Numerical model to determine the composition of H$_2$O–NaCl–CaCl$_2$ fluid inclusions based on microthermometric and microanalytical data

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Received 28 March 2010; accepted in revised form 13 September 2010; available online 8 October 2010

Abstract

Natural fluids approximated by the H$_2$O–NaCl–CaCl$_2$ system are common in a wide range of geologic environments, including sedimentary basins associated with hydrocarbon occurrences and MVT deposits, submarine hydrothermal systems, and other metamorphic, magmatic and hydrothermal environments. We present a comprehensive numerical model and Microsoft® Excel®-based computer program to determine the compositions of fluid inclusions in the H$_2$O–NaCl–CaCl$_2$ system based on microthermometric and microanalytical data. The model consists of six polynomial correlation equations that describe liquid salinity as a function of NaCl/CaCl$_2$ ratio and melting temperature on each of the ice, hydrohalite, halite, antarcticite, CaCl$_2$·4H$_2$O and CaCl$_2$·2H$_2$O vapor-saturated liquidus surfaces. The cotectic and peritectic boundaries are determined from the intersections of the liquidus surfaces. The model is implicitly internally consistent and topologically correct.

The model expands upon the compositional range of applicability and the data types that can be used for compositional determination. It reproduces experimental data for all compositions that lie within the H$_2$O–NaCl–CaCl$_2$·4H$_2$O compositional triangle in the H$_2$O–NaCl–CaCl$_2$ system and yields accurate reproductions of the H$_2$O–NaCl and H$_2$O–CaCl$_2$ binaries. Furthermore, in comparison to previously published models, the one presented here eliminates systematic errors, wavy isotherms and cotectic and peritectic curves with local “bumps.”

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1. INTRODUCTION

Aqueous fluids in which NaCl and CaCl$_2$ are the two most abundant salts and which may be adequately described by the system H$_2$O–NaCl–CaCl$_2$ are common in many geologic environments. Fluids of this composition are commonly found in sedimentary basins (Collins, 1975; Lowenstein et al., 2003; Hanor and McIntosh, 2007), Mississippi Valley-Type Pb–Zn deposits (Haynes and Kesler, 1987; Basuki and Spooner, 2002; Stoffell et al., 2008), Archean lode gold deposits (Robert and Kelly, 1987), skarn and greisen deposits (Kwak and Tan, 1981; Layne and Spooner, 1991; Samson et al., 2008), iron-oxide Cu–Au (IOCG)-type deposits (Xu, 2000), magmatic Cu–Ni deposits (Li and Naldrett, 1993), crystalline rocks of the Canadian Shield (Schiffries, 1990) and elsewhere (Nyman et al., 1990), and in sub-seafloor hydrothermal systems (Vanko, 1988; Vanko et al., 1988). Thus, fluid inclusions approximated by the system H$_2$O–NaCl–CaCl$_2$ are common in a diverse range of geologic environments, and a methodology to interpret microthermometric data obtained from these inclusions is necessary to better understand geologic processes such as diagene, hydrocarbon migration, evolution of hydrothermal systems, metal transport, metamorphism and crystallization of magmas.
The best source of information concerning the compositions of paleo-geologic fluids comes from fluid inclusions (Roedder, 1984). The temperatures at which phase changes occur within a fluid inclusion during heating can be used to estimate the fluid composition, assuming that PTX phase relationships of representative fluid systems are available. In addition, the elemental ratios in saline aqueous inclusions can be determined by microanalysis, for example by laser ablation ICPMS (LA-ICPMS) (Günther et al., 1998), which provides an additional constraint for determining the fluid composition when combined with microthermometric data.

The system H$_2$O–NaCl–CaCl$_2$ (Fig. 1) is a three-component system, and the phase rule requires that two variables must be specified to determine a unique liquid composition on the vapor-saturated liquidus, whereas one variable is sufficient to determine a unique liquid composition on any vapor-saturated, two-solid-plus-liquid boundary (cotectic or peritectic curve). The temperatures of last melting of solid phases, either on a cotectic or peritectic curve ($T_{pb,v}$) or on the one-solid liquidus ($T_{m,v}$), are two possible sources of data; elemental ratios determined from LA-ICPMS represent another data source. (Note that whereas several previous studies of the H$_2$O–NaCl–CaCl$_2$ system have used the term “$X_{NaCl}$” to refer to the weight ratio of NaCl relative to NaCl + CaCl$_2$, we adopt the more common notation such that $X_{NaCl}$ refers to the mole fraction of NaCl, and we instead denote the weight and molar ratios of NaCl relative to NaCl + CaCl$_2$ as $\Phi$ and $\Psi$, respectively. As discussed in detail below, depending upon which data are available, fluid inclusion compositions may be determined using a combination of either the temperature of melting on a cotectic or peritectic and a temperature of melting on the vapor-saturated liquidus surface ($T_{pb,v} + T_{m,v}$), or a temperature of melting on the vapor-saturated liquidus surface and the ratio of the amount of NaCl relative to the total amount of NaCl and CaCl$_2$. ($T_{m,v} + \Phi$ – the two compositional ratios can be directly converted to one another via the molar masses of the species) or the temperature of melting of one phase
on a cotectic or peritectic and the temperature of melting of a second phase on a cotectic or peritectic \((T_{px,cl} + T_{pm,n})\).

Compositions of \(\text{H}_2\text{O–NaCl–CaCl}_2\) fluid inclusions can be approximated using graphically-displayed phase equilibrium data (e.g., Konnerup-Madsen, 1979; Robert and Kelly, 1987) or using empirical or theoretical data (Oakes et al., 1990; Williams-Jones and Samson, 1990; Naden, 1996; Chi and Ni, 2007), and several computer packages have been developed to interpret data from fluid inclusions whose compositions are approximated by the system \(\text{H}_2\text{O–NaCl–CaCl}_2\) (Naden, 1996; Bakker, 2003; Chi and Ni, 2007). While each model works well over a limited range of \(T\)-\(X\) conditions, none of the currently available models is equipped to calculate fluid inclusion compositions over the complete range in compositions reported for natural \(\text{H}_2\text{O–NaCl–CaCl}_2\) fluid inclusions. Moreover, some of the previously published equations (Oakes et al., 1990; Naden, 1996; Chi and Ni, 2007) are characterized by structured residuals with respect to the experimental data, or have inflections (“bumps”) between data points and local extrema along calculated isotherms and univariant curves, as described in more detail below. Finally, none of the previously published models provide the ability to determine fluid compositions using the complete range of possible input data, such as the temperature of melting on a cotectic or peritectic and a temperature of melting on the vapor-saturated liquidus surface \((T_{px,cl} + T_{m,n})\) or a temperature of melting on the vapor-saturated liquidus surface and the weight fraction of NaCl relative to NaCl + CaCl\(_2\) \((T_{cm,n} + \phi)\), or the temperature of melting of one phase on a cotectic or peritectic and the temperature of melting of a second phase on a cotectic or peritectic \((T_{px,cl} + T_{pm,n})\), as described below. The model presented here incorporates those aspects of previous models that have been shown to be consistent with the phase equilibria determined from experimental data, and adds new equations and methods to expand the \(T\)-\(X\) range of applicability, remove anomalies inherent in some previous statistical models, and expands the range of input data that may be used to estimate the composition of \(\text{H}_2\text{O–NaCl–CaCl}_2\) fluid inclusions.

The goal of this study is to provide a comprehensive set of empirical equations that describe the portion of the vapor-saturated \(\text{H}_2\text{O–NaCl–CaCl}_2\) system that includes the range of compositions of natural fluid inclusions and the range of available experimental data. As such, this study covers a region within the ternary system bounded by the \(\text{H}_2\text{O}\) apex, the NaCl apex and the composition of \(\text{CaCl}_2\cdot4\text{H}_2\text{O}\) on the \(\text{H}_2\text{O–CaCl}_2\) binary (Fig. 1b). The equations derived in this study have been developed into a Microsoft® Excel®-based program to allow users to easily calculate fluid inclusion compositions in this complex system over the complete compositional range reported from natural fluid inclusions, using a variety of input data, including \(T_{px,cl} + T_{m,n} + \phi\) or \(T_{px,cl} + T_{pm,n}\). The program is available as an Electronic annex to this paper.

We emphasize that the model developed in this study applies to stable equilibrium melting behavior in the system \(\text{H}_2\text{O–NaCl–CaCl}_2\), but metastable melting phenomena are also frequently encountered in \(\text{CaCl}_2\)-bearing fluids (e.g., Potter and Clyne, 1978; Roedder, 1984; Vanko et al., 1988; Baumgartner and Bakker, 2009). For instance, Vanko et al. (1988) reported that some of their synthetic \(\text{H}_2\text{O–NaCl–CaCl}_2\) fluid inclusions could not be completely frozen, while others could only be frozen to a metastable phase assemblage. Likewise, Linke (1958) and Baumgartner and Bakker (2009) report the occurrence of several metastable phase assemblages in the \(\text{H}_2\text{O–CaCl}_2\) binary system. While we acknowledge that metastable behavior in the \(\text{H}_2\text{O–NaCl–CaCl}_2\) system does occur, the model presented in this study specifically represents only the stable phase relations on the vapor-saturated \(\text{H}_2\text{O–NaCl–CaCl}_2\) fluid.

