CRYOGENIC RAMAN SPECTROSCOPIC STUDIES IN THE SYSTEM NaCl–CaCl$_2$–H$_2$O AND IMPLICATIONS FOR LOW-TEMPERATURE PHASE BEHAVIOR IN AQUEOUS FLUID INCLUSIONS

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ABSTRACT

The character of Raman spectra in the O–H stretching region collected at low temperatures (~–180°C) from fine-grained aggregates of ice and salt hydrate (hydrohalite or antarcticite or both) in the system H$_2$O–NaCl–CaCl$_2$ reflects the composition of the parent solution and can be used to estimate the ratio of NaCl to CaCl$_2$ in the system. Comparison of these spectra with spectra collected from moderate-salinity natural fluid inclusions from the Oregon 3 granitic pegmatite, Colorado, allows non-destructive testing, and confirmation that these inclusions contain CaCl$_2$, as inferred from microthermometry. In both synthetic solutions in the H$_2$O–NaCl–CaCl$_2$ system and in natural fluid inclusions, Raman spectra collected after initial freezing indicate the presence of ice, but not salt hydrates. Upon warming, a phase change is observed at temperatures of between –70 and –50°C that appears as a darkening of the inclusion and that, during routine microthermometry, could be interpreted as a eutectic melting event. Raman spectra collected after this event indicate that it represents the crystallization of salt hydrates (hydrohalite and antarcticite), which we suggest occurs from an interstitial, hypersaline liquid. Many of the low "eutectic" temperatures reported in the literature may thus not represent first melting (stable or metastable), and inferences made about the composition of fluid inclusions from such measurements may be erroneous.

Keywords: fluid inclusions, composition, phase behavior, cryogenic Raman spectroscopy, eutectic, CaCl$_2$.

SOMMAIRE

Le caractère des spectres Raman dans la région de l'étirement O–H, prélevés à basse températures (~–180°C) sur des aggrégats à grains fins de glace et d'hydrate(s) de sel (hydrohalite ou antarcticite ou les deux) dans le système H$_2$O–NaCl–CaCl$_2$, dépend de la composition de la solution et peut servir à estimer le rapport de NaCl à CaCl$_2$ du système. Une comparaison de ces spectres avec des spectres obtenus d'inclusions fluides naturelles de salinité moyenne provenant de la pegmatite granitique Oregon 3, au Colorado, permet une évaluation non destructive, et confirme que ces inclusions contiennent le CaCl$_2$, comme le laissaient supposer les mesures microthermométriques. Aussi bien dans les solutions synthétiques du système H$_2$O–NaCl–CaCl$_2$ que dans les inclusions fluides naturelles, les spectres Raman prélevés après un gel initial indiquent la présence de glace, mais non des hydrates de sel. En réchauffant ces inclusions, nous observons un changement de phase entre –70 et –50°C, qui se manifeste par un assombrissement de l'inclusion, et qui serait interprété couramment comme une fusion eutectique du contenu de l'inclusion. Les spectres Raman prélevés après cet événement montrent qu'il s'agit bien de la cristallisation des hydrates de sel (hydrohalite et antarcticite), à notre avis à partir d'un liquide interstitiel hypersalin. Plusieurs des cas de faible température "eutectique" dans la littérature ne représenteraient donc pas l'initiation d'une fusion (stable ou métastable), et les inférences faites à propos de la composition des inclusions fluides à partir de telles mesures pourraient bien être erronées.

(Traduit par la Rédaction)

Mots-clés: inclusions fluides, composition, comportement des phases, spectroscopie Raman cryogénique, eutectique, CaCl$_2$.

INTRODUCTION

In the microthermometric analysis of aqueous fluid inclusions, the temperature of first melting of a frozen inclusion is generally used to infer something about the identity of the electrolytes dissolved in the aqueous phase (Crawford 1981, Roedder 1984). These measurements are important because they tell us whether or not a particular model for the major-element composition of an inclusion is appropriate. For example, an equilibrium first-melting temperature well below the H$_2$O–NaCl eutectic implies that this simple binary system is

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inappropriate for modeling phase behavior in this particular inclusion. First-melting temperatures below the equilibrium eutectic temperatures in the H_2O–$NaCl$ and the H_2O–$NaCl$–KCl systems (at –21.2 and –22.9°C, respectively) are generally used to infer that other cations (most commonly Ca^{2+}, Mg^{2+}, or Fe^{2+}) are present in solution (Crawford 1981, Roedder 1984, Goldstein & Reynolds 1994). However, such first-melting temperatures are notoriously difficult to observe, especially in small inclusions, and are thus prone to error and misinterpretation. Furthermore, it is generally difficult to be confident that a change during warming of a frozen inclusion is, in fact, the appearance of liquid at the stable eutectic temperature. Indeed, alternative interpretations have been advanced that involve melting of a metastable assemblage (Davis *et al.* 1990, Vanko *et al.* 1988) or devitrification of saline, aqueous glasses (Roedder 1984, p. 297).

