Low-temperature Raman spectroscopic analyses of fluid inclusions from granitoid-related mineral deposits and comparisons with decrepitate analyses.

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LOW-TEMPERATURE RAMAN SPECTROSCOPIC ANALYSES OF
FLUID INCLUSIONS FROM GRANITOID-RELATED MINERAL
DEPOSITS AND COMPARISONS WITH DECREPITATE
ANALYSES

by

Ryan Thomas Walker

A Thesis
Submitted to the Faculty of Graduate Studies and Research
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Partial Fulfillment of the Requirements for the
Degree of Master of Science at the
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1998
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ABSTRACT

Low-temperature laser Raman spectroscopy (LRS) has been used to obtain spectra from frozen fluid inclusions from granitoid-related mineral deposits. Spectra obtained from fine-grained aggregates produced by cyclical freezing and warming contain distinct salt hydrate peaks. This cyclical freezing method is essential in allowing for hydrate formation in fine-grained frozen inclusions, as inclusions that were simply frozen quickly, did not experience hydrate formation, resulting in spectra lacking hydrate and, in many cases, ice peaks. Spectra obtained in this manner provide a representation of the bulk chemistry of the inclusion. This is not so where spectra are obtained from inclusions that have been frozen slowly to grow large, single crystals (e.g. Dubessy et al., 1982). Large single crystals do allow for easy Raman spectroscopic identification, but do not give an indication of the bulk chemistry of the inclusion. Comparison of relative peak intensities in low-temperature Raman spectra of synthetic mixtures in the NaCl-CaCl₂-H₂O system allows for semi-quantitative estimates of the relative abundance of NaCl and CaCl₂ in some of the fluid inclusions studied. It was possible to obtain such spectra from very small, low salinity inclusions, although the peaks present in the spectra are of very low intensity. Ice, hydrohalite and antarcticite were detected by low-temperature LRS in inclusions from the South Platte fluorite-REE pegmatites, Colorado, however, only ice and hydrohalite were detected in inclusions from other environments, including the Mt. Pleasant Sn-W-Mo deposit, New Brunswick. These data confirm that the phase behaviour of fluid inclusions in these deposits can be modeled using the H₂O-NaCl and H₂O-NaCl-CaCl₂ systems.

EDS/WDS analyses of fluid inclusion decrepitates from the deposits studied, generally agree with the Raman results but indicate the presence of small concentrations of K in some cases. LRS investigation of daughter minerals in Mt. Pleasant fluid inclusions has indicated the common presence of a solid which is most likely tourmaline. EDS analyses of solid phases in Mt. Pleasant inclusions indicate the presence of halite, sylvite, alunite, biotite, wolframite/scheelite and potassium-feldspar. The presence of anhydrite in some South Platte inclusions is also indicated by LRS.
DEDICATION

I dedicate this thesis to my mother, Gail Walker, and Catherine and Aileen McLoughlin, who all loved and supported me throughout the writing of this thesis.
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Chapter 1: INTRODUCTION

Fluid Inclusions

Many naturally occurring minerals grow in the presence of some type of fluid medium, which often becomes trapped within the growing crystal as a "fluid inclusion". Trapping of the fluid in an inclusion can happen during or after crystal growth. As the crystal grows, irregularities in crystal faces are often produced. These irregularities or cavities in the crystal faces act as traps for the fluid. Inclusions can also be formed by healing fractures after crystal growth is complete. Solid phases present in the fluid medium can also become trapped. Such solids can act as obstacles to crystal growth and become entrapped with or without fluid as the crystal continues to grow around the obstacle.

As fluids may be trapped during or after crystal growth, fluid inclusions represent direct samples of fluids present during specific times in the life of a crystal. A variety of information can be retrieved from fluid inclusions. The information generally available includes trapping temperatures, trapping pressures and the composition of the fluid (Roedder, 1984). The variety of information available in fluid inclusions and their ubiquitous nature in geologic samples make them an indispensable tool in the study of a variety of geologic processes.

Fluid Inclusion Chemistry

Aqueous fluid inclusions can have concentrations of dissolved salts ranging from 0 to over 50 wt. %. The salts found in such inclusions typically comprise Na⁺, Ca²⁺, K⁺, Mg²⁺, Cl⁻ and SO₄²⁻. Lesser amounts of Li⁺, Al³⁺, Fe³⁺, BO₃³⁻, PO₄³⁻, B³⁺, Ba²⁺, Br⁻, Mn²⁺, NH₄⁺, F⁻, Si⁴⁺, HCO₃⁻ and CO₃²⁻ are also found (Roedder, 1990). Sodium and Cl⁻ are generally the most abundant. Free carbon dioxide may also be present and can be the dominant species present. Salt concentrations may be sufficiently high that saturation with a variety of minerals may occur during cooling of the inclusion from the trapping temperature. Such minerals are referred to as daughter minerals.

In general, the ionic chemistry of fluid inclusions is dominated by Na⁺ with subordinate concentrations of K⁺ (typically 10 to 50 % of the concentration of Na⁺). In
some cases, \( \text{Na}^+ \) is absent or subordinate to \( \text{Ca}^{2+} \) (Roedder, 1972). As \( \text{Na}^+ \) and \( \text{Cl}^- \) are the dominant ions present in fluid inclusions, halite is the most common daughter mineral found in inclusions.

