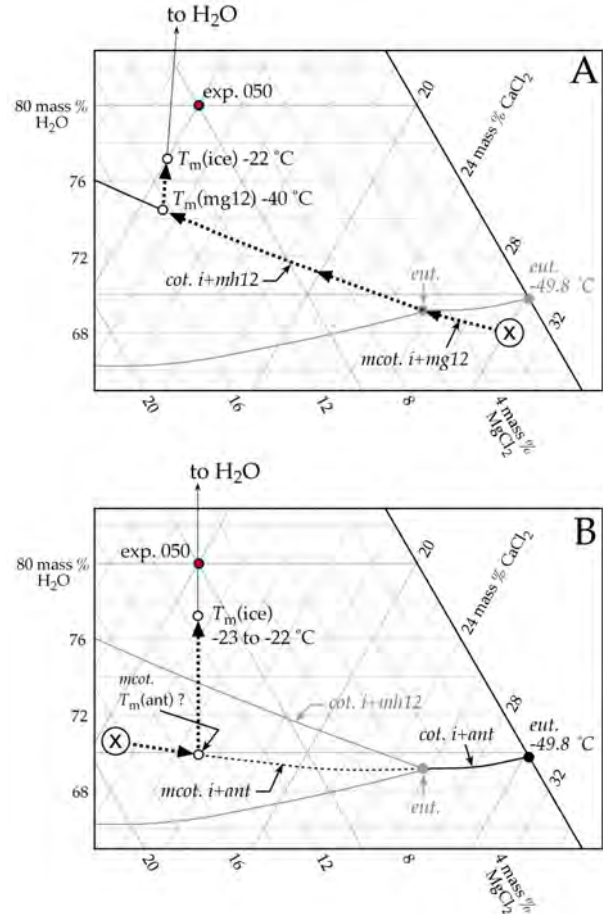


Figure 12. Trace of the brine composition (thick dashed lines) in fluid inclusions in the ternary H₂O- CaCl_2 - MgCl_2 system (*Exp 050*) during a heating experiment. The traces are illustrated for fluid inclusions that nucleate ice + $\text{MgCl}_2 \cdot 12\text{H}_2\text{O}$ (A), and ice + antarcticite (B). The symbol x indicates the approximate composition at about -190°C . See text and Figure 7 for further explanations.

from binary systems, which may also lack the presence of salt-hydrates at low temperatures [22].

The ice dissolution temperature can be interpreted in a binary H₂O-salt system, which is often used to illustrate an equivalent amount of mass salt at this temperature. In general, the equivalent mass NaCl is calculated; however, other types of salt, such as CaCl_2 , must be used at dissolution temperatures below the eutectic temperature of the H₂O-NaCl system. For example, the observed ice dissolution temperature of $-34.2 \pm 1.1^{\circ}\text{C}$ in *Exp 006* corresponds to 26.2 ± 0.4 eq mass % CaCl_2 . This calculated equivalent mass of salt may be a highly underestimated salinity in ternary H₂O-salt systems.

Fluid inclusions that reveal dissolution of two phases, e.g. ice and salt-hydrates, can only be interpreted in ternary

H₂O-salt systems. Ice and hydrohalite are often nucleated at low temperatures in fluid inclusions that also contain a second type of salt, such as CaCl₂ and MgCl₂. Nucleation of hydrates of these salts is usually inhibited in NaCl-bearing brines, whereas the brine remains present down to -190°C. Nucleation of hydrates of MgCl₂ and CaCl₂ mainly occurs in brines that are extremely poor in NaCl content.

Identification of salt-hydrates with Raman spectroscopy at low temperatures directly provides the primary types of salts that are present in fluid inclusions. The absence of salt-hydrates in cooled saline aqueous fluid inclusions represents a metastable fluid state and prevents the Raman detection of any salt-hydrates. However, the same inclusions may react differently to multiple cooling and heating cycles in microthermometry and may, occasionally, nucleate salt-hydrates. Within a homogeneous assemblage of fluid inclusions, equal salinities can be obtained from a completely different behaviour in microthermometric experiments. For example, final dissolution of ice in inclusions at -34°C corresponds to the same salinity as inclusions that reveal a final dissolution of hydrohalite at 0.0°C in the H₂O-NaCl-CaCl₂ system (see Figure 7A and B). Both dissolution processes occur within metastable phase assemblages.