Final ice-melting temperatures below the eutectic temperatures of the H_2O–$NaCl$ and H_2O–$NaCl$–KCl systems are less common, but are less ambiguous, and again require interpretation using a salt system in which such final ice-melting temperatures are possible. Inclusions with eutectic and final ice-melting temperatures below the stable eutectic in the H_2O–$NaCl$–KCl system are most often interpreted in terms of the H_2O–$NaCl$–$CaCl_2$ system, which is used to estimate salinity, and, in some cases, the ratio of $NaCl$ to $CaCl_2$ in the inclusion. It would be very useful to determine, nondestructively, whether or not Ca is responsible for low first-melting or final ice-melting temperatures in individual inclusions and, thus, whether or not the system H_2O–$NaCl$–$CaCl_2$ is appropriate for modeling such inclusions. We tackle this problem here in the context of our investigation of the system H_2O–$NaCl$–$CaCl_2$.

BACKGROUND INFORMATION

Dubessy *et al.* (1982) demonstrated that salt hydrates can be identified in individual fluid inclusions using Raman spectroscopy. This goal was achieved by growing large crystals (> 100 μm) in both synthetic solutions and in natural fluid inclusions, and collecting Raman spectra from these crystals at temperatures of between –170 and –175°C. They were able to distinguish various salt hydrates in inclusions by the character of spectra in the OH-stretching region (3000–3600 cm^{-1}) and by comparison with spectra collected from synthetic hydrates. At such low temperatures, band widths are narrower than at higher temperatures, allowing better resolution of the closely spaced hydrate peaks.

In the system H_2O–$NaCl$–$CaCl_2$, the stable solid assemblage below the eutectic temperature is ice – hydrohalite ($NaCl•2H_2O$) – antarcticite ($CaCl_2•6H_2O$) (Yanatieva 1946, Crawford 1981). Except in very $CaCl_2$-rich solutions, antarcticite will melt at the ternary eutectic temperature upon warming a frozen mixture in this system. It is therefore impossible to grow large crys-

tals of antarcticite in most natural inclusions from which Raman spectra could be obtained. An alternative approach, and one which we have employed here, is to collect spectra from the fine-grained aggregate of crystals that constitute the frozen inclusions. This approach has the added advantage that it can potentially provide information about the bulk composition of the inclusion because the relative proportions of the various hydrates should reflect the relative abundance of the electrolytes in the fluid inclusion.

We have carried out, and report here, a pilot study in which we have collected Raman spectra from frozen, synthetic solutions in the system H_2O–$NaCl$–$CaCl_2$ and from natural fluid inclusions which, based on microthermometric analysis, were considered to contain $CaCl_2$. This study was conducted to assess whether useful information about the bulk composition of aqueous fluid inclusions can be obtained with this method. We show that this is the case and, in addition, that some phase changes observed below the stable eutectic temperature represent crystallization, rather than melting events.

METHODS

All Raman spectra were collected on an I.S.A. Jobin Yvon THR 1000 Raman spectrometer fitted with a liquid-N_2-cooled CCD detector. Excitation was achieved using an ionized argon Lexel laser tuned to 514.5 nm. Integration times typically ranged from 3 to 10 s (up to 50 s); in most cases, three spectra were coadded. Low temperatures were achieved with a Linkam fluid inclusion system comprising a THM600 stage, TMS91 programmable temperature controller, and a CS196 liquid nitrogen pump. Spectra were obtained at temperatures between –175 and –185°C. Synthetic solutions were analyzed within thin (~<1 mm o.d.) capillary tubes manufactured by heating and stretching glass tubing. Fluid inclusions were analyzed in doubly polished wafers 100–200 μm thick.

Synthetic solutions

Synthetic solutions in the H_2O–$NaCl$, H_2O–$CaCl_2$, and H_2O–$NaCl$–$CaCl_2$ systems were prepared from Fisher analytical grade $NaCl$ and $CaCl_2$. The $NaCl$ and $CaCl_2$ binary solutions were prepared at 15 and 20 wt.% salt, respectively, to provide abundant salt hydrate upon freezing but to be below saturation with any solid phase at room temperature. Solutions in the ternary system were prepared by mixing these two stock solutions at weight ratios of 1:2, 1:1, and 2:1 ($NaCl$:$CaCl_2$).

