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

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Abstract—Halite solubility along part of the vapor-saturated liquidus in the system NaCl-CaCl₂-H₂O has been determined using the synthetic fluid inclusion technique. Data allow the construction of liquidus isotherms for temperatures up to 500°C and bulk compositions containing >60 wt% total salt and as much as 25 wt% CaCl₂. Combined with previous data for the binary system NaCl-H₂O and for the ternary system NaCl-CaCl₂-H₂O in the low-salinity, low-temperature region, a preliminary ternary phase diagram can be constructed that remains incomplete only in the CaCl₂-rich region.

Results are applied to the interpretation of saline fluid inclusions from quartz veins in oceanic metagabbros, and can be applied to many other natural inclusions containing aqueous solutions with NaCl and CaCl₂ as major solutes. Microthermometric measurements at equilibrium of the melting temperature of ice (Tm (ice)) and of the dissolution temperature of halite (Tm (halite)) are sufficient to determine the bulk composition of the NaCl-CaCl₂-H₂O fluid.

INTRODUCTION

EQUILIBRIUM PHASE RELATIONS

The synthetic fluid inclusion technique is fully described in Bodnar and Stern er (1987) and is only briefly summarized here. Experiments were conducted in Pt capsules to minimize contamination resulting from the corrosive effects of chloride brines at elevated temperatures. Three CaCl₂-H₂O solutions were prepared from reagent grade CaCl₂·4H₂O. A small weighed portion of one of the CaCl₂-H₂O fluids was added to each experimental capsule together with enough reagent grade NaCl to give a desired bulk fluid composition. The loaded capsules were weighed and heated overnight at >100°C to check for leaks. Surviving capsules were loaded into cold-seal hydrothermal bombs and run for 7 days at 700°C and 2.0 to 4.5 kbar (Table 1). The actual P-T conditions were chosen for each composition in light of previous data for the system NaCl-H₂O. The aim was to synthesize fluid inclusions that, on heating, would undergo nearly simultaneous halite dissolution and vapor disappearance.

RESULTS OF SYNTHETIC INCLUSION

MICROTHERMOMETRY

After quenching, the healed quartz cores were removed and sliced into 5-6 discs, each about 1 mm thick. These were polished for heating and freezing determinations, which were done on separate discs to avoid any complications from possible stretching or decrepitation.

Microthermometric measurements were made with a Fluid Inc.-adapted USGS-type heating/freezing stage mounted on a Zeiss petrographic microscope. Temperatures of phase changes were measured with a chromel-constantan thermocouple directly on the sample chip. Measurements were calibrated using synthetic fluid inclusions having known phase transitions at −56.6°C, 0.0°C, and +374°C. Occasional use was made of ice baths and of triply distilled H₂O (Tm = −38.89°C). During calibrations, the temperatures indicated by the thermocouple were always within 0.2°C of the 0.0°C standard and within 1.0°C of the 374°C standard. Therefore, the accuracy of measurements on unknowns is thought to be ±0.2°C during freezing runs and ±1.0°C during heating runs.

RESULTS OF SYNTHETIC INCLUSION
Table 1. Results of heating measurements on synthetic inclusions

<table>
<thead>
<tr>
<th>Sample Composition</th>
<th>P (kb)</th>
<th>Tm(halite)</th>
<th>Avg. Tm(halite)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>28.1/2</td>
<td>219.6-221.4</td>
<td>220.6 (12)</td>
</tr>
<tr>
<td>2</td>
<td>36.8/7</td>
<td>224.6-235.4</td>
<td>232.3 (10)</td>
</tr>
<tr>
<td>3</td>
<td>45.8/5</td>
<td>440.6-443.5</td>
<td>442.5 (13)</td>
</tr>
<tr>
<td>4</td>
<td>60.1/4</td>
<td>506.5-512.2</td>
<td>509.0 (19)</td>
</tr>
<tr>
<td>5</td>
<td>19.4/1</td>
<td>186.3-199.7</td>
<td>191.8 (12)</td>
</tr>
<tr>
<td>6</td>
<td>29.7/6</td>
<td>294.6-295.9</td>
<td>295.0 (13)</td>
</tr>
<tr>
<td>7</td>
<td>48.8/0</td>
<td>456.9-458.8</td>
<td>457.1 (14)</td>
</tr>
<tr>
<td>8</td>
<td>25.5/0</td>
<td>525.0-528.0</td>
<td>525.9 (17)</td>
</tr>
<tr>
<td>9</td>
<td>35.0/1</td>
<td>255.3-258.5</td>
<td>255.8 (13)</td>
</tr>
<tr>
<td>10</td>
<td>45.7/1</td>
<td>448.0-449.7</td>
<td>449.9 (12)</td>
</tr>
</tbody>
</table>