**The Analysis of Fluid Inclusions**

The composition and salinity of fluid inclusions are most commonly investigated by measuring the temperature at which phase changes occur in the inclusions and comparing these with phase equilibria in model systems. This method is generally referred to as microthermometry. While this method is widely practiced it is not without problems. As the method involves the observation of phase changes within fluid inclusions often only several micrometers in diameter, these phases may be impossible to identify with any certainty. Other techniques which rely on destruction of the inclusion are also commonly employed. For example, leachate analyses involve analyzing the diluted contents of an inclusion released by the fracturing of inclusions. This technique comes with the obvious cost of the destruction of the sample as well as the possible formation of artifacts in the inclusion contents upon opening. The technique also does not allow for the analysis of single inclusions of known genesis.

The use of Raman spectroscopy can overcome these problems. This technique allows for the non-destructive analyses of selected, single inclusions. The technique can not only provide information on the chemistry of the fluid within an inclusion but may also be used to identify daughter or trapped minerals within inclusions. The non-destructive nature of Raman spectroscopic analyses allows additional analysis to be performed after Raman spectra have been acquired. In most cases, the inclusion is left unchanged and ready for further analysis. A notable exception are hydrocarbon inclusions which may suffer thermal degradation due to absorption of the laser radiation.

Subsequent analysis may include other microbeam techniques. One such method involves the analysis of salt residues and daughter or trapped minerals using energy dispersive X-ray spectroscopy (EDS) or wavelength dispersive spectroscopy (WDS) in either a scanning electron microscope (SEM) or in an electron microprobe (EMP). This technique involves opening inclusions, either by breaking open small mineral fragments or by heating the inclusions until internal overpressuring causes the inclusions to rupture. In
the latter case, as the fluid contents reach the sample surface the water quickly evaporates at the elevated temperatures involved, leaving behind salt residues, called a decrepitate, which may then be analyzed by EDS or WDS.

**Low-Temperature (Cryogenic) Raman Spectroscopy**

At room temperature the electrolytes dissolved in the aqueous phase of fluid inclusions are almost totally dissociated. Therefore no strong bonds exist and consequently such solutions will provide very weak or no vibrational or Raman spectra with respect to the electrolytes themselves. However, information on these salts can be obtained by indirect means. In freezing the solutions, salt hydrates, which are unstable at room temperature, form in the inclusions. Such hydrates are Raman active.

Dubessy et al. (1982) investigated the application of laser Raman spectroscopy (LRS) in the determination of the electrolytes dissolved in the aqueous phase of fluid inclusions. In their paper, Dubessy et al. (1982) review the work of Mathieu and Couture-Gouthier (1953) and Guillermet and Novak (1969). These workers showed that the various types of vibrations in a stoichiometric hydrate \( M_x^{2+} Cl_{2x}^- \cdot n(H_2O) \), where \( M \) is a tetrahedrally or octahedrally co-ordinated metal, can be classified into: (1) fundamental internal vibrations of the water molecules; (2) lattice mode vibrations of the water molecules; (3) M-Cl vibrations and (4) M-O vibrations.

The most useful types of vibrations for hydrate identification are those which induce the most intense lines in the spectrum. The internal vibrations of the water molecules were found to fill this need. The fundamental internal modes of vibration of water molecules measured in the gaseous state are: (1) \( v_1A_1 = 3655.8 \text{ cm}^{-1} \) (symmetric stretching), \( v_3B_2 = 3756.7 \text{ cm}^{-1} \) (anti-symmetric stretching) and \( v_2A_1 = 1594.6 \text{ cm}^{-1} \) (bending). All of these modes are Raman active. In hydrate crystals, the water molecules are kept in their mean positions by hydrogen bonds between water and an ion (Cl---H-O-H) or between themselves. Raman spectra of crystalline hydrates also show lattice modes which are mixed vibrations due to rotary motions (vibrations) and translatory motions. The frequencies of the translatory modes are generally lower than 300 cm\(^{-1}\) and those of rotary are in the range 300-800 cm\(^{-1}\). Because the lattice modes do not result in strong Raman lines and also because these lines could easily be hidden by Raman bands of the
host crystal, Dubessy et al. (1982) chose the fundamental stretching and bending vibrations of the water molecules to identify the hydrates.

Dubessy et al. (1982) also present Raman spectra for ice. Intramolecular and intermolecular coupling of vibrations and the large number of hydrogen bonds result in a complex spectrum for ice. Dubessy et al. (1982) noted that it was important that the ice lines occurred at lower wavenumbers than those of the hydrates and that they had broader bandwidths. This means that there is no interference between the ice peaks and those of the hydrates. Spectra for NaCl•2H₂O (hydrohalite), CaCl₂•6H₂O (antarcticite), MgCl₂•6H₂O, MgCl₂•12H₂O, FeCl₃•6H₂O and KCl•MgCl₂•6H₂O (carnallite) were obtained by Dubessy et al. (1982) from slowly grown, large hydrate crystals formed from prepared synthetic solutions and from natural fluid inclusions. Relatively few Raman spectral studies of salt hydrates in naturally occurring fluid inclusions have been reported in the literature. Mernagh and Wilde (1989) present spectra obtained from frozen inclusions from the Alligator Rivers uranium district in the Northern Territory, Australia, however individual hydrate bands were not discernible in the spectra they obtained. Schiffries (1990) report low-temperature Raman spectra obtained from antarcticite daughter crystals in unusually Ca-rich inclusions from the Bushveld complex, South Africa. Dubessy et al. (1992) present spectra for hydrohalite and the Li-hydrate, LiCl•5H₂O, in a frozen inclusion from the Larderello geothermal system, Italy.

