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THEORETICAL ESTIMATION OF HALITE SOLUBILITY IN THE SYSTEM $NaCl-CaCl_2-H_2O$: APPLICATIONS TO FLUID INCLUSIONS*

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ABSTRACT

Calcium chloride has been shown to be a major component of halite-bearing fluid inclusions in a variety of geological settings. Routine estimation of the NaCl and $CaCl_2$ contents of such inclusions by microthermometry has, however, been precluded by a paucity of data on the high-temperature phase relationships in the system $NaCl-CaCl_2-H_2O$. Recently published Pitzer parameters that describe the behavior of aqueous species in the system permit activity coefficients of NaCl(aq.) and $CaCl_2$(aq.) and, in turn, halite solubility to be reliably calculated over a wide range of compositions and temperatures to 330°C. The data on halite solubility so calculated and previously published data on low-temperature phase relationships have been used to construct a temperature-contoured phase diagram for the system $NaCl-CaCl_2-H_2O$. This diagram can be used to make graphical estimates of the NaCl and $CaCl_2$ contents of halite-bearing aqueous fluid inclusions using the final melting temperature of ice and the temperature of halite dissolution.

Keywords: halite, solubility, theoretical, high temperature, system $NaCl-CaCl_2-H_2O$, phase relationships, fluid inclusions.

SOMMAIRE

Le chlorure de calcium est un composant important des fluides piégés et saturés en halite d'une variété de milieux géologiques. Une estimation routinière des contenus de NaCl et $CaCl_2$ de telles inclusions par microthermométrie s'est avérée impossible jusqu'à maintenant à cause d'un manque de données à propos des relations de phase dans le système $NaCl-CaCl_2-H_2O$ à température élevée. Les paramètres de Pitzer publiés récemment qui décrivent le comportement des espèces aqueuses dans ce système permettent un calcul des coefficients de l'activité de NaCl(aq.) et de $CaCl_2$(aq.), et, avec ces valeurs, la solubilité de la halite pour une grande étendue de compositions et de températures, jusqu' à 330°C. Les données sur la solubilité calculée de la halite et les données déjà dans la littérature sur les relations de phases à basses températures ont été utilisées pour construire un diagramme de phases avec contours de température pour le système $NaCl-CaCl_2-H_2O$. Avec ce diagramme, on peut se servir de la température de fusion finale de la glace et de la température de dissolution de la halite pour évaluer graphiquement les teneurs de NaCl et de $CaCl_2$ des inclusions fluides aqueuses saturées en halite.

(Traduit par la Rédaction)

Mots-clés: halite, solubilité, théorique, température élevée, système $NaCl-CaCl_2-H_2O$, relations de phases, inclusions fluides.

INTRODUCTION

It is becoming increasingly evident from studies of fluid inclusions in natural systems that $CaCl_2$ is an important component of brines in a variety of geological settings. In some cases, $CaCl_2$ has been shown to be the dominant salt in solution. Fluid inclusions with high contents of $CaCl_2$ have been found in a variety of ore deposits including: tungsten skarns (Kwak & Tan 1981), Mississippi Valley lead–zinc deposits (Haynes & Kesler 1987), sedimentary exhalative lead–zinc deposits (Samson & Russel 1987), lead–zinc vein deposits (Samson & Banks 1988), Archean gold deposits (Robert & Kelly 1987), granite-related copper stockwork deposits (Williams-Jones *et al.* 1989) and unconformity-type uranium deposits (Fuzikawa 1982). $CaCl_2$-rich fluid inclusions have been reported from evaporites (Roedder 1984) and low-grade metamorphic rocks (Crawford *et al.* 1979). It is also worth noting that deep groundwaters in the Canadian Shield commonly contain up to 15 wt.% $CaCl_2$ and have mole fractions of $CaCl_2$ with respect to total dissolved salts in excess of 0.7 (Frape *et al.* 1984).