### 1.1. Vapor-saturated phase relations in the \(\text{H}_2\text{O–NaCl–CaCl}_2\) system

Phase relations on the vapor-saturated liquidus of the \(\text{H}_2\text{O–NaCl–CaCl}_2\) ternary system are shown in Fig. 1. The system is characterized by at least eight fields in which a single solid phase is in equilibrium with liquid and vapor. Six of these fields are described in this study; two additional fields in the high salinity, CaCl\(_2\)-rich, low weight fraction NaCl \((\phi)\) part of the system (near the CaCl\(_2\) apex; Fig. 1a) are not considered here because experimental data are not available in that part of the ternary system (although these phases have been characterized along the \(\text{H}_2\text{O–CaCl}_2\) binary, e.g., Linke, 1958). Fig. 1 shows phase relationships in the part of the system that includes the range of reported compositions of natural fluid inclusions. The phase boundaries shown in Fig. 1c were calculated using the equations derived in this study and below we compare these calculated phase boundaries with experimental data.

Each field shown in Fig. 1 is labeled according to the solid phase that is in equilibrium with liquid and vapor. At low salinity, near the \(\text{H}_2\text{O}\) apex, the stable solid phase on the liquidus surface is \(\text{H}_2\text{O}\) ice (Fig. 1a and c). At intermediate to high salinity and \(\phi > 0.04\), halite (NaCl) is the stable solid phase (Fig. 1a and c). A field in which hydrohalite (NaCl\(_2\cdot2\text{H}_2\text{O}\)) is the stable solid phase separates the ice- and halite-stable fields (Fig. 1a and c). At intermediate to high salinity and \(\phi < 0.04\), calcium chloride hydrates are the stable solid phases: anatase (\(\text{CaCl}_2\cdot6\text{H}_2\text{O}\)) is the stable phase from about 30 to 50 wt% total salt, “tetrahydrate” (\(\text{CaCl}_2\cdot4\text{H}_2\text{O}\)) is the stable solid from 50 to about 57 wt% salt, and “dihydrate” (\(\text{CaCl}_2\cdot2\text{H}_2\text{O} = \text{sinjarite}\)) is stable from about 57 to 75 wt% salt (Fig. 1a and c). To our knowledge, ternary experimental data are not available for the \(\text{H}_2\text{O–NaCl–CaCl}_2\) system at salinities above 75 wt% total salt, thus the CaCl\(_2\cdot2\text{H}_2\text{O}\) and CaCl\(_2\) (anhydrous) stable fields are not included in this study (area near the CaCl\(_2\) apex on Fig. 1a labeled with a question mark, ?). Also shown in Fig. 1c are the compositions of hydrohalite (61.86 wt% NaCl on the \(\text{H}_2\text{O–NaCl}\) binary), anatase (50.07 wt% CaCl\(_2\) on the \(\text{H}_2\text{O–CaCl}_2\) binary), CaCl\(_2\cdot4\text{H}_2\text{O}\) (60.63 wt% CaCl\(_2\) on the \(\text{H}_2\text{O–CaCl}_2\) binary) and CaCl\(_2\cdot2\text{H}_2\text{O}\) (75.49 wt% CaCl\(_2\) on the \(\text{H}_2\text{O–CaCl}_2\) binary).
The fields in which one solid is in equilibrium with liquid and vapor are separated from each other by peritectic or cotectic boundary curves. Ice and hydrohalite are separated by the ice + hydrohalite (I + HH) cotectic, which extends from the ternary eutectic point (E) at −52 °C (Yanatieva, 1946) to the binary H₂O–NaCl eutectic (E') at −21.2 °C (Hall et al., 1988). Ice and antarcticite are separated by the ice + antarcticite (I + A) cotectic, which extends from the ternary eutectic (E) to the binary H₂O–CaCl₂ eutectic (E') at −49.8 °C (Yanatieva, 1946). The hydrohalite and antarcticite fields are separated from each other by the hydrohalite + antarcticite (HH + A) cotectic curve, which extends from the ternary eutectic (E) to the first ternary peritectic (P₁) at −22.4 °C (Yanatieva, 1946). The hydrohalite field is separated from the halite field by the hydrohalite + halite (HH + H) peritectic curve, which extends from the first ternary peritectic (P₁) to the binary H₂O–NaCl peritectic (P₁') at +0.1 °C (Linke, 1958). The halite field is separated from the antarcticite field by the halite + antarcticite (H + A) cotectic curve, which extends from the first ternary peritectic (P₁) to the second ternary peritectic (P₂) at +29 °C (Schiffries, 1990). The halite field is separated from the tetrahydrate field by the halite + tetrahydrate (H + Ca₄h) cotectic, which extends from the second ternary peritectic (P₂) to the third ternary peritectic (P₃) at approximately +45 °C (estimated from the data of Linke, 1958). The halite field is separated from the dihydrate field by the halite + dihydrate (H + Ca₂h) cotectic curve, which extends from the third ternary peritectic (P₃) to the fourth ternary peritectic at >110 °C (Linke, 1958). The antarcticite field is separated from the tetrahydrate field by the antarcticite + tetrahydrate (A + Ca₄h) peritectic curve, which extends from the second ternary peritectic (P₂) to the first binary H₂O–CaCl₂ peritectic (P₂') at +30.1 °C (Linke, 1958). Tetrahydrate is separated from dihydrate by the tetrahydrate + dihydrate (Ca₄h + Ca₂h) peritectic curve, which extends from the third ternary peritectic (P₃) to the second binary H₂O–CaCl₂ peritectic (P₃') at +45.1 °C (Linke, 1958). The locations of other boundary curves that occur at higher salinity conditions close to the CaCl₂ apex are not known. A detailed summary of the stable melting paths followed by H₂O–NaCl–CaCl₂ fluid inclusions having compositions in the various fields described above is provided in Appendix A.

2. SOURCES OF EXPERIMENTAL DATA

The experimental data used in the regression analysis are summarized in Table 1 and Fig. 2.

2.1. Phase boundaries

Phase boundaries on the vapor-saturated liquidus in the system H₂O–NaCl–CaCl₂ are broadly characterized by either cotectic relationships or peritectic relationships. Note that on a cotectic boundary, the phase change behavior that is observed upon heating is always “solid1 + solid2 → liquid”, whereas on a peritectic boundary, the reaction observed upon heating is “solid1 + liquid → solid2 + liquid → liquid”. In other words, as a fluid inclusion is heated, the inclusionist would observe two solids shrinking (melting) along a cotectic curve until one disappeared leaving behind the second solid and liquid, whereas s/he would observe one solid growing at the expense of the other along a peritectic curve.

In addition to the T–X data along the cotectic and peritectic phase boundaries summarized in Table 1 and Fig. 2, Schiffries (1990) reported the temperature at the second peritectic point (P₂) of +29 °C, which provides an additional constraint on the location of the A + Ca₄h, A + H and Ca₄h + H phase boundary curves.

2.2. Liquidus surfaces

In addition to compositions that lie on each divariant liquidus surface, data for the univariant boundary curves (peritectics or cotectics) adjacent to the surface were included in the regression for each liquidus surface. For example, in modeling the hydrohalite field, data from the I + HH, HH + A and HH + H phase boundaries were used in addition to the hydrohalite-only liquidus data. For each liquidus field, the number of data points that have been

<table>
<thead>
<tr>
<th>Source</th>
<th>Solid phase(s) on cotectic and peritectic curves and on liquidus surfaces¹</th>
<th>I + HH</th>
<th>I + A</th>
<th>HH + H</th>
<th>HH + A</th>
<th>H + A</th>
<th>H + Ca₂h</th>
<th>I</th>
<th>HH</th>
<th>H</th>
<th>A</th>
<th>Ca₄h</th>
<th>Ca₂h</th>
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<td>National Research Council (1928)</td>
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<tr>
<td>Yanatieva (1946)</td>
<td>9</td>
<td>3</td>
<td>6</td>
<td>7</td>
<td>8</td>
<td>57</td>
<td>30</td>
<td>13</td>
<td>20</td>
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<tr>
<td>Linke (1958)</td>
<td>4</td>
<td></td>
<td>1</td>
<td>2</td>
<td>21</td>
<td>1</td>
<td>57</td>
<td>15</td>
<td>7</td>
<td>12</td>
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<td>Potter and Clynne (1978)</td>
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<td>Vanko et al. (1988)</td>
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<td>Oakes et al. (1990)</td>
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<td>Oakes et al. (1992)</td>
<td>3</td>
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<tr>
<td>Sterner et al. (1988)</td>
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<tr>
<td>Sub-total</td>
<td>246</td>
<td>31</td>
<td>118</td>
<td>39</td>
<td>12</td>
<td>17</td>
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<td>61</td>
<td>137</td>
<td>58</td>
<td>12</td>
<td>19</td>
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</tbody>
</table>

¹ I = ice; HH = hydrohalite; H = halite; A = antarcticite; Ca₄h = tetrahydrate; Ca₂h = dihydrate.

For each one-solid liquidus surface, the total number of data points used in the regression analysis is the sum of the subtotal (data on the one-solid surface) plus the number of data points for the adjacent boundary curves.

Table 1
Summary of the number of published experimental T–X data points for the H₂O–NaCl–CaCl₂ system used in this study.
used in the regression, including data within the field and those on the phase boundary curves, are listed in Table 1.

For the halite liquidus, the high temperature data of Chou (1987) were omitted from the regression analysis, but these data are in excellent agreement with those of Sterner et al. (1988). In addition, the experimental data analyzed in this study include several liquidus temperature measurements along the anhydrous NaCl–CaCl₂ binary (Zhang et al., 1995), but those data are not included in the data set for regression.