Walker (1994) investigated the binary systems H₂O-NaCl and H₂O-CaCl₂ using cryogenic LRS. This study differed from that of Dubessy et al. (1982) in that the spectra were obtained from fine-grained ice/hydrate mixtures which were obtained by rapidly freezing synthetic solutions in microcapillaries. This method was employed as the fine-grained aggregate analyzed would be more reflective of the bulk composition of the inclusion fluid. Figure 1 shows spectra obtained by Walker (1994) from such fine-grained ice/hydrate mixtures. The spectrum shown in Figure 1a is that of a frozen H₂O-CaCl₂ mixture and shows peaks for antarcticite (CaCl₂•6H₂O) at 3385, 3407 and 3433 cm⁻¹. Figure 1b was obtained from a H₂O-NaCl mixture and shows hydrohalite (NaCl•2H₂O) peaks at 3402, 3422, 3435 and 3536 cm⁻¹. Both spectra also show a strong
Fig. 1  Raman spectra of frozen synthetic solutions from the systems; (a) H$_2$O-CaCl$_2$ (antarcticite) (peaks at 3385, 3401, 3407 and 3433 cm$^{-1}$), (b) H$_2$O-NaCl (hydrohalite) (peaks at 3402, 3422, 3435 and 3536 cm$^{-1}$) and (c) hexagonal ice with peaks at 3094, 3220 and 3330 cm$^{-1}$ (after Walker, 1994).
peak at around 3090 cm⁻¹ which indicates the presence of hexagonal ice in these mixtures. A spectrum acquired from frozen, triple-distilled water at -185 °C is shown in Figure 1c. In addition to the main peak at ~3090 cm⁻¹, a weaker peak is present at 3220 cm⁻¹; this peak is also evident in the salt solution spectra. In addition, Walker (1994) was able to semi-quantify the relative abundance of hydrohalite and antarcticite in solutions containing both NaCl and CaCl₂.

**Objectives of the Current Study**

The current study was initiated in order to investigate the application of cryogenic LRS to natural fluid inclusions and to compare the results with chemical data obtained using other methods. A particular goal was to analyze fine-grained aggregates rather than large single crystals, as had been done in most previous studies. A complimentary goal was to identify trapped and daughter minerals in the same suite of inclusions. The samples chosen for study (see below) had previously been investigated using microthermometric techniques which provided a basis for comparison with the Raman data. In addition, this study incorporated the analysis of the same suites of inclusions using EDS and WDS analyses of opened and decrepitated inclusions. All of the samples used came from mineral deposits, most of which are associated with felsic intrusive rocks. Ultimately, the chemical information obtained on inclusions from these deposits will result in a better understanding of the processes involved in forming the mineralization.

To summarize, the objectives are as follows:

1. To obtain Raman spectra of trapped and daughter minerals within the selected fluid inclusions.
2. To obtain Raman spectra of the frozen aqueous phase within the selected fluid inclusions.
3. To evaluate, using these data, the usefulness of cryogenic LRS in the chemical analysis of natural fluid inclusions, in part through a comparison with EDS and WDS data from the same suites of inclusions.
4. Finally, to improve our knowledge of the chemistry of mineralizing fluids in the felsic intrusive environment.
Samples used in the study

A number of well characterized suites of inclusions were available to the author from the collections of I. M. Samson. These included samples from the Mount Pleasant W-Mo-Sn deposits, New Brunswick, Canada; rare earth element (REE) pegmatites from the South Platte District, Colorado, USA; Au-quartz veins from Wawa, Ontario, Canada and fluorite-REE deposits in the Gallinas Mountains, New Mexico, USA.

Mount Pleasant (W-Mo-Sn) Deposit, N.B., Canada

The Mount Pleasant W-Mo-Sn deposits are associated with a series of subvolcanic, granite stocks on the margins of the Devonian St. George batholith (Kooiman et al. 1986; Sinclair et al., 1988). Based on microthermometry, the mineralizing fluids are thought to be sodium-dominated with salinity ranging from 10 to 60 wt. % eq. NaCl (Davis and Williams-Jones, 1985; Samson, 1990). Three types of fluid inclusion have been recognized and characterized by microthermometric means and interpreted in terms of the H₂O-NaCl-CaCl₂ system. The inclusion types are: low salinity (<10 wt % eq. NaCl + CaCl₂) liquid-rich, liquid-vapour inclusions, which homogenize to a liquid (Type 1), vapour-rich inclusions which homogenize to the vapour phase (Type 2) and high salinity (30 to 60 wt. % eq. NaCl) liquid-vapour-solid inclusions, most of which homogenize to the liquid phase (Type 3) (Samson, 1990).

The type 3 inclusions may be very complex, containing a vapour bubble, a liquid phase and one to six solid phases. The solids characterized by Samson (1990) from this group of inclusions include: 1) a nonbirefringent, low relief, cubic solid, 2) a nonbirefringent, low relief, anhedral solid, 3) a nonbirefringent, high relief, anhedral solid, 4) a prismatic or anhedral solid with blue-white interference colours, 5) a birefringent anhedral solid, 6) a possibly birefringent, rhombic solid, 7) a lathe or needle-like solid, which may show birefringence, and a number of solids that were too small to characterize (Samson, 1990). Microthermometric analyses performed by Samson (1990) of inclusions from this group left most of the solids unidentified. Solids 1 and 2 were tentatively identified as halite. The rhombohedral habit of solid 6 indicated that it was probably a carbonate. Raman spectra identified at least some of the crystals of solid 5 as calcite.
Solids 3, 4 and 8 remain unidentified and it was suggested that solids 3 and 4 may be the same mineral, simply in different orientations (Samson, 1990).