1 Wt % NaCl/ CaCl2/ H2O.
2 Temperatures in degrees C; number of inclusions measured in parentheses.
3 Measured Tm(halite) for seven inclusions having Tm(halite) less than the homogenization temperature.
4 Measured Tm(halite) for ten inclusions having Tm(halite) equal to the homogenization temperature; see text for discussion.

FORD (1981) and SHEPHERD et al. (1985), and are shown in Fig. 1. Phase boundaries and isotherms are based on the data of YANATIEVA (1946) and LINKE (1958). The ice-hydrohalite eutectic and the freezing point depressions along the NaCl-H2O binary between ice and hydrohalite are from HALL et al. (1988). The system has a ternary eutectic at about –52°C (Te; Fig. 1). The reaction curve separating the halite and hydrohalite (NaCl·2H2O) liquidus fields closely parallels the hydrohalite-ice eutectic (Fig. 1). Ice, hydrohalite, and antarcticite (CaCl2·6H2O) form the three solid phases at the eutectic. Bulk compositions of the fluid inclusions prepared for this study are plotted in Fig. 1. These were chosen so that the resulting inclusions would contain halite daughter crystals at room temperature, thus yielding information on halite solubilities where none existed previously.

The synthetic fluid inclusions appear similar to those produced in previous experiments (e.g., BODNAR et al., 1985). Most inclusions populate healed fracture surfaces that are planar or slightly curved. Inclusion sizes range from submicron to several tens of microns; they are usually fairly equant (Fig. 2) and distributed evenly along the healed fractures. Inclusions contain liquid, vapor, and a halite daughter crystal at room temperature. The majority have constant phase volume ratios, indicating that they contain similar bulk compositions. In addition, there exist a variable number of inclusions that are not well suited for study because it cannot be shown that they contain the desired bulk compositions. Most of these latter inclusions are large and irregular, with long thin extensions. Many appear to be filled with gas, which is probably air that entered the inclusions during the polishing. Other irregularly shaped inclusions appear to have spawned nearby inclusions, often containing different phase ratios, by necking down (ROEDDER, 1984).

Sample 5, although it has a bulk composition within the halite liquidus field, contains fluid inclusions that typically do not contain halite at room temperature. Thus, the phase assemblage in these inclusions is a metastable one, a problem not uncommon in saline inclusions only slightly oversaturated with halite at room temperature (ROEDDER, 1984). By freezing and warming these inclusions through several cycles halite could be nucleated, permitting the dissolution temperatures to be determined.

In several samples (numbers 4, 6, and 9), rare birefringent phases are discernable in the large irregular shaped inclusions. Maximum interference color is first order yellow, in a grain that appears to be only about 3 microns thick. The crystals form thin blades or platelets, with maximum dimension about 3 microns. Relief and refractive indices appear to be about the same as those of halite and quartz (i.e., positive relief relative to the fluid). On heating, the crystals dissolve (e.g., for sample 9, birefringent crystals dissolve at around 475°C). These crystals could be quartz or wollastonite; however, the birefringence seems too high for either, and the relief seems too low for wollastonite. Regardless of the identity of the crystals none have been observed within the abundant equant inclusions that contain liquid, vapor, and halite in constant proportions; i.e., in the inclusions that were taken as representative and were analyzed in this study.