Despite the impression created by the references given above, there are still comparatively few fluid-inclusion studies in which actual compositions have been reported. Many authors have described fluid inclusions with initial melting temperatures below -52°C (the eutectic temperature for the system $NaCl-CaCl_2-H_2O$; Linke 1958) and concluded, on this basis, that these inclusions probably contain significant $CaCl_2$. However, these authors have generally omitted providing compositions because of the lack of data on the high-temperature phase relationships in the above system and the difficulty in obtaining these compositions using non-microthermometric methods.

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At room temperature, the only phases that are typically present in high-salinity inclusions represented by the system $NaCl-CaCl_2-H_2O$ are liquid, halite, and vapor. Calcium chloride is extremely soluble and will only precipitate (as a hydrated phase) in solutions containing a mole fraction of $CaCl_2$ with respect to total chloride in excess of 0.95. Modeling of the high-temperature behavior of the system is thus largely a matter of knowing the solubility of halite. Until recently, this had been measured only to 94.5°C in the system $NaCl-CaCl_2-H_2O$ (Linke 1958). A few experimental points are now available for temperatures up to 500°C (Vanko *et al.* 1988). However, these are insufficient to completely characterize the solubility of halite in the system at these high temperatures. On the other hand, data on the properties of the aqueous species presented in studies by Brantley (1987) and Moller (1988) make it possible to model the solubility of halite over a significant part of the system at elevated temperatures.

In this paper we present theoretical estimates of the solubility of halite in the system $NaCl-CaCl_2-H_2O$ and describe how these data may be used, in conjunction with microthermometric data, to determine the NaCl and $CaCl_2$ contents of halite-bearing fluid inclusions.

CALCULATION OF HALITE SOLUBILITY

The solubility of halite in any solution can be calculated from the expression:

$$\ln K = \ln (m_{Na^+} \cdot \gamma_{Na^+} \cdot m_{Cl^-} \cdot \gamma_{Cl^-})$$

where K is the solubility product, m refers to molality, and γ is the activity coefficient of the subscripted species. Thus, given the solubility product, it is possible to determine the saturation molality of NaCl (*i.e.*, halite solubility) in an aqueous solution provided that the activity coefficients are known. The latter depend not only on temperature and ionic strength, but also on the nature of the other species in solution.

The data have previously been insufficient to characterize the thermodynamic behavior of solutions in the system $NaCl-CaCl_2-H_2O$ at elevated temperatures, and, in particular, to predict the activity coefficients of the aqueous ions. It is, however, now possible to model the behavior of solutions in this system for temperatures up to 350°C using the data of Brantley (1987) and Moller (1988). Brantley (1987) has measured vapor pressures of $NaCl-CaCl_2$ brines with ionic strengths up to 16.5 m at 200°, 250°, 300°, and 350°C and fitted these data to the ion interaction model of Pitzer (1973) to obtain values for the solute-adjustable Pitzer parameters $\beta^{(0)}$, $\beta^{(1)}$, C_ϕ, θ, and ψ. Moller (1988) has derived fitting equations for the same parameters for temperatures between 25° and 250°C and ionic strengths to 18 m for species in the system $Na-Ca-Cl-SO_4-H_2O$ using published solubility, e.m.f., and osmotic pressure data.

We have calculated the mean stoichiometric activity coefficients for NaCl and $CaCl_2$ using the following equation, simplified from Pitzer & Kim (1974), the data for $\beta^{(0)}$, $\beta^{(1)}$, C_ϕ, θ, and ψ from the sources referred to above, and values for A_ϕ tabulated in Pitzer *et al.* (1984):