Very little data exists on the chemistry of the fluids responsible for granite-related W-Sn deposits (Wood and Samson, in prep.). One of the best studied examples of this deposit type is that of Panasqueria in central Portugal. The mineralizing fluids are Na\(^+\) and Cl\(^-\) dominated with Na\(^+\) > Ca\(^{2+}\) > K\(^+\) and Cl\(^-\) > SO\(_4\)\(^{2-}\) (Norohna, 1992). FeCl\(_2\) has also been suggested as a major component in W and Sn mineralizing fluids (e.g. Eadington, 1983).

**South Platte District, Colorado**

Located in the northern portion of the Pikes Peak batholith, Colorado, the South Platte pegmatite district comprises abundant NYF (Niobium-Yttrium-Fluorine) REE pegmatites (Simmons and Heinrich, 1975). REE mineralization typically occurs at or near the boundary between the quartz cores and intermediate zones of the pegmatites. Precious little is known about the ionic composition of the fluids responsible for this hydrothermal REE mineralization. Microthermometric data indicates that the salinity of fluids which permeated the pegmatites ranged from 0 to 36 wt. % NaCl + CaCl\(_2\) (Levasseur and Samson, 1996; Levasseur, 1997).

Four types of inclusions were identified by Levasseur (1994): (1) aqueous liquid-vapour inclusions (0 to 30 wt. %) (2) liquid-vapour-solid inclusions (0 to 30 wt. %) in which the solid is generally birefringent, (3) liquid-vapour-halite ± solid inclusions (20 to 35 wt. %) and (4) aqueous-carbonic inclusions (< 10 wt. %).

**Wawa, Ont., Canada**

Deformation zones in the southwestern portion of the Archean Michipicoten greenstone belt host a large number of auriferous quartz vein systems (Samson et al., 1997). Some of these vein systems contain small gold deposits and are characterized by a wide variety of fluid inclusion types. These include aqueous inclusions with salinities ranging from 0 to 23 wt % NaCl equivalent and aqueous-carbonic inclusions with X\(_{CO2}\) values ranging from 0.05 to 0.26 and CO\(_2/CH_4\) ratios varying from 0.68 to 1.0 (Samson et al., 1997). Nahcolite-bearing (NaHCO\(_3\)) aqueous and aqueous-carbonic inclusions with high CO\(_2/CH_4\) ratios and salinities between 5 and 18 wt % NaCl equivalent are also present (Samson et al., 1997).


Gallinas Mountains, New Mexico

The fluorite-REE deposits of the Gallinas Mountains, New Mexico are associated with Tertiary alkaline, felsic intrusions that are associated with the waning stages of subduction (Allen and Foord, 1991). Three types of fluid inclusions have been reported; liquid-rich, aqueous liquid-vapour (LV), aqueous liquid-vapour-solid (LVS) and aqueous-carbonic inclusions (AC). The fluids responsible for mineralization in the Gallinas Mountains range in salinity from 14 to 19.5 eq. wt. % NaCl. with some as high as 25 eq. wt. % NaCl + CaCl₂ (Samson et al., 1997; Williams-Jones et al., 1997).

Thesis Structure

This thesis is divided into five chapters. The first chapter presents an introduction to fluid inclusions and their analysis and describes previous work on cryogenic LRS of fluid inclusions, in addition to the objectives and sample suites chosen for study. Chapter 2 outlines the methodology employed in this study. The results of the Raman, EDS and WDS analyses are presented in chapter 3. Chapter 4 contains a discussion of the results and Chapter 5 presents conclusions and recommendations for further work. A collection of Raman spectra are given in the appendices.
Chapter 2: METHODOLOGY

Raman Spectroscopy

Inclusion Selection

The most important criterion in the selection of an inclusion for Raman spectroscopic investigation was its size. The larger volume of fluid or solid phase in large inclusions, than in smaller ones, increased the probability that an acceptable spectrum would be obtained. In addition, only inclusions which were larger than the laser beam diameter were analyzed. Secondly, to minimize attenuation of the laser beam by the host mineral, inclusions close to the surface of the wafer were sought. Initially, in order to increase the probability that hydrates would be detected in frozen inclusions, high salinity, generally halite-bearing inclusions, were analyzed.

Raman Spectra

Raman spectra were obtained using a THR 1000 Laser Raman Spectrometer (I.S.A. Jobin Yvon) at the University of Windsor. The source of excitation was the 514.5 nm green line of a model 95 tuneable argon ion laser from the Lexel Corporation. This laser operated on 208 volts with a minimum supply of 35 amperes continuously. The spectra were obtained with the laser power set at 300 mW at output. The Raman spectrometer was calibrated on a daily basis using the 520 cm⁻¹ peak of silicon. In most cases, an acquisition routine using 3 reads with an integration time ranging between 3 and 10 seconds was used. In some instances 40 to 50 reads were employed in an attempt to resolve poorly defined lines. The multiple reads or spectra of the same region were added together automatically by the Prism® software. Instrumental interference commonly resulted in the presence of ‘spikes’ in the spectra. These spikes manifested themselves as very intense, narrow (less ≤ 1 cm⁻¹) peaks and were manually deleted from all spectra presented.

Low-temperature Raman Spectroscopy of Frozen Inclusions

For low-temperature spectra only, fluid inclusions in fragments of doubly polished rock wafers were placed in a quartz or glass crucible for a THM 600 heating/freezing stage which then sat in direct contact with the heating/freezing element of the stage. The
cooling system used comprised a Linkam THM 600 heating/freezing stage, a TMS 91 programmable temperature controller, and a CS196 liquid nitrogen pump. The THM 600 stage was then positioned on a BH-2 Olympus microscope stage under an Olympus x50 ultra-long working distance lens with 0.55 numerical aperture.