Fluid inclusions

The fluid inclusions used for analyses are from the Oregon 3 rare-element granitic pegmatite in Colorado. This is one of many rare-element granitic (NYF-type)

pegmatites that comprise the South Platte district within the northern portion of the Proterozoic, Pikes Peak batholith (Simmons & Heinrich 1980, Simmons *et al.* 1999). The quartz core of this pegmatite contains abundant, large, secondary aqueous inclusions. These comprise liquid–vapor inclusions and inclusions that contain one or more typically small crystals that include halite and anhydrite (Levasseur 1997, Levasseur & Samson 1996). The relative proportions of liquid, vapor and halite in the halite-bearing inclusions are consistent, indicating that the halite is a daughter mineral. Some halite-bearing inclusions also contain a birefringent, fibrous solid that has not been identified and that likely is a trapped phase. These fibrous crystals may also occur in halite-free inclusions. Some inclusions also contain one or more crystals of anhydrite, identified using Raman spectroscopy (Walker 1998).

First-melting temperatures of the halite-free inclusions, as measured by Levasseur (1997), were found to range from –71 to –17°C, whereas in the halite-bearing inclusions, they range from –63 to –29°C. Final ice-melting temperatures for the same inclusions were found to range from –49 to 0°C and –42 to –20°C, respectively (Levasseur 1997). The low eutectic and final ice-melting temperatures both indicate that the H_2O–NaCl system is inadequate as a model for this phase behavior. Given that this granitic pegmatite contains a significant quantity of both magmatic and hydrothermal fluorite (Simmons & Heinrich 1980), it is reasonable to hypothesize that the low temperatures are caused by $CaCl_2$ in the inclusions. This was subsequently borne out by the work reported here and by decrepitate analyses of the inclusions using scanning electron microscopy (SEM; Walker 1997, Walker & Samson 1998). When modeled in the H_2O–NaCl–$CaCl_2$ system, the phase behavior described above, along with temperatures of halite dissolution, indicate that the salinity of the inclusions ranges from 0 to 35 equiv. wt. % NaCl + $CaCl_2$. In this pilot study, we concentrated on inclusions of moderate to high salinity to maximize the likelihood of obtaining spectra with detectable hydrate peaks.

RESULTS

Synthetic solutions

Low-temperature Raman spectra for water and various solutions in the H_2O–NaCl, H_2O–$CaCl_2$, and H_2O–NaCl–$CaCl_2$ systems are shown in Figure 1. The spectral range shown (3000 to 3600 cm^{-1}) corresponds to the region containing the strongest Raman bands for ice and the salt hydrates. The bands are generated by internal stretching vibrational modes for the H_2O molecules in the hydrate structure (Falk & Knop 1973, Dubessy *et al.* 1982). A discussion of the assignments of the bands in this region for the common salt hydrates was given by Dubessy *et al.* (1982).

The spectrum for the H_2O solution (Fig. 1a) shows two prominent peaks at ~3092 and 3216 cm^{-1}, and some weaker features at higher wavenumbers. These peaks, which are also present in all of the salt–solution spectra (Figs. 1b through 1f), correspond to O–H stretching vibrations in ice (Taylor & Whalley 1964, Whalley 1977). Although Dubessy *et al.* (1982) assigned these peaks to hexagonal ice (Ih), the Raman spectra of cubic ice (Ic) and Ih are identical (Taylor & Whalley 1964, Whalley 1977); Ic should be the stable phase at the temperatures the spectra were collected (Bertie *et al.* 1963, Franks 1972).

Four peaks that cannot be ascribed to ice are evident in the H_2O–NaCl spectrum (Fig. 1b). These may be assigned to the O–H stretching modes in hydrohalite

FIG. 1. Raman spectra of the O–H stretching region (3000 to 3600 cm^{-1}) of frozen solutions of water, and various compositions in the H_2O–NaCl–$CaCl_2$ system. All spectra were collected at between –175 and –185°C in thin-walled glass capillary tubes. The NaCl solution contains 15 wt.% NaCl, and the $CaCl_2$ solution 20 wt.% $CaCl_2$. The ratios given for the NaCl–$CaCl_2$ mixtures (2:1, 1:1, and 1:2) refer to weight ratios of the two stock solutions that were mixed. The peaks shown in the H_2O spectrum (and which are also visible in the other spectra) correspond to ice. The additional peaks labeled in spectra b and f are from hydrohalite and antarcticite, respectively. These latter peaks form composite peaks in the mixed-solution spectra.