$$\begin{aligned}\ln\gamma_{MCl} = {} & Z_M f^\gamma + (2\nu_M / \nu)\, m_{Cl}\, [B_{MCl} + \Sigma m_{Cl} C_{MCl}] \\ & + (2\nu_{Cl}/\nu)\, [m_{Na}\, (B_{NaCl} + \Sigma m_{Cl} C_{NaCl} + \nu_M/\nu_{Cl}\theta_{MNa}) \\ & + m_{Ca}(B_{CaCl} + \Sigma m_{Cl} C_{CaCl} + \nu_M/\nu_{Cl}\theta_{MCa})] \\ & + m_{Na} m_{Cl}[Z_M B_{NaCl}{}' + \nu^{-1}\, (2\nu_M Z_M C_{NaCl} + \\ & \qquad \nu_M \psi_{NaCaCl})] \\ & + m_{Ca} m_{Cl}[Z_M B_{CaCl}{}' + \nu^{-1}(2\nu_M Z_M C_{CaCl} + \\ & \qquad \nu_M \psi_{NaCaCl})] \\ & + m_{Na} m_{Ca} \nu^{-1} \psi_{NaCaCl}\end{aligned}$$

where:

f^γ is the electrostatic term covering long-range interactions between species.

$$f^\gamma = -A_\phi(I^{1/2}/1 + 1.2I^{1/2}) + 2/1.2 \ln (1 + 1.2I^{1/2})$$

B_{MCl} is the second virial coefficient.

$$B_{MCl} = \beta^{(0)} + (2\beta^{(1)}/\alpha^2 I)[1-(1 + \alpha I^{1/2})\exp(-\alpha I^{1/2})]$$

$B_{MCl}{}'$ is the ionic strength derivative of B_{MCl}

$$B_{MCl}{}' = (2\, \beta^{(1)}/\alpha^2 I^2)[-1 + (1 + \alpha I^{1/2} + {\textstyle\frac{1}{2}}\alpha^2 I)\exp(-\alpha I^{1/2})]$$

and C_{MCl} is the third virial coefficient

$$C_{MCl} = C^\phi_{MCl}/2Z^{1/2}_M$$

In the above equations, γ refers to activity coefficient; M to metal; ν_M and ν_{Cl} to the stoichiometric coefficients of metal and chlorine in the metal chlorides; ν to the sum of ν_M and ν_{Cl}; Z_M to the charge of the cation; I to ionic strength; A_ϕ to the Debye-Hückel constant for the osmotic coefficient; α, $\beta^{(0)}$, $\beta^{(1)}$, to adjustable single-salt parameters used to calculate the second virial coefficient (α is set equal to 2 for 1 - 1 and 1 - 2 electrolytes); C^ϕ to an adjustable single-salt parameter used to calculate the third virial coefficient; and θ and ψ to the mixed-salt triple-ion interaction parameters. For further information on the Pitzer interaction model, the reader is referred to Pitzer (1973) or Pitzer & Kim (1974).

Activity coefficients calculated from the data of Brantley (1987) and Moller (1988) are very similar in the region of temperature overlap, provided, in the case of Brantley's data, that the mixed-salt parameters θ and ψ are set equal to zero. This is true even at the higher ionic strengths of 6 to 16.5 m, where quite sizable values are recommended for θ and ψ. Brantley (pers. comm.) has subsequently expressed doubt that use of any value other than zero for the above parameters is statistically justified. At high temperatures and ionic strengths, the fit of the data to the Pitzer model is comparatively poor because of significant ion-pairing between Ca^{2+} and Cl^- (Williams-Jones & Seward 1989) and possibly because of changes in the hydration sphere of the Ca^{2+} ion (Kumar & Atkinson 1983), which are not taken into account by the Pitzer equations.

We have opted to use the equations of Moller (1988) to calculate activity coefficients up to temperatures of 200°C, and rely on graphical interpolations of the values of the Pitzer parameters provided by Brantley (1987) to calculate activity coefficients at higher temperatures. This choice was guided in part by the slightly better fit of our modeled solubility of halite using the data of Brantley (1987) to the experimental solubility data of Vanko *et al.* (1988). This is discussed in more detail below.