In order to ensure that the sampling volume contained a mixture of solids that were representative of the bulk chemistry of the inclusion (i.e. a large number of small crystals in the small sample volume), the inclusion was frozen rapidly. To achieve this, the sample was held at a constant temperature (above the freezing point) in the heating/freezing stage while the pump was allowed to circulate liquid nitrogen through the tubing system and the heating/freezing stage in order to cool the system down. Nitrogen pumped into the stage also acted to evacuate any air and water vapour from within the stage. Any water vapour in the stage would condense and form ice on the surface of any sample subsequently placed in the stage and cooled. Ice on the surface of the sample would not only obscure the sample for any optical examination but would also cause the dispersion of the laser beam at the surface before it reached the target inclusion. The pre-cooling ensured that there would be no lag time in freezing the contents of the inclusion through having to cool the stage as well as the sample. After two minutes of circulation the temperature was allowed to drop very quickly (40-50°C/min.) thereby freezing the contents of the inclusion quickly and prohibiting large crystal growth. As shall be discussed in a subsequent section, such simple quick freezing of the sample did not always result in the formation of hydrates. Hydrate formation typically required subsequent temperature cycling.

As Raman bands broaden at increasingly higher temperatures causing an increased likelihood of peak overlap (Dubessy et al., 1982), spectra were acquired at the lowest temperatures possible (between -175 and -185 °C) in an attempt to ensure the highest degree of peak definition.

**Raman Spectroscopy of Trapped or Daughter Minerals**

Spectra of daughter or trapped minerals were obtained at room temperature by placing fragments of doubly polished rock wafers on a glass slide which was then placed directly on the microscope stage of the spectrometer. The acquisition parameters were the
same as those used for frozen inclusions.

**WDS and EDS Analyses**

**Decrepitates**

The major elemental composition of fluid inclusion contents can be obtained by analysing the salt residues left after evaporation of inclusion fluids (Eadington, 1974; Haynes et al., 1988). The contents of an inclusion are released when the inclusion ruptures as a result of internal overpressuring caused by heating. This rupturing is referred to as decrepitation. The liberated fluid contents of the burst inclusion travel to the surface of the sample along fractures that are generally induced by the decrepitation. At the surface, the solution quickly evaporates, leaving behind a residue of any salts present in the solution. Such residues are referred to as decrepitates. The decrepitates can then be analyzed using WDS or EDS in either an SEM or EMP.

**Sample Selection**

For the decrepitate analyses, samples were selected which had inclusions that were; 1) large, 2) numerous and 3) of predominately one generation. The latter is required as individual inclusions cannot be identified once decrepitation has occurred and the sample is in the SEM or EMP. In the case of the samples which were to be decrepitated, LV inclusions were chosen in order to avoid chemical inhomogeneity. It is possible that a solid phase in an LVS or LVHS inclusion may not dissolve before the decrepitation temperature is reached, resulting in a decrepitate that does not reflect the bulk chemistry of the fluid originally trapped in the inclusion. The solid contained in the inclusion may also, at the time of decrepitation, act as an obstacle to the ejection of the fluid contents of the inclusion onto the surface of the rock wafer itself, again resulting in a decrepitate which is not representative of the bulk fluid chemistry.

Fragments of doubly polished rock wafers, on the order of 100 to 200 μm in thickness, which contained the inclusions of interest were chosen using transmitted light microscopy. The surfaces of the wafers were cleaned with acetone, to prevent contamination of the small amount of fluid released upon decrepitation, and glued onto a glass slide, which was then labeled. This assembly was then placed in a THM 600
heating/freezing stage and heated to the point of decrepitation (400-500 °C). The decrepitation appeared as a darkening of the inclusions. The assembly was then carefully removed and kept in a desiccator, until a carbon coating was applied, to prevent recrystallization and to avoid inhomogeneity through CaCl₂ deliquescence or NaCl or KCl creep (Haynes et al., 1988). Heating periods must be kept brief in order to avoid the diffusion of alkalis into the host (Roedder, 1980).

Decrepitate Formation

The decrepitates occur as small mounds or in linear trails. The latter represent emission of fluid from fractures. Such linear trails were excluded from analysis as they may exhibit chemical inhomogeneity along their length (Haynes et al., 1988). The decrepitate mounds (Fig. 2) were generally 10 to 20 μm in diameter and the linear trails were up to 20 μm in length.

WDS analysis of the decrepitates was performed in the Department of Earth Sciences at the University of Western Ontario with a Jeol JXA-8600 Superprobe. Analytical conditions are listed in Table 1.

<table>
<thead>
<tr>
<th>Table 1. Microprobe/EDS and SEM/WDS instrument parameters</th>
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<tr>
<td>beam energy</td>
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All analyses were performed using a raster area that covered as much of the decrepitate surface as possible. Element concentrations were calculated using a ZAF correction procedure. The detection of elements by WDS is limited to those present in concentrations ≥ 0.1 wt. %.