For the tetrahydrate liquidus, Linke (1958) reports multiple polymorphs of CaCl₂·4H₂O coexisting with different salinity liquids. We have followed the suggestion of Potter and Clynne (1978), who point out that consideration of the phase rule indicates that the “beta” and “gamma” polymorphs are metastable, and so we have included only the “alpha” polymorph solubility data of Linke (1958).

3. EQUATIONS DESCRIBING THE LIQUIDUS AND PHASE BOUNDARY CURVES

The liquidus in a ternary system are divariant surfaces, and thus the total salinity (S_{tot}) can be represented as a function of the weight fraction of NaCl relative to NaCl + CaCl₂ (Φ) and the temperature of melting of the last solid phase on the vapor-saturated liquidus (T_{m,x}). The cotectic and peritectic curves are univariant lines and therefore both Φ and S_{tot} can be represented as a function of the temperature of melting of solid phase x on the cotectic or peritectic (T_{pb,x}). Previous studies have generally approached the problem of regression modeling of the vapor-saturated liquidus of ternary systems by fitting separate univariant regression equations to the experimental data on the phase boundary curves (e.g., Sterner et al., 1988; Naden, 1996). While that approach often produces a system of equations with small errors with respect to the experimental data, it also generally yields a model that is not internally consistent because predicted phase boundary curves will not necessarily intersect at the invariant points (eutectic and peritectic points) and predicted isotherms of adjacent fields will not always intersect at the univariant curves as they should. The approach taken in this study has been to regress the data for each liquidus surface, and weight the cotectic and peritectic curves appropriately to ensure that univariant curves represent the intersection of the adjacent liquidus surfaces. This approach has two advantages: First, it yields a model that is implicitly internally consistent, and secondly, it provides additional constraints on liquidus fields that are represented by sparse experimental data. For example, the only data available for the tetrahydrate field are along the H₂O–CaCl₂ binary (as described above). However, isotherms are available at the

![Diagram](image-url)
intersections of the tetrahydrate field with the adjacent antarcticite, halite and dihydrate fields, and these data, combined with data along the H2O–CaCl2 binary, provide reasonable constraints on the locations of isotherms within the tetrahydrate field.

Regression analyses were conducted using SAS® JMP 8 statistical software. The experimental data on each liquidus surface were regressed to find the equation that best satisfied three criteria: First, the equation was required to accurately reproduce the experimental data; secondly, the resulting isotherms were required to be smooth and monotonic, meaning free of local extrema and inflections; and thirdly, the equations for adjacent liquidus surfaces were required to intersect such that the cotectic and peritectic phase boundaries predicted by the intersection were consistent with experimental data. The percent residuals of each equation with respect to the experimental data were calculated by the expression \((1 - \text{calculated/ measured})\times100\).

3.1. Ice field

Salinities of fluid inclusions for which H2O ice is the final solid to melt are described by the following equation, modified from Naden (1996):

\[
S_{\text{mol}} = \sum_{i=0}^{5} a_i T_{m,\text{ice}}^i + \sum_{i=6}^{7} a_i \Phi^{i-5} + a_8 \Phi^{2} T_{m,\text{ice}} + a_9 \Phi T_{m,\text{ice}}^2
- 0.185 \exp(-T_{m,\text{ice}} - 52)
\tag{1}
\]

where \(T_{m,\text{ice}}\) is the final ice melting temperature in degrees Celsius and the \(a_i\)'s are fitting parameters given in Table 2. We have added the exponential term at the end of the equation originally provided by Naden (1996) to improve the intersection with the antarcticite field, as discussed below. The equation for the ice liquidus surface of Chi and Ni (2007) (their Eq. (4)) is based upon extrapolation from their I + HH boundary, and is therefore valid only at high salinity \((T_{m,\text{ice}} \leq -21 \, ^\circ\text{C})\, and it shows significant structure in the residuals as a function of salinity (Fig. 3). The equation of Oakes et al. (1990) (their Eq. (2)) fits the data well at salinities from 0 to 25 wt\%, but provides a poorer fit to the higher salinity data of Yanatieva (1946), with a negative-sloped, apparently linear structure in the residuals in the tetrahydrate field. Smol’s equation originally provided by Naden (1996) to improve the residuals as a function of salinity (Fig. 3). The equation of Oakes et al. (1990) (their Eq. (2)) fits the data well at salinities from 0 to 25 wt\%, but provides a poorer fit to the higher salinity data of Yanatieva (1946), with a negative-sloped, apparently linear structure in the residuals in the tetrahydrate field. Smol’s equation originally provided by Naden (1996) to improve the residuals as a function of salinity (Fig. 3).

3.2. Hydrohalite field

The salinity of fluid inclusions in which hydrohalite is the final solid phase to melt is described by:

\[
S_{\text{mol}} = \sum_{i=0}^{7} a_i (T_{m,\text{hh}} + 52)^i + a_8 \Psi^{-1} + \sum_{i=4}^{5} a_i \Psi^{i-2}
+ \sum_{i=6}^{9} a_i \Psi(T_{m,\text{hh}} + 52)^{i-4} + a_9 \Psi^2(T_{m,\text{hh}} + 52)
\tag{2}
\]

with the \(a_i\)'s listed in Table 2. Residuals associated with calculation of the total salinity in terms of weight percent \((S_{\text{mol}})\) using Eq. (2) are generally within ±5% of experimental values, excluding one outlier (Fig. 3). Eq. (2) does not significantly improve on the residuals associated with the equation of Naden (1996) for the hydrohalite field (Fig. 3); however, the equation of Naden (1996) tends to over-fit the data, and isotherms generated using Naden’s equation have local extrema between data points, (at some temperatures crossing the H + HH peritectic curve to predict compositions that are within the halite field) (Fig. 4). Isotherms generated using Eq. (2) are smooth and without local extrema (Fig. 4), and thus better reflect the geometry of the hydrohalite liquidus surface.

3.3. Halite field

The liquid salinity on the halite liquidus is described by:

\[
S_{\text{mol}} = \sum_{i=0}^{3} a_i (T_{m,\text{hh}} + 52)^i + a_2 \Psi^{-1} + \sum_{i=5}^{9} a_i \Psi(T_{m,\text{hh}} + 52)^{i-3}
+ \sum_{i=7}^{9} a_i \Psi^2(T_{m,\text{hh}} + 52)^{i-7} + \exp(-T_{m,\text{hh}} - 52)
\tag{3}
\]

### Table 2: Coefficients for Eqs. (1)-(6).

<table>
<thead>
<tr>
<th>(a_i)</th>
<th>Ice (Eq. (1))</th>
<th>Hydrohalite (Eq. (2))</th>
<th>Halite (Eq. (3))</th>
<th>Antarcticite (Eq. (4))</th>
<th>Tetrahydrate (Eq. (5))</th>
<th>Dihydrate (Eq. (6))</th>
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<td>2.275938E-4</td>
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<td>8.8841217E-9</td>
<td>1.0162876E-6</td>
<td>-2.95841861</td>
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<td>3.1094576E-6</td>
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</table>
Values of the fitting coefficients $a_i$ are listed in Table 2. Residuals for Eq. (3) are shown in Fig. 3. In addition, the data of Zhang et al. (1995) along the NaCl–CaCl$_2$ binary are predicted by Eq. (3) to within ±4%, even though the Zhang et al. data were not included in the regression analysis. In comparison to Eq. (3), the equation of Naden (1996) for the halite liquidus surface predicts wavy isotherms with local extrema, compared to the smooth, monotonic isotherms generated using Eq. (3) and shown on Fig. 5. The equation of Naden (1996) also does not adequately reproduce the high salinity H$_2$O–NaCl binary data of Sterner et al. (1988) (Fig. 3). Williams-Jones and Samson (1990) developed a theoretical equation to calculate halite solubility on the halite liquidus surface, and they report their results graphically as isotherms on the ternary phase diagram. Williams-Jones and Samson (1990) do not provide an error analysis of their model, and their model cannot be compared directly to our...
results because they do not provide the values for the Pitzer parameters, which they obtained from graphical interpolation. However, based on visual inspection, the isotherms presented by Williams-Jones and Samson (1990) appear to be in good agreement with those predicted by our Eq. (3).

Fig. 5. Comparison of the salinity on the +94.5 °C isotherm on the vapor-saturated halite liquidus predicted by the equation of Naden (1996) (dashed line) and by Eq. (3) from this study (solid line). Experimental data on the +94.5 °C isotherm from the National Research Council (1928) are shown as open circles. These experimental data were chosen for comparison because of the large number of data points extending over a wide range of compositions along the +94.5 °C isotherm in the NRC report.

Fig. 6. Liquidus curves for the H₂O–NaCl (top) and H₂O–CaCl₂ (bottom) binary systems, calculated from Eqs. (1)–(6). Experimental data are from National Research Council (1928) (halite); Yanatieva (1946) (ice, hydrohalite, halite, antarcticite); Linke (1958) (ice, hydrohalite, halite, antarcticite, tetrahydrate, dihydrate); Potter and Clynne (1978) (halite, antarcticite, tetrahydrate, dihydrate); Sterner et al. (1988) (halite); and Oakes et al. (1990) (ice).
3.4. Antarcticite field

The salinity on the antarcticite liquidus surface is described by the following relationship:

\[ S_{\text{mol}} = \sum_{i=0}^{4} a_i (T_{\text{m,ant}} + 52)^i + \sum_{i=6}^{7} a_i W^{i-4} (T_{\text{m,ant}} + 52)^{i-6} \]  

(4)

Values of the fitting parameters, \(a_i\), are listed in Table 2. Residuals associated with Eq. (4) are all within \(\pm 5\%\) of the experimental values (Fig. 3). To our knowledge, no equations have been published previously that describe the relationship between salinity and temperature on the \(\text{H}_2\text{O}–\text{NaCl}–\text{CaCl}_2\) ternary antarcticite liquidus surface.