(Dubessy *et al.* 1982) at 3403, 3420, 3435, and 3536 cm⁻¹. Similarly, the H_2O–$CaCl_2$ spectrum exhibits the principal O–H stretching bands for antarcticite at 3386, 3406, and 3432 cm⁻¹ (Dubessy *et al.* 1982). The NaCl–$CaCl_2$ mixtures (Figs. 1c, d, and e) all contain the hydrohalite peak at 3536 cm⁻¹ and a set of composite peaks in the 3380 to 3450 cm⁻¹ region. The 3420 cm⁻¹ hydrohalite peak is present in all three mixtures but diminishes in intensity relative to the other peaks with increasing Ca content (from Figs. 1d to 1c to 1e). The 3403 cm⁻¹ and 3406 cm⁻¹ peaks of hydrohalite and antarcticite overlap sufficiently to appear as a single peak at about 3404 cm⁻¹ in the mixtures. The same is true of the 3435 cm⁻¹ (hydrohalite) and 3432 cm⁻¹ (antarcticite) peaks, which combine to form a peak at 3434 cm⁻¹. Because the 3432 cm⁻¹ peak is the most intense of the antarcticite peaks, the composite peak at 3434 cm⁻¹ is the dominant peak in the Ca-rich mixture (Fig. 1e). The weakest of the antarcticite peaks (3386 cm⁻¹) only appears in the Ca-rich mixture as a shoulder (Fig. 1e).

Fluid inclusions

Spectra obtained after initial rapid freezing of most inclusions show the peaks of ice, but few other spectral features (Fig. 2). In the region between 3380 and

3550 cm⁻¹, where the principal hydrate peaks should occur, response is either relatively flat (Fig. 2b) or, more commonly, contains a broad peak centered at about 3440 cm⁻¹ (Fig. 2c).

Upon warming such frozen inclusions, a phase change was commonly observed between about –70 and –50°C, and in some cases, as low as –90°C. This is either manifested as a darkening of the solid assemblage or (less commonly) as a wave of darkening that sweeps across the inclusion. Similar phenomena were observed in the synthetic mixtures. After this phase change was observed, prior to any further warming, the inclusions were cooled quickly to ~–180°C and spectra taken. These spectra (Fig. 3) are characterized by the presence of peaks between 3350 and 3560 cm⁻¹, which correspond to the peak positions for hydrohalite and antarcticite, in addition to the ice peaks. During continued warming after the initial phase change, significant melting was observed at temperatures between –49 and –45°C.

FIG. 3.   Raman spectra of frozen, natural fluid inclusions from the Oregon 3 granitic pegmatite, Colorado. a. and b. Spectra obtained from liquid–vapor (LV) inclusions. c. Spectrum obtained from a liquid–vapor–halite (LVH) inclusion. d. Spectrum obtained from an aqueous inclusion containing liquid, vapor and a birefringent crystalline solid (LVS). Inclusions were initially frozen rapidly from room temperature, warmed to between –70 and –50°C until a darkening of the inclusion was observed, and then cooled to around –180°C, at which temperature the spectra were obtained. These spectra contain peaks that can be assigned to ice and hydrohalite, at 3092 and 3536 cm⁻¹, respectively, and a series of composite peaks between 3350 and 3460 cm⁻¹ that correspond to a mixture of hydrohalite and antarcticite (*cf.* Fig. 1).

FIG. 2.   Raman spectra taken from fluid inclusions frozen by rapid cooling from room temperature. These spectra are characterized by the prominent ice peak at ~3090 cm⁻¹ and by broad peaks at higher wavenumbers. a. Host quartz. b. and c. Typical spectra obtained from rapidly frozen aqueous fluid inclusions in quartz from the Oregon 3 granitic pegmatite, Colorado.

In comparison with the spectra obtained on synthetic solutions in Figure 1, it can be seen that they qualitatively most resemble the 2:1 NaCl:CaCl$_2$ mixture (Fig. 1c). The 3422 cm^{-1} peak is the most intense, and the 3406 and 3435 cm^{-1} peaks are subequal in intensity. The presence of antarcticite is indicated by the relatively high intensity of the 3435 cm^{-1} peak, which in the NaCl-only spectrum (Fig. 1b) is less intense than the 3403 cm^{-1} peak.

It was not always possible to obtain spectra with well-defined hydrate peaks, even after thawing and re-freezing the inclusion as described above. In such inclusions, the region in which the hydrate peaks should appear was typically marked by a weak to intense very broad peak, centered at approximately 3440 to 3450 cm^{-1} (Fig. 4).

Modeling

In order to evaluate the contributions of various hydrates to the composite peaks in the 3350 to 3460 cm^{-1} region of the inclusion spectra, we mathematically modeled the spectra obtained. Spectra were smoothed, and Lorentzian functions were fitted to the spectra over the range of interest (Fig. 5). In some cases, a baseline correction was applied prior to fitting. For each pair of graphs in Figure 5 (a through d), the individual points on the upper graphs represent the original, smoothed

FIG. 4. Raman spectra of two fluid inclusions that have been repeatedly frozen and thawed, but which did not yield peaks for salt hydrates. Rather, they are characterized by the main ice peaks and by broad peaks at higher wavenumbers.