High-temperature phase relations

The dissolution temperature of halite daughter crystals [Tm (halite)] was measured to locate isotherms in the liquid + halite field. Results of 135 heating measurements from 10 samples are summarized in Table 1 and Fig. 3. The range for a given sample is generally less than 2 to 3°C (i.e., nearly within the range of the maximum expected error); however, some samples exhibit substantially greater ranges. In the worst case, halite dissolution varied over a range of 11°C (12 measurements), but 10 of those twelve measurements have a range of only 3.4°C.

Nearly all inclusions underwent final homogenization via vapor bubble disappearance. Only in sample 3 was a subset of inclusions observed in which the vapor disappeared a few degrees before the halite. The Tm (halite) in both types of inclusions within sample 3, though, is indistinguishable (Table 1). For true vapor-saturated solubility determinations, the halite and the vapor bubble must disappear simultaneously.
Synthetic fluid inclusions. VIII

Fig. 2. Photomicrographs of sequential phase changes with varying temperature in a synthetic fluid inclusion (sample 2). The inclusion is about 33 microns long and 22 microns wide. (a) +20°C; inclusion contains liquid, vapor, and a halite daughter crystal at room temperature; (b) −41.5°C; after freezing and warming through several cycles, inclusion contains 5–6 large hydrohalite grains (low relief) and ice (moderate relief), as well as liquid (allowing the ice to appear rounded) and vapor; (c) −29.2°C; same phases as in the previous photo, but the liquid is greater and the ice (arrows) is smaller in volume; (d) −25.8°C; single tiny ice crystal (arrow) is present, and measured $T_m$ (ice) is −25.5°C; (e) +1.7°C; inclusion contains liquid, vapor, and metastable hydrohalite; note that the hydrohalite is little changed from the previous photo; (f) +16.0°C; metastable hydrohalite has transformed into stable halite, but as two crystals with complex boundaries; on heating, surface energy reduction will cause the halite to recrystallize into a single crystal with simple boundaries; (g) +318°C; halite and vapor are smaller due to dissolution and volume expansion of the liquid, respectively; (h) +351°C; halite is a tiny speck (arrow), with measured $T_m$ (halite) of +357°C; note that fluid at this stage approximates vapor-saturation, because vapor and halite disappearance are nearly simultaneous (see text).

In practice, it is difficult to achieve this condition. In our experiments the difference between vapor and halite disappearance was generally small, and even moderate differences have been shown to have very little effect on solubility determinations (CHOU, 1987; STERNER et al., 1988).

Resulting temperature contours on the halite liquidus are nearly straight (Fig. 3), and they tie in well along the NaCl-H₂O binary with data from CHOU (1987) and STERNER et al. (1988). The contours also parallel the trend of straight lines (hypothetical contours) that can be constructed between higher-temperature values of halite solubility along the NaCl-H₂O and NaCl-CaCl₂ binaries (STERNER et al., 1988; LEVIN et al., 1969).

Low-temperature phase relations

Metastable phase behavior is common in the inclusions at low temperature. For example, many of the inclusions in this study could not be frozen completely solid. This was the case particularly for the high-total salt samples (numbers 11 and 12, Fig. 1). Repeated quenching with liquid nitrogen failed to cause a change in the liquid plus vapor plus halite phase assemblage of these inclusions.

Fig. 3. Phase diagram for NaCl-CaCl₂-H₂O incorporating the measured $T_m$ (halite) of each of the synthetic fluid inclusions. Compositions are in weight percent. Solid isothermal contours are anchored along the NaCl-H₂O binary using average halite solubilities from CHOU (1987) and STERNER et al. (1988). The dashed line shows the portion of the join between (H₂O)₉₋₁₀(CaCl₂)₀ and NaCl that is drawn in Fig. 5.
Some degree of freezing is observed in all of the other samples. By sequential freezing (Haynes, 1985) it is easy to produce inclusions containing just a few hydrohalite and ice crystals (Fig. 2). The CaCl$_2$-rich interstitial liquid is then clearly visible and is very difficult to freeze. In fact, repeated attempts at quenching with liquid nitrogen failed to produce recognizable antarcticite, and the eutectic temperature of the system was not determined. Indirect observations of the onset of ice melting, determined by noting when euhedral ice boundaries become rounded, are often close to -52°C, but are as low as -73°C in one sample (sample 9, the most CaCl$_2$-rich one). Some of these lower temperature observations may correspond to metastable melting or recrystallization.