3.5. Tetrahydrate and dihydrate fields

Quantitative representation of the tetrahydrate and dihydrate fields is limited by the scarcity of available experimental data; however, the narrow compositional range of these fields (Fig. 1c) limits the absolute error in the weight fraction of \(\text{NaCl}\) in the solution (\(\Phi\)) to \(<0.058\). The form of each of the equations for the tetrahydrate and dihydrate fields was based in part on the requirement that the cotectic and peritectic curves bounding these fields must be predicted by the intersection of the equations for the adjacent liquidus fields, because the locations of isotherms in those fields are better constrained than those in the tetrahydrate and dihydrate fields and thus provide a means of checking
the validity of the expressions for those fields. The salinity on the tetrahydride liquidus surface is described by
\[
S_{mol} = \sum_{i=0}^{3} a_i (T_{m,CaCl_2} + 52)^{i/3} + \exp(100\Psi - 10)
\]  \hspace{1cm} (5)
and the salinity on the dihydrate liquidus surface is described by
\[
S_{mol} = \sum_{i=0}^{3} a_i (T_{m,CaCl_2} + 52)^{i/3} + a_i \Psi
\]  \hspace{1cm} (6)
The \(a_i\) parameters are listed in Table 2. Residuals of Eq. (5) are all within ±2% of experimental values, and those for Eq. (6) are within ±3%.

3.6. Comparison with data for the binary systems

The equations described above for modeling the ternary H₂O–NaCl–CaCl₂ system may also be used to predict liquid for the binary H₂O–NaCl and H₂O–CaCl₂ systems using Eqs. (1)–(6), as shown on Fig. 6. The predicted H₂O–NaCl eutectic (E') is at −21.18 °C, compared to the experimentally determined −21.2 °C (Hall et al., 1988). The predicted H₂O–NaCl peritectic point (P') is at +0.14 °C, compared to the experimental value of +0.1 °C (Linke, 1958). The predicted H₂O–CaCl₂ eutectic point (E') is at −49.9 °C, compared to the experimentally determined temperature of −49.8 °C (Yanatieva, 1946). The predicted first and second H₂O–CaCl₂ peritectic points (P₁' and P₂') are at +30.0 °C and +44.7 °C, respectively, compared to the experimental values of +30.1 °C and +45.1 °C (Linke, 1958).

3.7. Phase boundary curves

Each univariant curve is represented by the intersection of the adjacent divariant surfaces, rather than by a separate equation, as discussed above. For example, the liquid composition on the I + HH cotectic is represented by the intersection of the ice and hydrohalite liquidus, or in other words by the collection of T–X conditions that simultaneously satisfy Eqs. (1) and (2). Metastable extensions are not represented in this model. Residuals associated with determining the total salinity in weight percent (Swt) and the weight fraction of NaCl (Φ) along the phase boundary curves by this method are shown in Figs. 7 and 8, respectively. Residuals associated with salinity estimation are all within ±4% for the I + HH and HH + A cotectics, and within ±6% for the HH + H peritectic curve and H + CaCl₂·nH₂O cotectics (Fig. 7). Percent residuals associated with estimation of Φ on the phase boundary curves are generally larger, with ±20% for the I + HH curve, ±5% for the HH + A curve, ±60% for the HH + H curve, and ±50% for the H + CaCl₂·nH₂O curves (Fig. 8). These large percent errors in part reflect the fact that Φ is a small number (<1), such that small absolute errors yield large percent errors. It also reflects some scatter in the experimental data that we intentionally did not attempt to over-fit, owing to our requirement that the phase boundary curves predicted by the equations must be smooth and monotonic.

Identifying pairs of liquidus equations that provided smooth cotectic and peritectic curves that accurately reproduced the experimental values involved some trial and error. In some cases, while the individual equations for the liquidus fields adequately reproduced data in those fields, their intersections sometimes showed significant offset in isotherms on the cotectic or peritectic curves, or did not intersect at experimentally-determined T–X conditions on these curves, or produced topologies for the curves that were not supported by experimental data. As an example, we found that the equation for the H + HH peritectic curve from Naden (1996) that describes the weight fraction of NaCl (Φ) as a function of the melting temperature of hydrohalite on the peritectic curve (\(T_{pb,hh}\)) is over-fitted and predicts an unrealistic curvature, whereas the intersection of Eqs. (2) and (3) from this study is comparably much smoother (Fig. 9). Bakker (2003) incorporated the equations of Oakes et al. (1990) and Naden (1996), without modification, into a computer package that added the option to model the univariant curves by the intersections of the adjacent liquidus surfaces (the same approach taken...
in this study). However, the equations of Naden (1996) for the hydrohalite and halite liquidi intersect along a wavy curve with local extrema in salinity, which causes anomalous predictions from the computer package of Bakker (2003), whereas Eqs. (1) and (3) from the present study intersect more smoothly and without extrema (Fig. 10).

Some structure is observable in the residuals associated with the H + CaCl₂·6H₂O cotectics and the HH + A cotectic (Figs. 7 and 8). This structure could be reduced or eliminated by adjusting equations for the adjacent fields; however, this approach would then compromise the degree to which those equations for the adjacent fields would reproduce experimental data for those fields. As such, we chose to give preference to achieving the most accurate fit on the I + HH and HH + H boundaries, because phase changes along those boundaries are reported more commonly in studies of natural fluid inclusions. Thus, we have to some extent sacrificed the fidelity with which data along the less commonly reported HH + A and H + CaCl₂·nH₂O curves are reproduced. However, we believe that this approach is justified because the antarcticite, tetrahydrate and dihydrate fields encompass a very narrow range of weight fraction NaCl (Φ < 0.05), and the liquid salinity on each of those liquidi surfaces is not very sensitive to the weight fraction of NaCl. Furthermore, since Φ is always <0.05 in this part of the system, relatively large percent errors translate into small absolute errors in the weight fraction of NaCl in the inclusion.

4. METHODOLOGIES FOR DETERMINING INCLUSION BULK COMPOSITIONS

The model presented here allows fluid inclusion compositions to be determined using a variety of input data, including the melting temperature of a phase on a cotectic or peritectic boundary of the last solid on the liquidus surface (T_{ph,x1} + T_{ph,x2}), or the temperature of melting of the last solid on the liquidus surface and the weight ratio of NaCl in the inclusion determined from microanalysis (T_{m,x} + Φ), or the melting temperature of two phases on a cotectic or peritectic boundary, either melting simultaneously (T_{ph,x1} = T_{ph,x2}) or at different temperatures (T_{ph,x1} + T_{ph,x2}). The following sections describe the methodologies to determine bulk composition using the various types of input data.

4.1. Final melting on a cotectic curve (T_{ph,x1} = T_{ph,x2}, two solid phases dissolve simultaneously)

In the simplest case where two solids dissolve simultaneously on a cotectic curve, the bulk composition is uniquely specified by the melting temperature in accordance with the phase rule. The measured melting temperature can be used to calculate the fluid inclusion composition by solving for the intersection of the adjacent surfaces at that temperature, in other words by finding the value of the weight fraction of NaCl (Φ) for which the two adjacent liquidus surface salinity equations yield the same salinity at the measured temperature of melting. For example, consider a fluid inclusion in which ice and hydrohalite dissolve simultaneously at -25°C. The salinity in the ice field at -25°C and a given weight fraction of NaCl (Φ) can be found from Eq. (1), while the salinity in the hydrohalite field at -25°C and Ψ can be estimated from Eq. (2). By iteration, we find that a weight fraction of NaCl, Φ, of 0.57 yields a liquid salinity of 24.7 wt% at -25°C in both Eqs. (1) and (2). Thus, the intersection of the ice and hydrohalite liquidus surfaces occurs at a salinity of 24.7 wt% (NaCl + CaCl₂) and a weight fraction of NaCl of 0.57, and this represents the bulk composition of the fluid inclusion.

4.2. Last melting temperature (T_{m,x}) and NaCl weight fraction (Φ)

If available data include the melting temperature of the last solid obtained from microthermometry, and the weight fraction of NaCl (Φ) determined by microanalysis (e.g., LA-ICPMS), the fluid bulk composition is determined by finding the intersection of the isotherm of the final melting temperature with the pseudobinary defined by the NaCl weight fraction (Φ). Those two variables may be input directly into the appropriate equation (with Φ converted to Ψ where required). As an example, consider a fluid inclusion that contains a halite daughter mineral that dissolves at 200°C, and has a weight fraction of NaCl relative to NaCl + CaCl₂ (Φ) of 0.7 based on LA-ICPMS analysis of the inclusion. A weight fraction of NaCl of 0.7 equals a mol fraction, Ψ, of 0.815, and substituting those values of Ψ (0.815) and T_{m,h} (200°C) into Eq. (3) yields a total salinity on a mole fraction basis, S_{mol}, of 0.116, which corresponds to a total salinity of 33.1 wt%.