5.2. Experimental difficulties

Salinities obtained from dissolution temperatures of ice, salt hydrates, and salt from synthetic fluid inclusions at stable and metastable conditions partially correspond to the intended experimental conditions (Table 1). Fluid inclusions from experiments in the H₂O-NaCl-CaCl₂ system reveal higher salinities, but similar NaCl/CaCl₂ mass ratios. The loss of H₂O can be concluded from these observations, as evaporation may have occurred during welding of the Au-capsules that are used in the experimental synthesis. A second argument for apparent higher salinities, as obtained from dissolution temperatures, is illustrated by Bakker [26]. Final dissolution in fluid inclusions occurs on the SLV curve (coexistence of solid, liquid, and vapour) and cannot be directly used to estimate bulk salinities. The properties of the vapour phase (density and volume fraction) cannot be neglected, and bulk properties of fluid inclusions can only be obtained from a combination of final dissolution temperature, total homogenization temperature, and/or volume fraction of the vapour phase. Salinities obtained from only the final dissolution temperatures are always overestimated values [26].

Fluid inclusions from experiments in the H₂O-NaCl-MgCl₂ system reveal lower salinities than the initial experimental conditions (Table 1). The measured composi-

tions are depleted in MgCl₂, enriched in H₂O, and contain approximately the same amount of NaCl as was initially present. MgCl₂ has strong hygroscopic properties, and it attracts water vapour when exposed to air. The weighing procedure for loading the Au-capsules with specific amounts of salt may have resulted in an overestimated mass of MgCl₂, which is composed of MgCl₂ and adsorbed H₂O. Consequently, the fluid composition in the capsule is enriched in H₂O and depleted in MgCl₂. The minor differences in experiments within the H₂O-CaCl₂-MgCl₂ system are caused by similar weighing errors.

5.3. Inconsistent models

The quality of purely empirical and thermodynamic modelling of ternary H₂O-salt systems is difficult to assess due to the lack of experimental data. The variety of models may result in inconsistent salinity estimations, for example in the H₂O-NaCl-MgCl₂ system, c.f. [6] and [10]. Significant differences also exist between purely empirical models of the same system, for example the H₂O-NaCl-CaCl₂ system, c.f. [14] and [15], Figure 8. Knowledge of these ternary systems can be extended with experimental studies of synthetic fluid inclusion, if metastabilities are well documented and understood.

6. Conclusions

Unpredictable phase change behaviour of fluids at low temperatures makes careful observations of fluid inclusions necessary to use microthermometric data as a credible indicator of salinity. Synthesis of fluid inclusions of well known compositions and trapping conditions (temperature and pressure) allow experimental studies of fluid behaviour to act as the basis for the interpretation of natural systems. Eutectic temperatures are normally used to define the salt system in natural aqueous fluid inclusions. The assumption for this application is the presence of stable phase assemblages and reliable data for phase relationships. As the present study reveals, salt-hydrate nucleation may completely be inhibited in ternary water-salt inclusions, or only one salt-hydrate may precipitate in the absence or presence of ice during cooling. Stable phase assemblages below eutectic temperatures, which are more common in binary water-salt systems, are not observed among inclusions synthesised in ternary water-salt systems. Consequently, eutectic temperatures cannot be detected in these inclusions. Nevertheless, most ice and salt-hydrate final dissolution occurs in a stable state (phase assemblage); therefore, these temperatures are still reliable indicators of the salinity of those in-

clusions and can be used for salinity estimations. Raman spectroscopy at low temperatures must be applied to identify the major types of salt present in the system, as detected from the nucleation of specific Raman-active salt-hydrates. Furthermore, Raman spectroscopy can be used to obtain accurate dissolution temperatures through changing phase assemblages in a heating experiment that are otherwise difficult to detect by optical means.

Acknowledgements

We greatly acknowledge the comments of three anonymous reviewers. This project is partly financed by the Austrian Research Fund (FWF), project number P18209-B06.