spectrum. The lower graphs show the individual Lorentzian peaks used to model the spectrum, and the solid line on the upper graphs represents the modeled spectrum based on these peaks. Excellent fits to the spectra acquired from synthetic solutions are obtained with peaks centered at 3402, 3420, and 3435 cm^{-1} for H$_2$O–NaCl (Fig. 5a) and at 3389, 3406, and 3433 cm^{-1} for H$_2$O–CaCl$_2$ (Fig. 5b). These six peaks also provide very good fits of the composite peaks in spectra obtained from mixed H$_2$O–NaCl–CaCl$_2$ solutions (Fig. 5c), and indicate that the mixed spectra are simply combinations of the peaks present in the binary mixtures. Very good fits also were found from spectra obtained from inclusions (Fig. 5d) in models using the same peak positions of hydrohalite and antarcticite used to model the synthetic solutions. This agreement indicates that Na and Ca are the only abundant hydrate-forming cations present in the inclusions. Spectra of Mg and Fe hydrates are sufficiently distinct from those of hydrohalite and antarcticite (Dubessy *et al.* 1982) that the strong Raman bands for these phases would not be masked by the bands of hydrohalite and antarcticite, and thus would be visible if Mg or Fe hydrates were present in sufficient quantities in the inclusions.

DISCUSSION AND CONCLUSIONS

As the data presented in Figure 1 clearly show, the character of Raman spectra of the hydrates in the stretching region obtained from fine-grained aggregates of synthetic solutions reflects the bulk composition of the fluid. In this study, only qualitative statements can be made with any confidence about the presence or absence of CaCl$_2$, although some semiquantitative statements about the relative abundance of NaCl and CaCl$_2$ are possible. Whether this technique could be used to quantify the relative amounts of NaCl and CaCl$_2$ will require further study. Even if an acceptable calibration curve can be constructed using synthetic solutions (either in capillary tubes or in synthetic inclusions), application of this approach to natural inclusions will be limited by the quality of spectra obtained from the latter, as such spectra tend to show significant noise. Nevertheless, we have been able to obtain spectra of sufficient quality from natural fluid inclusions to allow us to determine whether or not dissolved CaCl$_2$ is present in the inclusions studied.

The spectra obtained after initial cooling of inclusions indicates that ice typically forms during initial freezing, but that hydrates do not (Fig. 2). In other words, a disequilibrium solid assemblage exists in these inclusions upon simple cooling. Subsequent warming of these inclusions induces a phase change, typically between approximately –70 and –50°C, that represents the crystallization of hydrohalite and antarcticite. This is indicated by the character of Raman spectra collected after this event, which contain peaks for these compounds (Fig. 3). The crystallization of these phases

FIG. 5. Lorentzian models of smoothed Raman spectra. In some cases, a baseline correction was applied prior to fitting. For each pair of graphs, the individual points on the upper graph represent the original, smoothed spectrum. The lower graphs show the individual Lorentzian peaks used to model the spectrum, and the solid line on the upper graph represents the modeled spectrum based on these peaks. a. NaCl. b. $CaCl_2$. c. NaCl–$CaCl_2$, 1:2 mixture. d. A natural fluid inclusion.

could either occur at the expense of a hypersaline liquid interstitial to the ice crystals, or of a saline, aqueous glass. In the latter case, the crystallization would represent devitrification.

At low temperatures, H_2O may exist as a variety of amorphous solids (glasses) that include high-density amorphous ice and low-density amorphous ice (Handa et al. 1986, Tulk et al. 1998). With increasing temperature, such amorphous phases convert to crystalline ice. The transition temperature for high-density to low-density amorphous ice is reported to be –159°C by Handa et al. (1986). When amorphous ice crystallizes, it does so as cubic ice (Ic) at temperatures of between –129 and –114°C (Handa et al. 1986, Hallbrucker et al. 1989), and then converts to hexagonal ice at higher tempera-

tures. The temperature of transformation from cubic to hexagonal ice does not appear to be well constrained, as several different values have been measured; Bertie et al. (1963) place the transition at between –130 and –120°C, McMillan & Los (1965), at around –87°C, and Handa et al. (1986), at between –89 and –41°C. The variability, at least in part, appears to reflect heating rates and the thermal history of the sample (Bertie et al. 1963, Handa et al. 1986). There is also some evidence that amorphous ice may convert directly to hexagonal ice, particularly where relict crystals of hexagonal ice serve as nucleation sites (Handa et al. 1986).

The Raman spectra of the amorphous ice phases are characterized by a broad Raman peak that varies in position from ~3280 to 3340 cm^{-1} depending on the phase

measured (Klug *et al.* 1987, Tulk *et al.* 1998). The breadth of this peak, at least in part, reflects a wide range in the strength of the hydrogen bond (Tulk *et al.* 1998). The broad peaks in our spectra (Fig. 2) are centered at higher wavenumbers (~3430–3470 cm^{-1}) than would be expected for amorphous ice.