4.3. Two unique melting temperatures, T_{ph,x1} ± T_{m,x2} or T_{ph,x1} ± T_{ph,x2}

If available data include two unique melting temperatures from microthermometry – either a cotectic (or peritectic curve) melting temperature (T_{ph,x1}) plus the temperature
of melting of the last solid phase on the liquidus \((T_{m,cl})\), or a cotectic melting temperature \((T_{pb,cl})\) plus a univariant peritectic melting temperature \((T_{pb,tt})\) – various calculation procedures may be used depending on which solid phases and phase changes are involved. On Fig. 11, the ternary system is divided into several numbered fields that identify compositions within the \(\text{H}_2\text{O–NaCl–CaCl}_2\) ternary that involve the same phase changes as input data or follow similar calculation procedures.

4.3.1. Field 1 – \(T_{pb,hh} < T_{m,ice}\)

During heating from the eutectic temperature, fluids with compositions in field 1 (Fig. 11) lose hydrohalite along the \(I + HH\) cotectic and ice is the last solid phase to melt on the ice liquidus surface. The composition of the liquid at the temperature of hydrohalite dissolution on the cotectic is determined from the intersection of the hydrohalite and ice liquidus at the temperature of hydrohalite melting \((T_{pb,hh})\), from Eqs. (1) and (2). After hydrohalite disappears, because the last remaining solid is pure \(\text{H}_2\text{O}\) ice (solid solution between solid phases in this system is negligible), the weight fraction of NaCl \((\Phi)\) of the liquid phase does not change during continued heating and ice melting, and the liquid composition moves directly towards the \(\text{H}_2\text{O}\) apex. Thus, the weight fraction of NaCl \((\Phi)\) of the melt is determined from the temperature of hydrohalite melting on the cotectic and the final ice melting temperature \((T_{m,ice})\), can be input directly into Eq. (1) to determine the bulk salinity.

4.3.2. Field 2 – \(T_{pb,ant} < T_{m,ice}\)

The calculation procedure to determine the composition of fluids that exhibit antarcticite dissolution on the \(I + A\) cotectic, followed by final melting of ice on the ice liquidus surface (field 2; Fig. 11) is analogous to that for fluids in field 1, substituting \(T_{pb,ant}\) for \(T_{pb,hh}\) and substituting Eq. (4) for Eq. (2).

4.3.3. Field 3 – \(T_{pb,ice} < T_{m,h}\)

For fluid inclusions in which ice is the phase that disappears along the \(I + HH\) cotectic and which subsequently show hydrohalite as the last solid to melt on the hydrohalite liquidus (field 3; Fig. 11), the liquid composition at the temperature of ice melting on the \(I + HH\) cotectic is determined from the intersections of Eqs. (1) and (2), as described previously for field 1. After ice melts on the ice-hydrohalite cotectic curve, with further heating the liquid composition evolves along a straight line extending from the composition of the liquid at \(T_{pb,ice}\) to the composition of hydrohalite \((61.86\ \text{wt}\% \text{NaCl})\). The intersection of that line with the isotherm of final halite melting on the \(I + HH\) cotectic determines the unique bulk fluid composition. As an example, consider a fluid inclusion in which ice melts on the \(I + HH\) cotectic at \(-25^\circ\text{C}\) and hydrohalite is the last solid to melt at \(-10^\circ\text{C}\). At the last ice melting temperature, the liquid contains \(14.3\ \text{wt}\% \text{NaCl}\) and \(10.4\ \text{wt}\% \text{CaCl}_2\), from the intersection of Eqs. (1) and (2) at \(T_{pb,ice} = -25^\circ\text{C}\). The fluid inclusion bulk composition lies on a mixing line between the composition of the liquid on the \(I + HH\) cotectic and the composition of hydrohalite. The equation of the mixing line can be determined using the slope and intercept method, where the \(x-\) and \(y-\)axes are wt% NaCl and wt% CaCl\(_2\), respectively, and the input \(xy\) coordinates are the compositions of liquid \((14.3\ \text{wt}\% \text{NaCl}, 10.4\ \text{wt}\% \text{CaCl}_2\) and hydrohalite \((61.9\ \text{wt}\% \text{NaCl}, 0\ \text{wt}\% \text{CaCl}_2\). The equation of this line (in \(xy\) coordinates) is also the equation of the vertical plane containing the line (in \(xyz\) coordinates, where the \(z\)-axis is temperature), because the linear equation of the mixing line is independent of temperature. Thus, by iteratively solving for the pair of values of wt% NaCl and wt% CaCl\(_2\) that satisfy both this linear equation and Eq. (2), we find the bulk composition. In our example, a composition of \(16.4\ \text{wt}\% \text{NaCl}\) and \(9.9\ \text{wt}\% \text{CaCl}_2\) satisfies both equalities, and is thus the bulk fluid composition of the inclusion.

4.3.4. Field 4 – \(T_{pb,ant} < T_{m,h}\)

For fluid inclusions that exhibit antarcticite melting in the presence of hydrohalite along the \(HH + A\) cotectic, followed by hydrohalite final melting (field 4; Fig. 11), the calculation procedure is analogous to that for field 3, the only difference being that \(T_{pb,ant}\) is substituted for \(T_{pb,hh}\) and the liquid composition on the \(HH + A\) boundary is determined from the intersections of Eqs. (2) and (4).

4.3.5. Field 5 – \(T_{pb,hh} < T_{m,h}\)

Fluid inclusions that have compositions within field 5 (Fig. 11) show halite as the last solid phase to melt, and hydrohalite as the next-to-last solid phase to melt. The calculation procedure for fluid inclusion compositions in this field depends on the input data that are available.

For fluid inclusions in field 5 with compositions to the high-salinity side of the line extending from \(\text{CaCl}_2-6\text{H}_2\text{O}\) to \(\text{NaCl}-2\text{H}_2\text{O}\) (Figs. 1 and 11) (field 5a), the sub-solidus assemblage is halite + hydrohalite + antarcticite, and first melting occurs at the first peritectic \(P_1\) (Fig. 1). At this temperature \((\sim 22.4^\circ\text{C})\), antarcticite is consumed and the liquid composition subsequently evolves along the \(HH + H\) peritectic curve, until hydrohalite is consumed at \(T_{pb,hh}\). The liquid composition at \(T_{pb,hh}\) is determined from the intersection of Eqs. (2) and (3). The liquid composition on the peritectic curve is recast in terms of the molar proportion of \(\text{CaCl}_2\) relative to \(\text{CaCl}_2 + 6\text{H}_2\text{O}\) \((\Omega)\) according to:

\[
\Omega = \frac{S_{mol} - S_{ant} \Psi}{1 - S_{mol} \Psi}
\]  

Upon departure from the \(HH + H\) peritectic curve, the value of \(\Omega\) of the liquid remains constant with further heating, as the liquid composition evolves along a straight line towards the \(\text{NaCl}\) apex. The fluid inclusion bulk composition is found as the intersection of the vertical plane containing that line of constant \(\Omega\) with the isotherm of final halite melting.

For fluid inclusions in field 5 that lie within the ice-hydrohalite-antarcticite triangle (fields 5b and 5c) (Fig. 11), first melting occurs at the eutectic and the liquid composition evolves along either the \(HH + A\) or \(HH + I\) curve until either ice or antarcticite is consumed, after which the liquid composition evolves across the hydrohalite field along a straight line towards the composition of hydrohalite. Upon intersecting the \(HH + H\) peritectic curve, halite nucleates and the liquid composition evolves...
along the HH + H curve until hydrohalite is consumed. The composition then evolves along a straight line towards the NaCl apex with further heating until halite is completely consumed. For each of the fields 5b and 5c, there are thus three melting temperatures that may be observed and recorded (\(T_{pb, ice}\) (or \(T_{pb, ice}\)) + \(T_{pb, hh}\) + \(T_{m,h}\)) and any pair of these is sufficient to fix the bulk fluid composition. Vanko et al. (1988) describe the methods by which either pair of these data may be used to determine the fluid bulk composition. If the data available are \(T_{pb, hh}\) and \(T_{m,h}\), the method used to calculate the inclusion composition is the same as outlined above for field 5a. However, as discussed by Roedder (1984) and Vanko et al. (1988), the final melting of hydrohalite can be difficult to observe, and hydrohalite may persist metastably for several degrees Celsius above the equilibrium melting temperature. For those reasons, it is sometimes more practical to measure \(T_{pb, ice}\) (Vanko et al., 1988). In that case, the liquid composition is determined at \(T_{pb, ice}\) using Eqs. (1) and (2), and the equation of the straight line that extends from the cotectic liquid composition at \(T_m, h\) to the composition of hydrohalite (as described above for field 3) (Fig. 12). The intersection of the vertical plane containing that line with the isotherm of \(T_m, h\) on the halite liquidus (Eq. (3)) represents the bulk fluid composition (Vanko et al., 1988) (Fig. 12). Fluid inclusions with compositions in field 5c are treated in a similar manner to those in field 5b, substituting \(T_{pb, ice}\) for \(T_{pb, ice}\) and substituting Eq. (4) for Eq. (1).