Relative to the fluid, ice has moderate negative relief about equal to that of halite, which has moderate positive relief (Fig. 2). Regrown ice crystals are often bladed or hexagonal tabular, the morphology depending on the available space. Ice melting ($T_m(\text{ice})$) was measured in the range -38.7°C to -23.3°C (Table 2).

Hydrohalite typically regrows on cooling as bladed crystals (Fig. 2). Hydrohalite melting, accompanied by growth of halite crystals with square or rectangular outlines, occurred at temperatures ranging from several degrees below zero to several degrees above zero, and is assumed to be metastable in most cases.

Observations of Becke lines indicate that ice has moderate negative relief, hydrohalite has low positive relief, and both halite and quartz have moderate positive relief relative to the fluid:

\[ n_{\text{ICE}} < n_{\text{FLUID}} < n_{\text{HH}} < n_{\text{HAL}} \approx n_{\text{QTZ}} \]

where \( n \) is average refractive index. These relations may vary depending on the fluid composition, which could explain why some previous reports differ (e.g., Burruss and Holister, 1979, p. 167; Shepherd et al., 1985, p. 107).

Stable phase assemblages in this system can be predicted using the phase diagram. Consider the equilibrium crystallization of a bulk composition at point a in Fig. 4 (note that the following discussion differs slightly from that of Shepherd et al., 1985, p. 107). On cooling to the liquidus temperature (point a) halite forms and the composition of the liquid moves directly away from NaCl, assuming negligible solid solution of Ca in halite. The liquid composition reaches the halite-hydrohalite reaction curve at point b, where hydrohalite begins to form and halite begins to resorb. The liquid composition then moves down the halite-hydrohalite reaction curve toward point c. There, halite is completely resorbed (the inclusion contains hydrohalite, liquid of composition c, and vapor of negligible mass), and the liquid composition is free to move across the hydrohalite liquidus field toward point d, along a line directly away from hydrohalite. At point d ice joins the assemblage, and ice and hydrohalite co-crystallize as the liquid moves to the eutectic, point e.

In theory, the equilibrium melting path on heating is simply the reverse of the cooling path. In practice, metastability complicates both cooling and heating paths. For instance, hydrohalite persists metastably to temperatures several degrees above the expected equilibrium (Roedder, 1984; and see Fig. 2, for example). One equilibrium phase transition that can be reliably reproduced is the ice melting temperature (point d, Fig. 4). This has been determined for several inclusions that lose ice along the ice-hydrohalite cotectic, and results of 52 freezing measurements are given in Table 2. When compared to the temperatures predicted by extrapolation of the data of Yanatieva (1946), differences of several tenths to less than two degrees show the consistency of the two data sets. The low angle of intersection between the isotherms and the cotectic precludes more exact agreement.

In three samples, some or all inclusions failed to nucleate hydrohalite on freezing (Table 2). In these cases, at low temperatures, the metastable ice melting temperature in the presence of halite, vapor, and liquid was determined reproducibly. In theory, this temperature should be the same for all three samples, because they all have bulk compositions along the pseudobinary between NaCl and (CaCl$_2$)$_2$(H$_2$O)$_n$ (Fig. 3 and Fig. 5). The actual measured temperatures differed by 0.2°C.