The presence of the ice peaks in our spectra indicates that crystalline ice has formed. It is conceivable, however, that the residual saline liquid forms a vitreous solid. Although vibrational spectroscopic studies have been carried out on glasses formed in aqueous salt systems (*e.g.,* Tao *et al.* 1991), we are not aware of any spectra measured in the O–H-stretching region, nor of any assessment of the incorporation of salt into the structure of amorphous ice, which would presumably cause shifts in the position of the Raman bands. Certainly, O–H-stretching vibrations in silicate glasses produce broad Raman bands between 3300 and 3700 cm^{-1} (McMillan *et al.* 1983, Mysen & Virgo 1985, McMillan & Remmele 1986), such that this is not an unreasonable suggestion.

Alternatively, the broad peak represents O–H-stretching vibrations in liquid H$_2$O, which form a broad asymmetrical peak at ~3450 cm^{-1} (Walrafen 1964, 1972) and which represent overlapping peaks corresponding to H$_2$O molecules in different structural configurations. With increasing salinity, the shape of this band becomes more symmetrical but remains centered at ~3450 cm^{-1} as the intensities of the lower-frequency peaks diminish (Walrafen 1962, Mernagh & Wilde 1989). The position and shape of the broad band in our spectra are, therefore, more consistent with the presence of a saline, aqueous solution, rather than a glass, although without Raman spectra of saline glasses, the latter possibility cannot be ruled out. The rapidity with which the hydrates crystallize also suggests that they form from a liquid rather than a glass (*cf.* Roedder 1984).

However, there is experimental evidence that aqueous glasses liquify prior to crystallization of ice upon warming; the temperature at which the glass converts to a liquid is known as the glass transition (T$_g$). In pure H$_2$O, the glass transition has been measured at between –144 and –135°C (McMillan & Los 1965, Johari *et al.* 1987, Hallbruker *et al.* 1989), although not all investigators interpret this transition as a change from glass to liquid (Fisher & Devlin 1995). With the addition of salt, T$_g$ is raised and increases with increasing salinity (Angell & Sare 1970). LiCl, the only chloride salt of a monovalent cation studied by Angell & Sare (1970), had less effect on T$_g$ than chloride salts of polyvalent cations or nitrate and sulfate salts. If NaCl has a similar effect, T$_g$ would be raised to around –110°C in a solution containing 25 mole % salt. Calcium chloride has a more pronounced effect and would require concentrations of approximately 20 mole % to raise T$_g$ to –60°C. Thus, significant concentrations of dissolved salt in the residual liquid in the inclusions could allow glass to

exist up to the temperatures at which the hydrates crystallize in our inclusions. However, aqueous glasses are difficult to form by supercooling liquid H$_2$O (Brüggeller & Mayer 1980) except from aerosols (Brüggeller & Mayer 1980, Mayer 1985), and are more commonly formed by vapor deposition (Burton & Oliver 1935) or through the conversion of ice at high pressures (Mishima *et al.* 1984). All of the evidence we have favors a model in which ice forms on initial cooling, leaving a residual, interstitial, hypersaline liquid. On warming, the salt hydrates crystallize from this liquid.

Phase transitions in synthetic inclusions in the system NaCl–CaCl$_2$–H$_2$O at temperatures between –90 and –70°C have been attributed to melting events at metastable eutectics and on liquidi above these eutectics (*e.g.*, Davis *et al.* 1990, Vanko *et al.* 1988). We do not dispute that such melting may occur; the data presented above, however, indicate that at least some phase transitions between about –70 and –50°C represent a crystallization event and not a melting event. Significant melting is observed in the inclusions studied at temperatures slightly above (~–49°C) the equilibrium eutectic temperature in the system NaCl–CaCl$_2$–H$_2$O (–52°C); this presumably represents a case of equilibrium melting. In interpreting low-temperature phase equilibria in the system NaCl–CaCl$_2$–H$_2$O, Davis *et al.* (1990) suggested that a CaCl$_2$ hydrate generally forms (either stable CaCl$_2$•6H$_2$O or metastable CaCl$_2$•4H$_2$O), but that hydrohalite commonly does not form. Our data suggest that, typically, no hydrates form.

The character of this phase change and the temperatures at which it occurs would, in most inclusions, lead to the interpretation that this is a eutectic melting event. If interpreted as a stable eutectic, the interpretation that the fluid contains salts other than NaCl and CaCl$_2$ would be wrong. Thus because of the demonstrated existence of crystallization events in this study and the possibility of metastable melting events (Davis *et al.* 1990, Vanko *et al.* 1988), apparent eutectic temperatures below –50°C in natural fluid inclusions may be erroneous, and the interpretation of such measurements in terms of a complex fluid chemistry may be unwarranted.