![Fig. 12. Schematic heating sequence for a fluid inclusion with a composition within field 5b (Fig. 11), showing the melting events that may be observed during microthermometry. Isotherms of the relevant phase changes are shown as dotted lines. Antarcticite is lost at the eutectic (point “E”). The liquid composition then evolves along the I + HH eutectic with further heating until ice is consumed at point “a” (\(T_{pb, ice}\)). At this point, because hydrohalite is the only solid phase present, the liquid composition evolves along a straight line towards the composition of hydrohalite with further heating (segment a → b). The HH + H curve is intersected at point “b,” where halite nucleates (\(T_{pb, hh}\)). On further heating, the liquid composition evolves along the HH + H peritectic curve (segment b → c), until hydrohalite is consumed at point “c” (\(T_{pb, hh}\)). At this point, halite is the only remaining solid phase, so with further heating the liquid composition evolves towards the NaCl apex until intersecting the \(T_m, h\) isotherm at point “d,” which is the bulk fluid inclusion composition. Note that the bulk composition lies along the mixing line “a-NaCl·2H2O” (between the liquid composition at \(T_{pb, ice}\) and pure hydrohalite), and the mixing line “c-NaCl” (between the liquid composition at \(T_{pb, hh}\) and pure halite), therefore any pair of \(T_{pb, ice}\), \(T_{pb, hh}\) or \(T_{m, h}\) is sufficient to fix the bulk composition.

![Fig. 13. Comparison of the compositional ranges over which the model presented in this study (top) and previously published models of the H2O-NaCl-CaCl2 system are valid (middle and bottom). Top: The compositional range of applicability of the model presented in this study. Middle: The shaded field shows the range of applicability of the model AqSo1e (Bakker, 2003) and is also the range for the model of Chi and Ni (2007), except for a small region near the H2O-CaCl2 binary as described in the text. Bottom: The shaded area shows the range of applicability of the model AqSo2e (Bakker, 2003) and CalcicBrine (Naden, 1996).](image-url)
4.3.6. Field 6 – Tpb,ant, Ca4h or Ca2h < Tm,h

The calculation method for fluid inclusions that exhibit cotectic melting of one of the three CaCl2 hydrates in the presence of halite, followed by halite dissolution as the last solid phase, is similar for each of the three halite + CaCl2–H2O cotectics. Field 6a includes fluid inclusion compositions for which antarcticite disappears on the H + A cotectic, field 6b includes those that lose tetrahydrate along the H + Ca4h cotectic, and field 6c includes those that lose dihydrate on the H + Ca2h cotectic (Fig. 11). The method employed for each of these fields is to determine the liquid composition (Ω) on the cotectic at the temperature of last halite melting from the intersection of Eq. (3) with either Eqs. (4), (5) or (6), (depending on the last hydrate to melt). The fluid inclusion bulk composition is found as the intersection of the vertical plane containing the line of constant Ω with the isotherm of final halite melting (Tm,h).

4.3.7. Field 7 – Tpb,X < Tm,ant, Ca4h or Ca2h

Field 7 (Fig. 11) includes a narrow compositional range near the CaCl2 binary, and is characterized by at least seven possible melting sequences and pairs of input data, although observation of melting sequences in this part of the system has yet to be reported unequivocally for natural fluid inclusions.

Because the weight fraction of NaCl (Φ) in this part of the system is everywhere less than 0.05, the fluid bulk composition can be estimated with reasonable precision from Tm,CaCl2-nH2O alone. The liquid Φ on the appropriate cotectic or peritectic curve can be determined directly as outlined for the other fields, by the intersection of the adjacent liquidus, and the bulk composition lies on the straight line that extends from that composition to the composition of the final melting of solid CaCl2 hydrate. Again, the weight fraction of NaCl (Φ) in the bulk fluid in this part of the system does not significantly affect the calculated total salinity and, in the absence of a next-to-last melting temperature, Φ must be between 0 and 0.05.

5. DESCRIPTION OF THE NUMERICAL MODEL

The numerical model developed in this study has been built into a Microsoft® Excel® program that estimates H2O–NaCl–CaCl2 fluid inclusion compositions. The program is available for download as an Electronic annex to this paper. Compositions that may be calculated using the model are defined by a triangle bounded by the H2O apex, the NaCl apex and the composition of CaCl2·4H2O on the H2O–CaCl2 binary (Fig. 13). For comparison, the compositional limits of other published numerical models (CalcicBrine (Naden, 1996); AqSo1e and AqSo2e (Bakker, 2003); “H2O–NaCl–CaCl2” (Chi and Ni, 2007) ) are also shown in Fig. 13. The compositional range of the numerical model developed in this study extends the applicability to fluid inclusions that have liquid compositions that evolve along an antarcticite-bearing cotectic curve, as well as fluid inclusions that exhibit first melting at the first or second ternary peritectic, for which the composition cannot be determined using the previously published models. The programs “H2O–NaCl–CaCl2” (Chi and Ni, 2007) and “AqSo2e” (Bakker, 2003) do not allow the input of a known weight fraction of NaCl (Φ) to calculate fluid inclusion bulk composition. Furthermore, “AqSo2e” (Bakker, 2003) does not allow the input of the combination of melting of ice on a cotectic or peritectic (Tpb,X) and melting of halite on the liquidus surface (Tm,h).

6. EXAMPLES OF APPLICATION OF THE MODEL

Application of the numerical model developed in this study to interpretation of natural fluid inclusions can be demonstrated using data from previously published studies. Where available, data for individual fluid inclusions have been input into the numerical model derived in this study to determine bulk fluid compositions. In other cases, ranges of measured temperatures of phase transitions have been
Table 3
Compositions of natural fluid inclusions estimated using the numerical model developed in this study. The compositions reported in the original studies are shown for comparison.

<table>
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<th>Source</th>
<th>Measured melting temperatures</th>
<th>Salinity</th>
<th>(\Phi)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(T_{pb, hh})</td>
<td>(T_{m, hh})</td>
<td>From source</td>
</tr>
<tr>
<td>Nyman et al. (1990)</td>
<td>(-44.5) to (-33.5)</td>
<td>(-40.1) to (-25.0)</td>
<td>27</td>
</tr>
<tr>
<td>Vanko et al. (1988)</td>
<td>(-38.0)</td>
<td>(+280)</td>
<td>41</td>
</tr>
<tr>
<td>Schiffries (1990) – “Type 1”</td>
<td>(+21.0) to (+29.0)</td>
<td>(+160) to (+201)</td>
<td>–</td>
</tr>
<tr>
<td>Schiffries (1990) – “Type 3”</td>
<td>(+31.0) to (+39.0)</td>
<td>(+173) to (+225)</td>
<td>–</td>
</tr>
</tbody>
</table>

Fluid inclusions that show ice as the final solid phase to melt are reported in many studies (e.g., see Basuki and Spooner (2002) for references). The “Stage III” inclusions in epidoite of Layne and Spooner (1991) are used as examples here to demonstrate the applicability of the numerical model developed in the present study. The compositions of these fluid inclusions, determined using the microthermometric data of Layne and Spooner (1991) in the numerical model developed in this study range from 17.4 to 26.5 wt% total salt, and a weight fraction of NaCl \((\Phi)\) of 0.064–0.081 (Fig. 14). These compositions are in good agreement with those reported by Layne and Spooner (1991), differing by less than 1 wt% total salinity for each inclusion (Table 3).

Fluid inclusions in which hydrohalite is the last solid to melt have been reported by, among others, Nyman et al. (1990), Layne and Spooner (1991), and Xu (2000). The microthermometric data of Nyman et al. (1990) are reported only as temperature ranges, and the minimum and maximum melting temperatures were used to estimate the range of fluid inclusion compositions using our numerical model (Fig. 14 and Table 3). The range in salinities determined here based on the microthermometric data of Nyman et al. (1990) is 26.4–30.4 wt% NaCl, with a range in weight fraction of NaCl \((\Phi)\) of 0.16–0.63, whereas Nyman et al. (1990) report salinities of 26–27 wt% NaCl and \(\Phi\) from 0.6 to 0.7. The difference in \(\Phi\) reported by Nyman et al. (1990) compared to values determined in this study is likely due to the inaccuracy associated with graphically interpolating isotherms in the hydrohalite field that was used in the previous study, compared to the numerical methods used here. However, the bulk salinities estimated by Nyman et al. (1990) are in good agreement with those estimated here.

Fluid inclusions in which halite is the final solid to melt are described by Vanko et al. (1988), Nyman et al. (1990), Schiffries (1990), Layne and Spooner (1991) and Xu (2000). Microthermometric data from Vanko et al. (1988) for individual fluid inclusions in quartz from a vein in hornblendite from the Mathematician Ridge, East Pacific Rise, have been used to estimate fluid inclusion compositions (Fig. 14). Those fluid inclusions from Vanko et al. (1988) in which ice melts in the presence of metastable halite have been excluded in this example. The compositions of the fluid inclusions determined using our numerical model are in good agreement with the compositions determined by Vanko et al. (1988), differing by less than 2 wt% for each inclusion (Table 3).

Microthermometric data from “Type 1” and “Type 3” inclusions from the Bushveld Complex reported by Schiffries (1990) include coticetic melting temperatures of various CaCl₂ hydrates. Schiffries (1990) did not estimate a bulk fluid composition due the uncertainty in locating the H + A and H + Ca₂h coticetic curves, and the small number of experimental data in this part of the phase diagram (Schiffries, 1990). The “Type 1” inclusions exhibit eutectic melting, and the liquid evolves along the H + A coticetic before losing antarcticite \((T_{pb, am})\) and undergoing final melting by halite dissolution \((T_{m, hh})\). The data for “Type 1”
inclusions indicate salinities ranging from 46 to 51 wt% total salt and weight fraction of NaCl (Φ) ranging from 0.15 to 0.24 (Fig. 14 and Table 3). The “Type 3” inclusions of Schiffries (1990) show first melting at the second ternary peritectic (P₂) (Fig. 1), and the liquid evolves along the H + Ca4h cotectic before losing tetrahydrate (T_{pb,Ca4h}), and the last solid phase to melt is halite (T_{m,h}). The ranges of T_{pb,Ca4h} and T_{m,h} from Schiffries (1990) indicate salinities for the “Type 3” inclusions of 49–54 wt% total salt, with Φ ranging from 0.14 to 0.25 (Fig. 14 and Table 3).