We calculated the solubility product (Ksp) of halite from activity coefficient data for halite-saturated aqueous solutions presented in Pitzer *et al.* (1984) and the halite-solubility function of Potter *et al.* (1977).

The method used to estimate fluid-inclusion compositions, which is described in the next section, requires that a polythermal projection of the ternary system H_2O–NaCl–$CaCl_2$ be prepared showing isotherms on the halite saturation surface. The locations of the isotherms were determined by calculating the solubility product for a given temperature, and, for given total molalities of dissolved salts, determining the particular fractions of NaCl and $CaCl_2$ that would generate an equivalent activity product of Na^+ and Cl^-. In practice, the latter was achieved by an iterative technique known as solution by halves. This involved calculating the ionic strength and, in turn, the activities of the species in two end-member solutions and a solution with a composition midway between them, testing to determine which pair of compositions generated activity products bracketing the solubility product of halite, and repeating the process with the bracketing pair as the new end-members. These steps were repeated for each point until satisfactory convergence on the

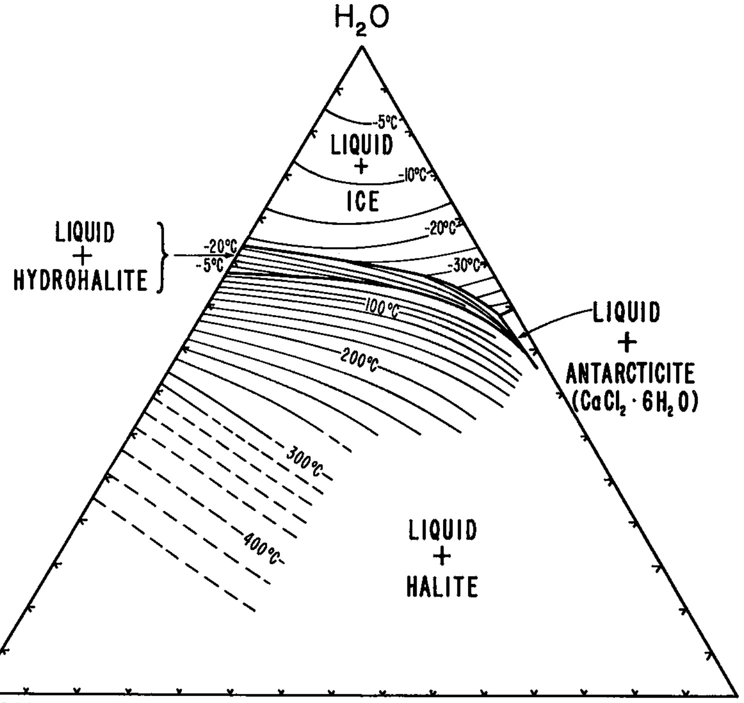

FIG. 1. A phase diagram for the ternary system NaCl–$CaCl_2$–H_2O contoured for temperature. The data used to construct the phase boundaries and subzero isotherms are from Linke (1958). The isotherms for the halite saturation surface, shown at 20°C intervals (solid lines), were calculated as described in the text. Also shown are aproximate isotherms (dashed lines) for halite saturation at temperatures above 320°C constructed by extending lines parallel to the 300°C isotherm from the compositions given by the equations of Potter *et al.* (1977) or Chou (1987) for temperatures below or above 382°C, respectively (discussed further in the text).

solubility product was achieved.

The solid lines in the halite field of Figure 1 represent contours of halite saturation computed at 20°C intervals by the procedure described above. It will be noted that at low temperatures these contours cover most of the field, whereas at higher temperatures they are increasingly restricted to the NaCl–H_2O side of the diagram. This distribution is due, in part, to the fact that with increasing temperature, the solubility of halite increases and with it the ionic strength of the solution. As has already been noted, there are maximum limits on the ionic strengths of the solutions for which the activity coefficients may be calculated. We have also noted that at the higher temperatures, the solubility model appeared to break down at increasingly lower ionic strengths; indeed, we were not able to calculate halite solubility above 330°C. This breakdown of the model presumably reflects the Ca^{2+} - Cl^- ion pairing that we referred to earlier.