Mathematical modeling of the inclusion spectra indicates that the composite hydrate peaks in the 3380–3450 cm^{-1} region can be adequately explained by hydrohalite and antarcticite peaks. This is consistent with data obtained from SEM examination with analysis of decrepitate residues by energy-dispersion spectrometry (EDS) (Walker 1998, Walker & Samson 1998) and from laser-ablation inductively coupled plasma – mass spectrometry (ICP–MS) analyses (Samson *et al.* 1998) on the same inclusions, which indicate that NaCl and CaCl$_2$ are the dominant salts in solution. We recommend that, wherever possible, interpretation of phase behavior, such as low eutectic temperatures, in aqueous fluid inclusions using multicomponent systems be based on elemental analysis of inclusions.

REFERENCES

ANGELL, C.A. & SARE, E.J. (1970): Glass-forming composition regions and glass transition temperatures for aqueous electrolyte solutions. *J. Chem. Phys.* **52**, 1058-1068.

BERTIE, J.E., CALVERT, L.D. & WHALLEY, E. (1963): Transformations of ice II, ice III, and ice V at atmospheric pressure. *J. Chem. Phys.* **38**, 840-846.

BRÜGGELLER, P. & MAYER, E. (1980): Complete vitrification in pure liquid water and dilute aqueous solutions. *Nature* **288**, 569-571.

BURTON, E.F. & OLIVER, W.F. (1935): The crystal structure of ice at low temperatures. *Proc. R. Soc.* **A153**, 166-172.

CRAWFORD, M.L. (1981): Phase equilibria in aqueous fluid inclusions. *In* Fluid Inclusions: Applications to Petrology (L.S. Hollister & M.L. Crawford, eds.). *Mineral. Assoc. Can., Short Course Handbook* **6**, 75-100.

DAVIS, D.W., LOWENSTEIN, T.K. & SPENCER, R.J. (1990): Melting behavior of fluid inclusions in laboratory-grown halite crystals in the systems $NaCl-H_2O$, $NaCl-KCl-H_2O$, $NaCl-MgCl_2-H_2O$, $NaCl-CaCl_2-H_2O$. *Geochim. Cosmochim. Acta* **54**, 591-601.

DUBESSY, J., AUDEOUD, D., WILKINS, R. & KOSZTOLANYI, C. (1982): The use of the Raman microprobe mole in the determination of the electrolytes dissolved in the aqueous phase of fluid inclusions. *Chem. Geol.* **37**, 137-150.

FALK, M. & KNOP, O. (1973): Water in stoichiometric hydrates. *In* Water, a Comprehensive Treatise. 2. Water in Crystalline Hydrates Aqueous Solutions of Simple Nonelectrolytes (F. Franks, ed.). Plenum Press, New York, N.Y. (55-113).

FISHER, M. & DEVLIN, J.P. (1995): Defect activity in amorphous ice from isotopic exchange data: insight into the glass transition. *J. Phys. Chem.* **99**, 11584-11590.

FRANKS, F. (1972): The properties of ice. *In* Water, a Comprehensive Treatise. 1. The Physics and Physical Chemistry of Water (F. Franks, ed.). Plenum Press, New York, N.Y. (115-149).

GOLDSTEIN, R.H. & REYNOLDS, T.J. (1994): Systematics of fluid inclusions in diagenetic minerals. *S.E.P.M. Short Course* **31**, S.E.P.M., Tulsa, Oklahoma.

HALLBRUCKER, A., MAYER, E. & JOHARI, G.P. (1989): Glass transition in pressure-amorphized hexagonal ice. A comparison with amorphous forms made from the vapor and liquid. *J. Phys. Chem.* **93**, 7751-7752.

HANDA, Y.P., MISHIMA, O. & WHALLEY, E. (1986): High-density amorphous ice. III. Thermal properties. *J. Chem. Phys.* **84**, 2766-2770.

JOHARI, G.P., HALLBRUCKER, A. & MAYER, E. (1987): The glass–liquid transition of hyperquenched water. *Nature* **330**, 552-553.

KLUG, D.D., MISHIMA, O. & WHALLEY, E. (1987): High-density amorphous ice. IV. Raman spectrum of the uncoupled O–H and O–D oscillators. *J. Chem. Phys.* **86**, 5323-5328.

LEVASSEUR, R. (1997): *Fluid Inclusion Studies of Rare Element Pegmatites, South Platte District, Colorado*. M.Sc. thesis, Univ. of Windsor, Windsor, Ontario.

_____ & SAMSON, I.M. (1996): Fluid inclusion characteristics of REE–Y–Nb pegmatites, South Platte District, Colorado. *Geol. Assoc. Can. – Mineral. Assoc. Can., Programs Abstr.* **21**, A56.