No examples are given in Fig. 14 and Table 3 of fluid inclusions in which antarcticite is the last solid phase to melt, because fluid inclusions of this type have not been unequivocally identified in previous studies. The apparent lack of fluid inclusions of this type may be due in part to the narrow compositional range of the antarcticite field (Fig. 1), but also possibly due to the difficulty of recognizing antarcticite in fluid inclusions (see Roedder, 1984). For example, Robert and Kelly (1987) identified salt hydrate as the last melting phase of some H₂O–NaCl–CaCl₂ fluid inclusions from gold-bearing quartz veins at the Sigma Mine, but were unable to determine whether the phase was hydrohalite or antarcticite. Ulmer-Scholle et al. (1993) report antarcticite as the final solid phase in fluid inclusions in diagenetic quartz from the Delaware Basin (Texas and New Mexico), but the identification was based on melting temperatures up to +3.1 °C for fluid inclusions with homogenization temperatures of 53–81 °C (Ulmer-Scholle et al., 1993). Fluid inclusions with such low homogenization temperatures tend to eliminate the vapor bubble upon freezing, due to the volume expansion associated with the water–ice transition, and thus the melting temperatures were obtained under vapor-absent conditions. Under such conditions, the temperatures of solid–liquid phase transitions cannot be properly interpreted with respect to experimental data for the vapor-saturated liquidus (Roedder, 1967). As shown by Roedder (1967), a final melting temperature of +3.1 °C is not incompatible with metastable melting of ice in the pure H₂O system under vapor-absent conditions.

Although fluid inclusions that have antarcticite as the final solid phase to melt have not been unambiguously identified, fluid inclusions with low NaCl weight fraction (Φ) (e.g., Kwak and Tan, 1981; Layne and Spooner, 1991) as well as those described by Schiffries (1990) in which the liquid composition evolves along the H + A and H + Ca₄h cotectics, indicate that fluid compositions in the CaCl₂-rich portion of the phase diagram occur in nature. Furthermore, Raman analysis has been used to identify CaCl₂ hydrates in fluid inclusions (Dubessy et al., 1982; Samson and Walker, 2000; Baumgartner and Bakker, 2009). The numerical model developed in this study allows fluid compositions to be determined in this part of the phase diagram, and will be useful if fluid inclusions with high salinity and low weight fraction of NaCl (Φ) are discovered in the future.

7. SUMMARY

The empirical equations developed in this study completely describe the geometry of the liquidus surface and cotectic curves for the part of the H₂O–NaCl–CaCl₂ phase diagram between the H₂O apex, the NaCl apex and the composition of CaCl₂·4H₂O on the H₂O–CaCl₂ binary. The numerical model described herein incorporates this comprehensive set of equations to allow fluid inclusion compositions to be determined anywhere within that compositional range, using a variety of combinations of input data. The model has been applied to estimate compositions of natural fluid inclusions using microthermometric data reported in the literature. The Microsoft® Excel® program that implements the model to estimate fluid inclusion compositions is available for download as an Electronic annex to this paper. The authors recommend that the model presented here should be used in preference to CalciteBrine.

ACKNOWLEDGMENTS

The authors thank Dave Vanko, Iain M. Samson and an anonymous reviewer for their comments and suggestions that significantly clarified, improved and shortened an earlier version of this manuscript. The authors also thank Associate Editor Bob Burruss for his comments and sage advice on editorial issues. Thanks to Tobias Schlegel for testing the computer package and suggesting some improvements to the user interface. This material is based upon work supported by the National Science Foundation under Grant Nos. EAR-0711333 and OCE-0928472. The Institute for Critical Technology and Applied Science (ICTAS) at Virginia Tech provided support for Steele-MacInnis. Naden publishes with the permission of the Executive Director, British Geological Survey (NERC).

APPENDIX A. STABLE MELTING PATHS OF H₂O–NACl–CaCl₂ FLUID INCLUSIONS

The compositions of natural fluid inclusions that are described by the system H₂O–NaCl–CaCl₂ may be determined based on the temperature and sequence of phase changes observed during heating from low temperatures. The temperatures of phase changes and the sequence of phase changes, in turn, depend on the bulk composition of the inclusion. The temperature of first melting provides an indication of which representative system is appropriate for interpreting the fluid inclusion composition, and may also provide an indication of the compositional range (e.g., first melting at the eutectic versus first melting at a peritectic point). However, the phase changes that are most often used to determine bulk compositions of fluid inclusions from microthermometric data are the melting temperatures of the last and next-to-last solid phases, so it is not necessary to measure the temperatures of all phase changes. The reader is referred to Schiffries (1990) for a complete discussion of the many potential stable melting pathways in the H₂O–NaCl–CaCl₂ system, and to Vanko et al. (1988) and Baumgartner and Bakker (2009) for some examples of metastable melting sequences. Note that if the last or next-to-last solid phase to melt is metastable, it can lead to misinterpretation of the fluid inclusion composition, as discussed by Roedder (1984) and Baumgartner and Bakker (2009).
The system $\text{H}_2\text{O}–\text{NaCl–CaCl}_2$ 37

Fig. A1. Example melting pathways, or liquid lines of ascent (up temperature), for select compositions in the $\text{H}_2\text{O}–\text{NaCl–CaCl}_2$ system. (a) A fluid with composition “a2” shows first melting at the eutectic (point E, $-52^\circ\text{C}$) where antarcticite is consumed. The liquid composition evolves along the $\text{I} + \text{HH}$ cotectic until hydrohalite is consumed at point “a1” ($T_{\text{pb,hh}}$), after which the liquid evolves toward the $\text{H}_2\text{O}$ apex until ice is consumed at point “a2” ($T_{\text{m,ice}}$), representing the fluid inclusion bulk composition. A fluid with composition “a4” shows hydrohalite melting at the eutectic (point “E”) and the liquid evolves along the $\text{I} + \text{A}$ cotectic until point “a3,” ($T_{\text{pb,ant}}$) where antarcticite melts, with final melting at point “a4” ($T_{\text{m,ant}}$), representing the fluid inclusion bulk composition. (b) A fluid of composition “b2” will show the same initial melting sequence as that for composition “a2” except that ice is consumed before hydrohalite on the $\text{I} + \text{HH}$ cotectic at point “b1” ($T_{\text{pb,ice}}$), whereupon the liquid composition evolves directly towards the composition of hydrohalite until $T_{\text{m,hh}}$ at point “b2”. For composition “b4” ice is lost at the eutectic (point E) and the liquid composition then evolves along the $\text{I} + \text{A}$ cotectic until $T_{\text{pb,ant}}$ at point “b3” where antarcticite is consumed. The liquid then evolves along a straight line toward the composition of hydrohalite until $T_{\text{m,h}}$ at point “b4”. (c) For composition “c4” first melting occurs at the eutectic (point “E”) where antarcticite is lost. The liquid then evolves along the $\text{I} + \text{HH}$ cotectic until ice is completely consumed at point “c1” ($T_{\text{pb,hh}}$). The liquid composition then evolves directly towards the composition of hydrohalite until the $\text{HH} + \text{H}$ curve is intersected at point “c2”, whereupon halite begins to grow at the expense of hydrohalite, and the liquid composition evolves along the $\text{HH} + \text{H}$ peritectic curve. Hydrohalite is finally consumed at point “c3” ($T_{\text{pb,ant}}$), and the liquid composition then evolves towards the NaCl apex until halite melts at $T_{\text{m,h}}$ (“c4”), representing the fluid inclusion bulk composition. Fluid inclusions with composition “c8” follow an analogous pathway, but lose ice at the eutectic (point “E”) and next lose antarcticite on the $\text{HH} + \text{A}$ cotectic at point “c5” ($T_{\text{pb,ant}}$). The liquid composition then evolves towards the composition of hydrohalite until the $\text{HH} + \text{H}$ curve is intersected at point “c6,” where halite first nucleates. The liquid composition then evolves along the $\text{HH} + \text{H}$ curve as halite grows at the expense of hydrohalite with further heating. Hydrohalite is completely consumed at point “c7” ($T_{\text{pb,hh}}$), whereupon the liquid composition evolves directly toward the composition of halite until reaching $T_{\text{m,h}}$ at point “c8”, representing the bulk composition. Fluid inclusions with composition “c10” have first melting at the first ternary peritectic point (“P”) where hydrohalite is lost, and the liquid evolves along the $\text{H} + \text{A}$ cotectic until intersecting the second ternary peritectic point (“P’”), where a reaction occurs and tetrahydrate grows at the expense of antarcticite by incongruent melting. The liquid composition then evolves along the $\text{H} + \text{Ca}_4\text{h}$ cotectic until tetrahydrate is completely consumed at point “c9” ($T_{\text{pb,Ca4h}}$). The liquid then evolves towards the NaCl apex until final halite melting at point “c10” ($T_{\text{m,h}}$). (d) For a fluid inclusion with bulk composition “d2,” first melting occurs at the eutectic (“E”) where hydrohalite is consumed. The liquid then evolves along the $\text{I} + \text{A}$ cotectic curve until ice is completely consumed at point “d1” ($T_{\text{pb,ice}}$), whereupon the liquid composition evolves directly towards the composition of antarcticite until antarcticite is completely consumed at point “d2” ($T_{\text{m,ant}}$). A fluid inclusion with composition “d4” loses ice at the eutectic (point “E”), after which the liquid evolves along the $\text{HH} + \text{A}$ cotectic until hydrohalite is consumed at point “d3” ($T_{\text{pb,hh}}$). The liquid then evolves towards the composition of antarcticite until antarcticite is consumed at point “d4” ($T_{\text{m,ant}}$).
Fluid inclusions approximated by the system H₂O–NaCl–CaCl₂ and having compositions that lie within the ice-hydrohalite-antarcticite triangle (triangle "1"; Fig. 1b) are characterized by the sub-solidus assemblage ice + hydrohalite + antarcticite, and have first melting at the ternary eutectic (E) at −52 °C (Fig. 1c). The vapor bubble (the presence of which is required to demonstrate vapor-saturated conditions) is considered to be of negligible mass and does not contribute to the fluid composition (except perhaps for high temperature (≥400 °C) fluid inclusions that contain a vapor bubble larger than a few 10⁻⁶ of volume percent at the time of last melting). Inclusions with compositions that lie within the hydrohalite + halite + antarcticite triangle (triangle "2"; Fig. 1b) contain the sub-solidus assemblage hydrohalite + halite + antarcticite. For these compositions, first melting occurs at the first peritectic point (point "P₁"; Fig. 1c), and the first solid phase to be consumed is antarcticite. Schiffries (1990) has also identified fluid inclusions that are liquid-absent at room temperature and characterized by the sub-solidus assemblage hydrohalite + halite + tetrahydrate (triangle "3"; Fig. 1b) and exhibit first melting at the second ternary peritectic (P₂) (Fig. 1c) at +29 °C (Schiffries, 1990). Fluid inclusions showing second peritectic (or higher) first melting behavior are liquid-absent at room temperature and can be easily overlooked or mistaken for mineral inclusions during routine petrographic examination (Schiffries, 1990).