**EDS Analyses of Solids within Fluid Inclusion Cavities**

In order to carry out EDS analysis of solids present in inclusion cavities a different method was employed. Samples previously characterized to have a high density of solid-bearing inclusions were cut into small slabs on the order of 3mm x 3mm x
Fig. 2 SEM micrographs of the various decrystalline formations observed (the white bar represents 10 μm in each case).
10mm. These slabs were then broken into two pieces and glued to a glass slide with the newly exposed fracture surface facing up. The samples were then quickly coated with carbon. A surface was initially scanned at low magnification to locate inclusion cavities. Once a cavity containing one or more solids was located, higher magnifications were used for the EDS analysis; up ~300 000 X for spot analyses of extremely small solids. In some cases, the electron beam was rastered to analyze larger solids or aggregates of crystals. These analyses were carried out at McGill University on a JSM-840A scanning electron microscope. Element concentrations were calculated using a ZAF correction procedure.

The analysis parameters are listed in Table 1. Under ideal conditions, analysis by EDS allows for the detection of light elements (Z<12) present in concentrations of about 1.0 wt. %, and heavier elements 0.5 wt. %. However, given the uneven sample surface and non-ideal geometry of the electron beam and backscattered radiation relative to the sample surface, element concentrations below 1.0 wt. % are untrustworthy and concentrations in the 2-3 wt. % range must be treated with caution.

Element volatility has been shown to be a function of beam current density in EDS and WDS analyses. Elements such as Na, Ca, K and Cl may volatilize or 'burn off' when beam current densities exceeded 0.5 nanoamps/μm² (Haynes et al., 1988). In this study a current of 9.6 nanoamps was employed. Those solids and decrepitates which were analyzed using a rastered beam over an area of 10 μm², resulting in a beam current density of 0.096 nanoamps/μm², had low enough beam current densities to prevent loss of elements during analysis. However, in those analyses which required smaller beam diameters it is possible that some loss of light elements occurred.
Chapter 3: RESULTS

Raman Spectra of Trapped or Daughter Minerals within Fluid Inclusions

Mt. Pleasant Inclusions

As described earlier, three types of fluid inclusions have been characterized at Mt. Pleasant (Samson, 1990). Type 3 inclusions contain a variety of solids, many of which remain unidentified. In an attempt to further characterize these solids, Raman spectra were obtained from a selection of solids in such inclusions. Spectra obtained from the majority of the solids only show peaks for the host quartz (see Appendix I, Figs. 1 to 4). This implies that these solids are either Raman inactive or the Raman bands are too weak to show up. However, solid 4 (Samson, 1990), which is characterized by blue-white birefringence colours and forms ranging from prismatic to hexagonal, produced peaks in the spectra obtained.

Raman Spectra obtained from Solid 4

Spectra have been acquired from solid 4 in a number of different samples. The best spectra were acquired from a group of complex inclusions in sample B10-174. The spectral features described below from this group of inclusions were seen in all examples of this solid. Longitudinal, prismatic sections of solid 4 show distinct peaks at 618 and 1021 cm\(^{-1}\) (Figs. 3a and b; see also Figs. 5, 7, 13, and 25 in Appendix I). These spectra also show peaks for the host quartz positioned at 210, 266, 323, 394, 401, 466, 699, 795, 807, 847, 903, 922, 1069, 1087, and 1164 cm\(^{-1}\) (Fig. 3c). In addition to the peaks noted above, several very distinct peaks occur in the wavenumber range 3000 to 4000 cm\(^{-1}\) at 3551, 3577 and 3624 cm\(^{-1}\) (Fig. 4a; see also Figs. 6, 8, 14, 26, 27, and 28 in Appendix I). These peaks are superimposed on a broad band centred at about 3478 cm\(^{-1}\). The spectrum of the host quartz (Fig. 4c) has no real peaks over the same wavenumber range.

Spectra acquired from hexagonal forms of solid 4 show the same spectral characteristics. Peaks at 618, 1024, 3551, 3576 and 3625 cm\(^{-1}\) are again obvious (Figs. 5 and 6), although less intense than in the spectra acquired from longitudinal sections of the mineral.
Fig. 3 (a) and (b) represent Raman spectra of solid 4, an elongate, birefringent crystal in inclusion B10-174-1-1 (inset) acquired with ten and three reads, respectively. (c) Raman spectrum of the host quartz.
Fig. 4  (a) and (b) represent Raman spectra of solid 4, an elongate, birefringent crystal in inclusion B10-174-1-1 (inset). (c) Raman spectrum of the host quartz.
Fig. 5 Raman spectra of solid 4, a prismatic, birefringent crystal in inclusion B10-174-1-3 (inset sketch). Spectrum (a) (b) and (c) were acquired with: 50, 5 and 15 reads, respectively. (d) The spectra were acquired from various spots on the solid. (d) Raman spectrum of the host quartz.
Fig. 6 (a) Raman spectra of solid 4, an elongate, birefringent crystal in inclusion B10-174-1-3 (inset sketch). (b) Raman spectrum of the host quartz.
A spectrum acquired from a rectangular, high relief solid which has the optical characteristics of solid 4 (Fig. 7a), in inclusion B10-45-1-1 is slightly different from spectra acquired from other examples of solid 4 in that it has a peak at 630 cm\(^{-1}\). The peak at 618 cm\(^{-1}\) is indistinct and there appears to be no peak present at 1024 cm\(^{-1}\). However, the peaks at 3551 and 3578 cm\(^{-1}\) are present (Fig. 8a). It is not known whether or not there is a peak at 3625 cm\(^{-1}\) as this spectrum was acquired over the range 3000-3600 cm\(^{-1}\).

**South Platte Inclusions**

Some LVS and LVHS inclusions from quartz in the South Platte Pegmatites contain birefringent, prismatic crystals. The spectrum shown in Figure 9a was acquired from one such solid in sample RL 94-60 and is characterized by peaks at 417, 628, 678, 1019 and 1131 cm\(^{-1}\), in addition to those of the host quartz (Fig. 9b).