MAYER, E. (1985): New method for vitrifying water and other liquids by rapid cooling of their aerosols. *J. Appl. Phys.* **58**, 663-667.

MCMILLAN, J.A. & LOS, S.C. (1965): Vitreous ice: irreversible transformations during warm-up. *Nature* **206**, 806-807.

MCMILLAN, P.F., JAKOBSSON, J.R., HOLLOWAY, J.R., & SILVER, L.A. (1983): A note on the Raman spectra of water-bearing albite glasses. *Geochim. Cosmochim. Acta* **47**, 1937-1943.

_____ & REMMELE, R.L., JR. (1986): Hydroxyl sites in SiO_2 glass: a note on infrared and Raman spectra. *Am. Mineral.* **71**, 772-778.

MERNAGH, T.P. & WILDE, A.R. (1989): The use of the laser Raman microprobe for the determination of salinity in fluid inclusions. *Geochim. Cosmochim. Acta* **53**, 765-771.

MISHIMA, O., CALVERT, L.D. & WHALLEY, E. (1984): "Melting ice" I at 77 K and 10 kbar: a new method of making amorphous solids. *Nature* **310**, 393-395.

MYSEN, B.O. & VIRGO, D. (1985): Raman spectra and structure of fluorine- and water-bearing silicate glasses and melts. *In* Advances in Materials Characterization II (R.L. Snyder, R.A. Condrate, Sr. & P.F. Johnson, eds.). Plenum Publishing Corp., New York, N.Y. (43-55).

ROEDDER, E. (1984): Fluid inclusions. *Rev. Mineral.* **12**.

SAMSON, I.M., CHEN, ZHONXING, FRYER, B.J. & WALKER, R.T. (1998): High sensitivity in-situ analysis of cation/anion compositions of individual fluid inclusions by LAM–ICP–MS using a cold plasma ionization source. *Geol. Soc. Am., Abstr. Program* **30**, A-81.

SIMMONS, W.B. & HEINRICH, E.W. (1980): Rare earth pegmatites of the South Platte district, Colorado. *Colorado Geol. Surv., Resource Ser.* **11**.

_____, WEBBER, K.L. & FALSTER, A.U. (1999): NYF pegmatites of the South Platte district, Colorado. *Can. Mineral.* **37**, 836-838.

TAO, N.J., LI, G., CHEN, X., DU, W.M., & CUMMINS, H.Z. (1991): Low-frequency Raman-scattering study of the liquid–glass transition in aqueous lithium chloride solutions. *Phys. Rev. A* **44**, 6665-6676.

TAYLOR, M.J. & WHALLEY, E. (1964): Raman spectra of ices Ih, Ic, II, III, and V. *J. Chem. Phys.* **40**, 1660-1664.

TULK, C.A., KLUG, D.D., BRANDERHORST, R., SHARPE, P. & RIPMEESTER, J.A., (1998): Hydrogen bonding in glassy liquid water from Raman spectroscopic studies. *J. Chem. Phys.* **109**, 8478-8484.

VANKO, D.A., BODNAR, R.J. & STERNER, S.M. (1988): Synthetic fluid inclusions. VIII. Vapor-saturated halite solubility in part of the system $NaCl–CaCl_2–H_2O$, with application to fluid inclusions from oceanic hydrothermal systems. *Geochim. Cosmochim. Acta* **52**, 2451-2456.

WALKER, R.T. (1998): *Low Temperature Raman Spectroscopic Analyses of Fluid Inclusions from Granitoid-Related Mineral Deposits and Comparisons with Decrepitate Analyses.* M.Sc. thesis, Univ. of Windsor, Windsor, Ontario.

_____ & SAMSON, I.M. (1998): Cryogenic Raman spectroscopic investigations of fluid inclusions in the $NaCl–CaCl_2–H_2O$ system. *Int. Mineral. Assoc., 17th Gen. Meeting, Abstr. Programme*, A3.

WALRAFEN, G.E. (1962): Raman spectral studies of the effects of electrolytes on water. *J. Chem. Phys.* **36**, 1035-1042.

_____ (1964): Raman spectral studies of water structure. *J. Chem. Phys.* **40**, 3249-3256.

_____ (1972): Raman and infrared spectral investigations of water structure. *In* Water, a Comprehensive Treatise. 1. The Physics and Physical Chemistry of Water (F. Franks, ed.). Plenum Press, New York, N.Y. (151-214).

WHALLEY, E. (1977): A detailed assignment of the O–H stretching bands of ice I. *Can. J. Chem.* **55**, 3429-3441.

YANATIEVA, O.K. (1946): Polythermal solubilities in the systems $CaCl_2–MgCl_2–H_2O$ and $CaCl_2–NaCl–H_2O$. *Zh. Priklad. Khim.* **19**, 709-722 (in Russ.).