Natural H₂O–NaCl–CaCl₂ fluid inclusions that show ice as the last solid phase to melt have been described in many studies and are common in MVT deposits (e.g., see Basuki and Spooner, 2002). For inclusions that ice as the last solid phase to melt the liquid composition may evolve along either the I + HH cotectic (path E → a₁; Fig. A1a) or the I + A cotectic (path E → a₃; Fig. A1a) during heating from the eutectic temperature, depending on the bulk composition. Thus, the melting temperature of ice (T₈₈₅₅) will be preceded by melting of hydrohalite (Tₚₜₕₜₜₜ) (path E → a₁ → a₂, Fig. A1a) for inclusions that contain more than 0.058 weight fraction of NaCl (Φ) relative to NaCl + CaCl₂, corresponding to the composition at the eutectic, but the melting temperature of ice will be preceded by Tₚₜₚₜₜₜ (path E → a₃ → a₄, Fig. A1a) if the bulk composition lies to the CaCl₂-rich side of the eutectic composition (Φ = 0.058).

For fluid inclusions whose bulk composition lies within the hydrohalite field, hydrohalite is the last solid phase to melt and either ice or antarcticite must be the next-to-last solid phase to melt. Thus, the melting temperature of hydrohalite (Tₘₜₜₜₜ) is preceded by either the melting of ice (Tₚₜₚₜₜₜ, path E → b₁ → b₂; Fig. A1b) or the melting of antarcticite (Tₚₜₚₜₜₜ, path E → b₃ → b₄; Fig. A1b). The fluid composition evolves directly toward the composition of hydrohalite upon departure from the I + HH or HH + A cotectic (path segments b₁ → b₂ and b₃ → b₄, respectively; Fig. A1b), until final melting occurs by hydrohalite disappearance (points "b₂" and "b₄"; Fig. A1b). Natural fluid inclusions that show hydrohalite as the last solid to melt have been described by Nyman et al. (1990), Layne and Spooner (1991) and Xu (2000).

Fluid inclusions with bulk compositions at the eutectic, CaCl₂, corresponding to the composition at the eutectic, have first melting at the ternary eutectic (E) at −52 °C (Fig. 1c). Fluid inclusions whose bulk composition lies to the CaCl₂-rich side of the eutectic composition (E) at −52 °C (Fig. 1c) have first melting at the ternary eutectic (E) at −52 °C (Fig. 1c). For example, consider a fluid inclusion with bulk composition shown by point "c₄" in Fig. A1c. First melting occurs at the eutectic (point "E," Fig. A1c), where antarcticite is completely consumed. The liquid composition then evolves along the I + HH cotectic upon further heating until ice is completely consumed at point "c₁" (Fig. A1c). Then, the liquid composition evolves across the hydrohalite field along a straight line toward the composition of hydrohalite on the H₂O–NaCl binary. Upon intersection of the HH + H reaction curve at point "c₂" hydrohalite reacts to produce halite + liquid. The liquid composition then evolves along the HH + H peritectic curve as halite grows at the expense of hydrohalite, until all hydrohalite is consumed at point "c₃," and the liquid composition then evolves along a straight line towards halite with further heating, until final melting of halite at point "c₄," representing the fluid inclusion bulk composition (Fig. A1c). This melting sequence can theoretically yield temperatures for the melting of ice along the I + HH cotectic (Tₚₜₚₜₜₜ) (point "c₁"; Fig. A1c) or melting of antarcticite along the HH + A cotectic, (Tₚₜₚₜₜₜ) (point "c₅"), the melting of hydrohalite along the HH + H peritectic (Tₚₜₚₜₜₜₜ) and the melting of halite on the vapor-saturated halite liquidus (Tₚₚₜₜₜₜ) (Fig. 2c). However, in practice the disappearance of the first phase to melt, either ice or antarcticite, may be difficult to recognize, or the melting temperature of hydrohalite may be difficult to determine accurately owing to sluggish melting or metastability, for instance due to the kinetic barrier to halite nucleation on the HH + H peritectic curve. Fluid inclusions that follow this melting sequence have been described in natural samples by Vanko et al. (1988), Nyman et al. (1990), Layne and Spooner (1991) and Xu (2000).

Fluid inclusions with compositions in the halite field may lose ice on the I + HH cotectic (path E → c₁ → c₂ → c₃ → c₄; Fig. A1c) or lose antarcticite on the HH + A cotectic (path E → c₅ → c₆ → c₇ → c₈; Fig. A1c). For example, consider a fluid inclusion with bulk composition shown by point "c₄" in Fig. A1c. First melting occurs at the eutectic (point "E," Fig. A1c), where antarcticite is completely consumed. The liquid composition then evolves along the I + HH cotectic upon further heating until ice is completely consumed at point "c₁" (Fig. A1c). Then, the liquid composition evolves across the hydrohalite field along a straight line toward the composition of hydrohalite on the H₂O–NaCl binary. Upon intersection of the HH + H reaction curve at point "c₂" hydrohalite reacts to produce halite + liquid. The liquid composition then evolves along the HH + H peritectic curve as halite grows at the expense of hydrohalite, until all hydrohalite is consumed at point "c₃," and the liquid composition then evolves along a straight line towards halite with further heating, until final melting of halite at point "c₄," representing the fluid inclusion bulk composition (Fig. A1c). This melting sequence can theoretically yield temperatures for the melting of ice along the I + HH cotectic (Tₚₜₚₜₜₜ) (point "c₁"; Fig. A1c) or melting of antarcticite along the HH + A cotectic, (Tₚₜₚₜₜₜ) (point "c₅"), the melting of hydrohalite along the HH + H peritectic (Tₚₜₚₜₜₜₜ) and the melting of halite on the vapor-saturated halite liquidus (Tₚₚₜₜₜₜ) (Fig. 2c). However, in practice the disappearance of the first phase to melt, either ice or antarcticite, may be difficult to recognize, or the melting temperature of hydrohalite may be difficult to determine accurately owing to sluggish melting or metastability, for instance due to the kinetic barrier to halite nucleation on the HH + H peritectic curve. Fluid inclusions that follow this melting sequence have been described in natural samples by Vanko et al. (1988), Nyman et al. (1990), Layne and Spooner (1991) and Xu (2000).
Natural fluid inclusions exhibiting this sequence of phase changes have been described by Schaffries (1990).

As pointed out by Schaffries (1990), several phase change sequences corresponding to compositions within the expected range of geologic fluid compositions have yet to be reported in natural H₂O–NaCl–CaCl₂ fluid inclusions. Most notably, natural fluid inclusions in which the last solid phase to melt is a CaCl₂ hydrate have yet to be unequivocally identified; although some previous studies have reported a salt hydrate, thought to be antarcticite, as the last solid phase to melt (e.g., Ulmer-Scholle et al., 1993), and final melting of CaCl₂ hydrates has been observed in synthetic H₂O–CaCl₂ fluid inclusions (Baumgartner and Bakker, 2009).

Several possible sequences of phase changes are contained within the compositional range of the CaCl₂ hydrate liquidus (e.g., paths E → d1 → d2 and E → d3 → d4; Fig. A1d).

APPENDIX B. SUPPLEMENTARY DATA


REFERENCES


*Associate editor: Robert C. Burruss*