**Raman Spectra of Frozen Fluid Inclusions**

**South Platte Inclusions**

Three types of fluid inclusions in quartz were analyzed from the South Platte pegmatites using cryogenic LRS: LV, LVS and LVH.

**Spectra obtained after initial rapid freezing**

Spectra obtained from inclusions which were frozen rapidly from room temperature to about -185 °C do not show many spectral features in the OH-stretching region (~3000 to 4000 cm\(^{-1}\)). Figure 10 shows several such spectra obtained from an LV inclusion in sample RL94-60. These spectra have broad peaks at 3090 and 3225 cm\(^{-1}\) along with a very weak, broad band centred at about 3440 cm\(^{-1}\). Similar results are seen in the spectrum from other inclusions in this group (Fig. 11a). A spectrum obtained from another LV inclusion but from a different group is very similar with peaks at 3092 and 3220 cm\(^{-1}\) (Fig. 12a).
Fig. 7 (a) Raman spectrum of solid (c) in inclusion B10-45-1-1 (inset). (b) Raman spectrum of the host quartz.
Fig. 8 (a) Raman spectrum of solid (c) in inclusion B10-45-1-1 (inset). (b) Raman spectrum of the host quartz.
Fig. 9  (a) Raman spectrum of an Anhydrite crystal in inclusion RL94-60-2-1 (inset). (b) Raman spectrum of the host quartz.
Fig. 10 (a to d) Raman spectra of inclusion RL94-60-3-2-1 (inset) after quickly freezing to -185 °C. (e) Raman spectrum of the host quartz.
Fig. 11  Raman spectra of inclusion RL94-60-3-2-2 (inset) after; (a) quickly freezing to -185°C, (b) slow freezing to grow large crystals, (c) application of a freeze-thaw cycle warming to -60 °C, and (d) freeze-thaw cycle, warming to -50 °C.
Fig. 12 Raman spectra of inclusion RL94-60-3-1-3 (inset) collected after; (a) freezing the inclusion quickly to -185 °C and (b) subsequent warming to -64 °C and quickly refreezing to -185 °C.
Spectra obtained after growth of large crystals and subsequent refreezing

In most LV inclusions ice was the last phase to melt upon warming frozen inclusions (Levasseur, 1997). However in some inclusions hydrate crystals remained after all the ice crystals had melted. In order to help identify these crystals, presumed to be hydrates, spectra were obtained from these crystals. This was achieved by slowly growing large crystals within the inclusions. After initial rapid freezing to -185 °C, the inclusions were heated to the point where only one or two hydrate crystals remained in the inclusion. The temperature was then slowly lowered to allow crystal growth. Eventually, the liquid surrounding these large crystals refroze (between ~ -60 and -90 °C) to a fine-grained aggregate which formed a matrix to the large hydrate crystals.

The spectra shown in Figure 13 were obtained from the large hydrate crystals and can be seen to be markedly different than the spectra described above. These spectra show a broad peak at 3084 cm\(^{-1}\) along with more intense, narrower peaks at 3401, 3420, 3433 and 3536 cm\(^{-1}\).

The spectra obtained from the fine-grained matrix (Fig. 14a, b and c) also have narrow peaks positioned at 3402, 3420, 3433 and 3536 cm\(^{-1}\) and a broad peak at 3084 cm\(^{-1}\). However, in this case, the 3084 cm\(^{-1}\) peak is the more intense. Similar results were obtained from another inclusion in this group although the peaks in the 3400 to 3550 cm\(^{-1}\) range are not as well defined, even when the laser beam was focused on the large crystals (Fig. 11b).

This technique was also applied to an LV inclusion RL94-60-4-5. The spectrum collected has very broad and weak bands centred at about 3094 and 3450 cm\(^{-1}\) (Fig. 15a).

Spectra obtained after partial thawing and rapid refreezing

In his study of synthetic solutions in the NaCl-CaCl\(_2\)-H\(_2\)O system, Walker (1994) found that hydrate formation could be induced in frozen solutions by slow warming up to temperatures of about -80 to -60 °C. Hydrate crystallization was generally seen as a dark wave which passed through the frozen mixture. This phenomenon has also been observed in natural fluid inclusions. In general, a technique was employed whereby rapidly frozen inclusions were warmed to temperatures of between -67 and -20 °C and
Fig. 13 (a) and (b) Raman spectra of large, slowly-grown hydrate crystals in inclusion RL94-60-3-2-1 (inset).
Fig. 14 Raman spectra of fine-grained matrix surrounding large, slowly grown crystals in inclusion RL94-60-3-2-1 (inset). (a), (b) and (c) represent spectra acquired from different spots in the inclusion.
Fig. 15  (a) and (b) are Raman spectra of inclusion RL94-60-4-5, taken after a freeze-thaw cycle, with warming to -60 °C and (c) after subsequent melting to a few crystals and refreezing slowly.
then rapidly refrozen. In most cases, hydrate crystallization was induced after a single freeze-thaw cycle as indicated by the appearance of peaks in the region 3400 to 3550 cm\(^{-1}\). However, in some cases, two or more such freeze-thaw cycles, generally thawing to higher temperatures each time, were required in order to crystallize hydrates. In some cases, hydrate could not be crystallized. The extent to which the inclusion was thawed was controlled by the visible changes within the inclusion. These changes included; waves of crystallization across the inclusion, the coarsening and or darkening of the preexisting fine-grained aggregate, and melting. On observation of these changes thawing was ceased and the temperature held constant for about 1 minute, before rapidly refreezing the inclusion to -185 °C.