CALCULATED VERSUS EXPERIMENTALLY DETERMINED SATURATION OF HALITE

Figure 2 shows experimental solubility data for halite saturation in the system NaCl–$CaCl_2$–H_2O and theoretically determined contours for halite saturation at the corresponding temperatures calculated using the methods described in the previous section. As previously noted, 94.5°C was the highest temperature for which experimentally determined values of saturated halite solubility in the system NaCl–$CaCl_2$–H_2O were available until the recent work of Vanko *et al.* (1988). The earlier data for 50° and 94.5°C, compiled in Linke (1958), define contours of halite saturation that are similar to the model contours, as may be seen from Figure 2. The higher-temperature data on halite saturation determined by Vanko *et al.* (1988) are limited to 11 compositional points, of which only four are in the temperature range for which halite-saturation contours have been

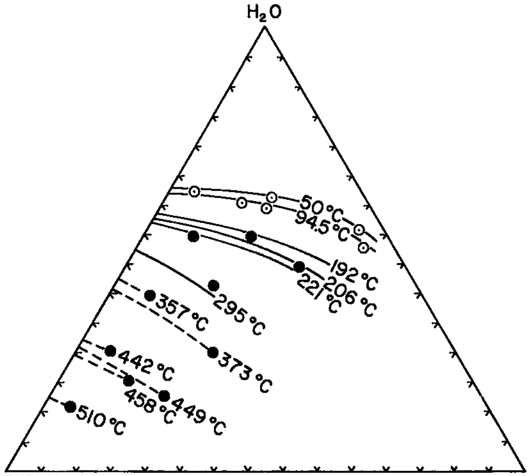

FIG. 2. The NaCl-$CaCl_2$-H_2O ternary system showing selected isotherms on the halite-saturation surface calculated in this study (solid curves) and experimentally determined compositions of halite-saturated liquids at the same temperatures. The open circles are from Linke (1958), and the closed circles from Vanko *et al.* (1988). Also shown are lines (dashed) extended from the composition of the liquid at halite saturation on the NaCl–H_2O binary (Potter *et al.* 1977, Chou 1987) to corresponding experimentally determined points in the ternary system at the same temperatures. Note that these high-temperature isotherms are essentially parallel to the calculated 295°C isotherm.