### Table 2. Measured $T_m$(Ice) for synthetic inclusions

<table>
<thead>
<tr>
<th>Sample</th>
<th>Range</th>
<th>Average$^1$</th>
<th>Predicted$^2$</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>-23.0 to -23.9</td>
<td>-23.8 (4)</td>
<td>25.4</td>
</tr>
<tr>
<td>2</td>
<td>-25.1 to -25.8</td>
<td>-25.3 (9)</td>
<td>27.4</td>
</tr>
<tr>
<td>3</td>
<td>-25.7 to -27.2</td>
<td>-25.3 (10)</td>
<td>28.0</td>
</tr>
<tr>
<td>4</td>
<td>-28.8 to -31.8</td>
<td>-29.9 (3)</td>
<td>-33.6</td>
</tr>
<tr>
<td>5</td>
<td>-33.9 to -34.2</td>
<td>-34.1 (6)$^2$</td>
<td>-40.4</td>
</tr>
<tr>
<td>6</td>
<td>-32.1 to -38.7</td>
<td>-38.1 (3)$^2$</td>
<td>-40.4</td>
</tr>
<tr>
<td>7</td>
<td>-34.1 to -34.3</td>
<td>-34.2 (5)$^3$</td>
<td>-40.4</td>
</tr>
<tr>
<td>8</td>
<td>-34.1 to -34.3</td>
<td>-34.3 (3)$^3$</td>
<td>-40.4</td>
</tr>
</tbody>
</table>

$^1$ Temperatures in degrees C; number of inclusions measured in parentheses.

$^2$ These values determined by interpolating from Yanatieva (1946).

$^3$ For these inclusions, $T_m$(Ice) is in the presence of metastable halite, not hydrohalite; see text for discussion.

### Applications to Natural Oceanic Fluid Inclusions

We have used the new halite liquidus data to estimate the bulk compositions of fluid inclusions from a mid-ocean ridge...
in the present study, as has the temperature of ice melting in the presence of metastable halite (~34.2°C). The ice and hydrohalite liquidus curves are interpolated from data of VANATIEVA (1946).

spreading center. Quartz-veined metagabbros dredged from the Mathematician Ridge, East Pacific, contain abundant fluid inclusions (VANKO, 1988; STAKES and VANKO, 1986). Individual samples record episodes of fluid trapping ranging from as high as 700°C (primary inclusions) to 150°C (secondary inclusions). In two samples, coexisting dense halite-saturated inclusions and low-density, low-salinity vapor-rich inclusions (average 45 and 2 wt% NaCl equivalent) attest to an episode of phase separation, which is interpreted to have occurred at 600–700°C and 60–100 MPa pressure (VANKO, 1988).

Initial melting in the halite-saturated inclusions is in the range ~50 to ~70°C. Components such as CaCl₂ and MgCl₂ can lower the eutectic temperatures of natural NaCl-rich fluids to these values, but evidence from deep-sea hot springs strongly suggest that mature oceanic hydrothermal fluids are essentially devoid of magnesium, probably as a result of extensive cation exchange between seawater and oceanic crustal rocks within the downgoing portions of convective systems (e.g., EDMOND et al., 1979; MOTTL, 1983). Consequently, the inclusions are modeled in the system NaCl-CaCl₂-H₂O (VANKO, 1988).

Reconnaissance measurements of \( T_m \) (ice) and \( T_m \) (halite) for several inclusions are shown in Table 3. Where ice melts in the presence of hydrohalite, liquid, and vapor, \( T_m \) (ice) is a stable equilibrium temperature analogous to point d in Fig. 4. The bulk composition of the fluid lies somewhere along the tie line between the liquid composition and the bulk composition of hydrohalite (e.g., d-c-a in Fig. 4). A second constraint on the bulk composition is obtained from \( T_m \) (halite). Given both \( T_m \) (ice) and \( T_m \) (halite), the bulk composition lies at the intersection of the tie line described above and the \( T_m \) (halite) isotherm on the halite liquids. These two curves intersect at a relatively high angle, providing a good estimate of the bulk composition.

Several measurements of \( T_m \) (ice) were also made at the metastable transition when ice melts in the presence of liquid, vapor, and metastable halite. In these inclusions, halite never transformed to hydrohalite on cooling. Similar behavior was observed in several of the synthetic fluid inclusions, particularly those with high CaCl₂ and high total salt contents. In these cases, well-constrained bulk compositional estimates cannot be obtained because only one temperature is known along the metastable reaction curve (Fig. 5). However, assuming that the metastable curve parallels the stable ice-hydrohalite eutectic, and that temperatures along the metastable curve are uniformly about 3°C lower than the eutectic temperatures at the same H₂O-CaCl₂ ratio (i.e., along pseudobinaries toward NaCl), then bulk compositions can be estimated crudely (Table 3).