References

- [1] Roedder E., Fluid Inclusions, Rev. Mineral. 12, Min. Soc. Amer., USA, 1984
- [2] Yardley B.W., Graham J.T., The origins of salinity in metamorphic fluids. *Geofluids*, 2002, 2, 249-256
- [3] Borisenko A.S., Study of the salt composition of solutions of gas-liquid inclusions in minerals by the cryometric method. *Geol. Geofiz.*, 1977, 18/8, 16-27
- [4] Linke W.F., Solubilities: Inorganic and metal-organic compounds. Volume I, American Chemical Society, Washington. 1958
- [5] Linke W.F., Solubilities: Inorganic and metal-organic compounds. Volume II, American Chemical Society, Washington. 1965
- [6] Spencer R.J., Møller N., Weare J.H., The prediction of mineral solubilities in natural water: A chemical equilibrium model for the Na-K-Ca-Mg-Cl-SO₄-H₂O system at temperatures below 25 °C. *Geochim. Cosmochim. Acta*, 1990, 54, 575-590
- [7] Harvie C.E., Møller N., Weare J.H., The prediction of mineral solubilities in natural water: The Na-K-Mg-Ca-H-Cl-SO₄-OH-HCO₃-CO₃-CO₂-H₂O system to high ionic strengths at 25°C. *Geochim. Cosmochim. Acta*, 1984, 48, 723-751
- [8] Bodnar R.J., Revised equation and table for determining the freezing point depression of H₂O-NaCl solutions. *Geochim. Cosmochim. Acta*, 1993, 57, 683-684
- [9] Baumgartner M., Bakker R.J., CaCl₂-hydrate nucleation in synthetic fluid inclusions. *Chem. Geol.*, 2009, 265, 335-344
- [10] Dubois M., Marignac C., The H₂O-NaCl-MgCl₂ ternary phase diagram with special application to fluid inclusion studies. *Econ. Geol.*, 1997, 92, 114-119
- [11] Wilkinson J.J., Fluid inclusions in hydrothermal ore deposits. *Lithos*, 2001, 55, 1-4, 229-272
- [12] William-Jones A.E., Samson I.M., Theoretical estimation of halite solubility in the system NaCl-CaCl₂-H₂O: Applications to fluid inclusions. *Can. Mineral.*, 1990, 28, 299-304
- [13] Oakes C.S., Bodnar R.J., Simonson J.M., The system NaCl-CaCl₂-H₂O: I. The ice liquidus at 1 atm pressure. *Geochim. Cosmochim. Acta*, 1990, 54, 603-610
- [14] Naden J., CalcicBrine: A Microsoft Excel 5.0 Add-in for calculating salinities from microthermometric data in the system NaCl-CaCl₂-H₂O. PACROFI VI, Program and Abstracts, Madison, USA, 1996, 97-98
- [15] Steele-MacInnes M., Bodnar R.J., Naden J., Numerical model to determine the composition of H₂O-NaCl-CaCl₂ fluid inclusions based on microthermometric and microanalytical data. *Geochim. Cosmochim. Acta*, 2011, 75, 21-40
- [16] Prutton C.F., Tower O.F., The system calcium chloride-magnesium chloride-water at 0, -15, and -30°. *J. Amer. Chem. Soc.* 1932, 54, 3040-3047
- [17] Yanatieva C.K., Polythermal solubilities. *Zh. Prikl. Khim.* 1946, 19, 709-722 (in Russian; translated by Berthold R. and Wolfram M.)
- [18] Vanko D.A., Bodnar R.J., Sterner M., Synthetic fluid inclusions: VIII. Vapor-saturated halite solubility in part of the system NaCl-CaCl₂-H₂O, with application to fluid inclusions from oceanic hydrothermal systems. *Geochim. Cosmochim. Acta*, 1988, 52, 2451-2456
- [19] Davis D.W., Lowenstein T.K., Spencer R.J., Melting behaviour of fluid inclusions in laboratory-grown halite crystals in the systems NaCl-H₂O, NaCl-KCl-H₂O, NaCl-MgCl₂-H₂O, and NaCl-CaCl₂-H₂O. *Geochim. Cosmochim. Acta*, 1990, 54, 591-601
- [20] Schiffries C.M., Liquid-absent aqueous fluid inclusions and phase equilibria in the system CaCl₂-NaCl-H₂O. *Geochim. Cosmochim. Acta*, 1990, 54, 311-619
- [21] Dubois M., Monnin C., Castelain T., Coquinot Y., Gouy S., Gauthier A., Coffé B., Investigation of the H₂O-NaCl-LiCl system: a synthetic fluid inclusion study and thermodynamic modeling from -50° to +100°C and up to 12 mol/kg. *Econ. Geol.*, 2010, 329-338
- [22] Bakker R.J., Raman spectra of fluid and crystal mixtures in the system H₂O, H₂O-NaCl and H₂O-MgCl₂ at low temperatures: applications to fluid inclusion research. *Can. Mineral.*, 2004, 42, 1283-1314
- [23] Baumgartner M., Analysis of salt-bearing aqueous solutions in synthetic fluid inclusions by microthermometry and cryogenic Raman spectroscopy. PhD

- thesis, University of Leoben, Austria, 2009
- [24] Bodnar R.J., Sterner S.M., Synthetic fluid inclusions. In: G.C. Ulmer, H.L. Barnes (Eds.) *Hydrothermal Experimental Techniques*. John Wiley & sons, New York, 1987, 423–457
- [25] Baumgartner M., Bakker R.J., Raman spectra of ice and salt hydrates in synthetic fluid inclusions. *Chem. Geol.*, 2010, 275, 58–66
- [26] Bakker R.J., Can the vapour phase be neglected to estimate bulk salinity of halite-bearing aqueous fluid inclusions. *Cent. Eur. J. Geosci.*, (this issue).