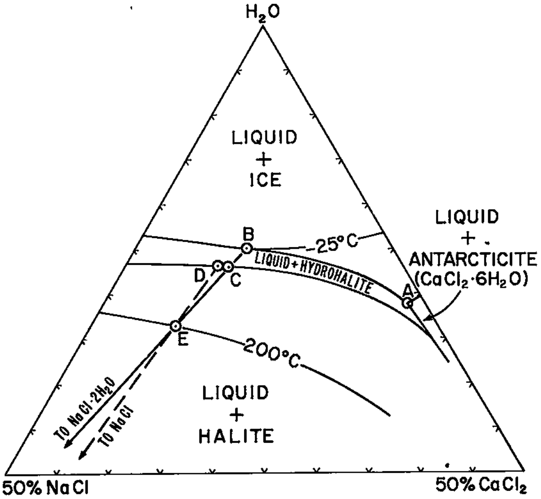

FIG. 3. A phase diagram for the system NaCl–$CaCl_2$–H_2O illustrating the method for estimating the composition of an initially frozen fluid inclusion that contained halite as a daughter mineral at room temperature. Point A shows the eutectic composition, point B the temperature of final melting of ice, point C the temperature at which hydrohalite reacts to form halite, point D the composition at which all the hydrohalite has been converted to halite, and point E the final dissolution temperature of halite. The bulk composition of the fluid inclusion is given by the intersection of the appropriate halite-saturation isotherm with a line extending from the composition at the final melting temperature to the composition of hydrohalite (on the NaCl–H_2O join). In the illustrated example, an inclusion with a final melting temperature of ice of -25°C and a final dissolution temperature of halite of 200°C will contain 25.3 wt.% NaCl and 8.3 wt.% $CaCl_2$. The bulk composition can, in theory, also be obtained from the intersection of the dashed line with the appropriate isotherm. However, the position of the former cannot generally be well constrained owing to metastable persistence of hydrohalite to anomalously high temperatures.

calculated. Those four points plot close to the corresponding model contours and thus provide support for the validity of the model (Fig. 2). Their remaining data consist of single points for various temperatures ranging from 357° to 510°C. If lines are drawn joining these compositions to the composition at halite saturation on the NaCl–H_2O binary join, approximate contours of halite saturation at high temperatures in the ternary system can be obtained (Vanko *et al.* 1988). The latter were obtained using the equation of Potter *et al.* (1977) for temperatures below 382°C and the equation of Chou (1987) for higher temperatures. These lines are also shown on Figure 2. With one exception, all the lines below 449°C are essentially parallel to the model curves computed at 300°C and 320°C. This suggests that the approximate positions of the higher-temperature saturation curves in the ternary system may be estimated by drawing lines parallel to the 300°C model curve (the curve for 320°C only extends to 6 wt.% $CaCl_2$) from the appropriate saturation composition on the NaCl–H_2O binary join.

ESTIMATING COMPOSITIONS OF FLUID INCLUSIONS

The NaCl and $CaCl_2$ contents of halite-bearing aqueous fluid inclusions may be reliably estimated using the final melting temperature of the ice and the temperature of halite dissolution. The method, as previously discussed by Vanko *et al.* (1988) and outlined below, derives directly from consideration of the warming path of a frozen fluid inclusion whose composition is represented by the system NaCl–$CaCl_2$–H_2O (point E on Fig. 3). From Figure 3, it can be seen that melting of such an inclusion starts at the eutectic (point A) and that the liquid composition changes, with increasing temperature, along the cotectic joining hydrohalite, ice, and liquid until the disappearance of the final ice crystal (point B). At this temperature, the composition of the liquid moves into the field of hydrohalite and liquid and changes along a line extended to the composition of hydrohalite until a reaction boundary is reached, where hydrohalite breaks down to form halite (point C). The composition of the liquid then changes along this boundary until all the hydrohalite has reacted (point D). Thereafter the composition of the liquid moves into the field of halite and liquid along a line extended to the NaCl apex of the diagram until the final dissolution of halite. The bulk composition of the fluid inclusion lies at the intersection of this line with the appropriate isotherm of saturated halite-solubility (point E). In practice, hydrohalite is generally very difficult to see and commonly melts metastably several degrees above its equilibrium temperature (Roedder 1984). Thus the line joining point D to the NaCl apex cannot be accurately positioned. However, from the preceding discussion, it can be seen that the bulk composition of the system also must lie somewhere along the line joining the final melting temperature of ice (point B) with the composition of hydrohalite (line B–C represents a binary mixture of hydrohalite and liquid). It follows, therefore, that this line also must pass through point E. Fortunately, temperatures of final melting of ice and dissolution of halite can be accurately determined, and thus a reliable estimate of the composition of the fluid inclusion can be obtained from the intersection of this second line with the halite-saturation isotherm.

CONCLUSIONS

The data are now available to reliably determine activity coefficients for the aqueous ions in the system NaCl–$CaCl_2$–H_2O at temperatures up to 350°C and at high ionic strengths. These data permit halite solubility to be accurately modeled at these elevated temperatures and have thus enabled construction of a phase diagram that allows satisfactory estimates to be made of the compositions of halite-bearing fluid inclusions that can be represented by the above system.

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