The Na/Cl weight ratios determined for the natural fluid inclusions range from 2.9 to 7.3 (Table 3 and Fig. 4). These values are substantially below the seawater ratio of 26, but are close to hypothetical hydrothermal end-member fluids (i.e., sampled fluids with the effects of admixed seawater removed; EDMOND et al., 1979) inferred from chemical analyses of hot spring solutions. In particular, the hydrothermal end-members at the southern Juan de Fuca Ridge have Na/Cl of 4.5 to 5.8 (VON DAMM and BISCHOFF, 1987), and the 13°N East Pacific Rise end-member solution has Na/Cl of 6.1 (MICHARD et al., 1984). Saline fluid inclusions from the Mathematician Ridge therefore possess Na/Cl ratios identical to those seen in some modern "black smoker" hot springs in the deep sea, although the total salinities are many times greater. Phase separation of a seawater-derived hydrothermal fluid accounts for these observations (VANKO, 1988).

**CONCLUSIONS**

1. Halite solubilities in the ternary system NaCl-CaCl₂-H₂O have been determined for compositions with as much as 25 wt% CaCl₂, total salinities > 60 wt%, and temperatures up to 500°C, using the synthetic fluid inclusion technique. Results appear to tie in smoothly with previous high-temperature data for the binaries NaCl-H₂O and NaCl-CaCl₂.

2. By measuring \( T_m \) (ice) and \( T_m \) (halite) in inclusions that are saturated with halite at room temperature, the bulk compositions of inclusions can be estimated graphically.

3. Application of the technique to some natural saline inclusions from a mid-ocean ridge hydrothermal system shows that the Na/Cl ratio determined is the same as that found in active high-temperature "black smokers" on the seafloor.

**Table 3.** Results of heating and freezing measurements on natural fluid inclusions (temperatures in °C)

<table>
<thead>
<tr>
<th>Sample</th>
<th>( T_m ) (ice)</th>
<th>( T_m ) (halite)</th>
<th>NaCl/CaCl₂/H₂O</th>
<th>Na/Cl (wt)</th>
</tr>
</thead>
<tbody>
<tr>
<td>B-11</td>
<td>-30.9</td>
<td>278</td>
<td>30.2/10.8/59.0</td>
<td>3.0</td>
</tr>
<tr>
<td>B-1k</td>
<td>-35.8</td>
<td>402</td>
<td>44.6/6.7/58.7</td>
<td>7.3</td>
</tr>
<tr>
<td>A-1e</td>
<td>-29.9</td>
<td>286</td>
<td>31.3/10.0/58.5</td>
<td>3.4</td>
</tr>
<tr>
<td>A-ic</td>
<td>-26.6</td>
<td>287 (ass)</td>
<td>31.4/9.0/59.6</td>
<td>3.3</td>
</tr>
<tr>
<td>A-1b</td>
<td>-30.8</td>
<td>286</td>
<td>31.0/10.0/58.5</td>
<td>3.2</td>
</tr>
<tr>
<td>A-1h</td>
<td>-38.27</td>
<td>392</td>
<td>40/14/60</td>
<td>3.1</td>
</tr>
<tr>
<td>A-1l</td>
<td>-43.55</td>
<td>412</td>
<td>42/16/42</td>
<td>2.9</td>
</tr>
<tr>
<td>A-in</td>
<td>-42.0</td>
<td>411</td>
<td>42/16/42</td>
<td>2.9</td>
</tr>
</tbody>
</table>

1. All inclusions are from a quartz vein in hornblende, sample 7-45, section II (VANKO, 1988).
2. Metastable ice melting temperature in the presence of liquid, vapor, and metastable halite. Estimates of bulk composition are discussed in the text.
REFERENCES


ROBERT F. and KELLY W. C. (1987) Ore-forming fluids in Archean gold-bearing quartz veins at the Sigma Mine, Abitibi greenstone belt, Quebec, Canada. Econ. Geol. 82, 1464-1482.