Two general types of spectra (Types I and II) were thus obtained from inclusions which have been subjected to freeze-thaw cycles. Type I spectra, either have no distinct peaks or have peaks at about 3090 and 3225 cm\(^{-1}\), with perhaps a very weak, broad band centred at about 3440 cm\(^{-1}\), and represent those inclusions in which no hydrates crystallized. Type II spectra also have peaks at about 3090 and 3225 cm\(^{-1}\), but, in addition, have at least four additional peaks in the region between 3400 to 3550 cm\(^{-1}\).

*Type I Spectra*

A spectrum obtained from the LV inclusion RL94-60-3-1-3, after quickly freezing to -185 °C, followed by warming to -64 °C, and subsequent refreezing to -185 °C, has two weak peaks at 3092 and 3422 cm\(^{-1}\) (Fig. 12b). The spectrum shown in Figure 16c was collected from the LVHS inclusion RL94-60-4-2 after it was quickly frozen to -185 °C, warmed to -44°C, and then quickly refrozen to -185°C. With the exception of a possibly very broad, weak band centred at about 3422 cm\(^{-1}\), the spectrum shows no peaks. Further warming to -51 °C, followed by refreezing to -185 °C was applied to this inclusion and the spectra shown in Figures 16a and 16b were then obtained. These spectra show a broad, low intensity peak at 3092 cm\(^{-1}\), along with the very broad, weak band centred at about 3422 cm\(^{-1}\). More intense, very broad bands, centred around 3440 cm\(^{-1}\) are also seen in the spectra obtained from the LVHS inclusion RL94-60-4-5 after quickly freezing to -185 °C, warming to -60 °C, followed by quickly freezing to -185 °C (Fig. 15b and c).
Fig. 16 Raman spectra of inclusion RL94-60-4-2 (inset) after freeze-thaw cycles. (a) and (b) were collected after warming to -51 °C with subsequent refreezing and (c) was collected after warming to -44 °C and refreezing.
**Type II Spectra**

The spectra shown in Figures 17a and 17b were obtained from the LV inclusion RL94-60-3-2-1, after quickly freezing to -185 °C, followed by warming to -50 and -60 °C, respectively and then quickly freezing to -185 °C. Peaks are present at about 3405, 3422 and 3538 cm\(^{-1}\). A shoulder is also present between about 3433 to 3440 cm\(^{-1}\). Spectra were also collected from the LV inclusion RL94-60-3-2-2, using the same freeze-thaw cycle described above. These spectra, shown in Figures 11c and 11d, have broad, weak peaks at about 3100, 3403, 3424 and 3537 cm\(^{-1}\) with a shoulder at approximately 3433 to 3440 cm\(^{-1}\). The spectra acquired from the LV inclusion RL94-60-3-2-3 were again recorded after using the same freezing routine as above. The spectra show broad, intense peaks at about 3090 cm\(^{-1}\) with narrow peaks at 3404, 3422 and 3537 cm\(^{-1}\) (Fig. 18a and b). Again, a shoulder is present between 3433 and 3438 cm\(^{-1}\).

The spectrum shown in Figure 19a was obtained from the LVHS inclusion RL94-60-4-1 after quick freezing to -185 °C, followed by warming to -60 °C, and subsequent refreezing to -185 °C. The spectrum has a very intense, broad peak at 3095 cm\(^{-1}\) and narrower, more intense peaks at 3404, 3422, 3434, and 3536 cm\(^{-1}\). Weaker peaks are seen at 3225 and 3439 cm\(^{-1}\). The broad, intense peak at about 3090 cm\(^{-1}\) is again present in the spectra obtained from the LVHS inclusion RL94-60-4-3, which were recorded after quickly freezing to -185 °C, followed by warming to -44 °C and subsequent quick refreezing to -185 °C. Upon warming to -44 °C, two, visually distinct areas of crystallization formed. The spectrum shown in Figure 20a was acquired from an area of 'darker' crystals and the spectrum shown in Figure 20b was acquired from an area of clearer crystals. Both spectra show broad, intense peaks at 3092 cm\(^{-1}\), with more intense, narrower peaks at 3404 and 3422 cm\(^{-1}\). Weaker, less distinct lines are seen at 3537 and 3220 cm\(^{-1}\). The band between 3433 and 3438 cm\(^{-1}\) is broader and weaker than the adjacent peak at 3422 cm\(^{-1}\). In addition, the spectrum obtained from the area of darker crystals (Fig. 20a) shows more noise than the spectrum acquired from the clear area of crystals (Fig. 20b).
Fig. 17  Raman spectra of inclusion RL94-60-3-2-1 (inset) after freeze-thaw cycle, warming to (a) -50 °C, then refreezing to -185°C and (b) then warming again to -60 °C and refreezing to -185°C.
Fig. 18  Raman spectra of inclusion RL94-60-3-2-3 (inset) after quickly freezing to -185°C, then warming to (a) -50 °C followed by quickly refreezing to -185 °C and then (b) subsequently to -60 °C and refreezing.
Fig. 19  (a) Raman spectrum of inclusion RL94-60-4-1(inset) after freeze-thaw cycle, warming to -60 °C and quickly refreezing to -185 °C (halite crystal did not disappear). (b) Raman spectrum of the host quartz.
Fig. 20 Raman spectra of inclusion RL94-60-4-3 after freeze-thaw cycle, warming to -44 °C. Spectrum (a) was collected from an area of darker crystals and spectrum (b) from an area of clearer crystals.
A spectrum obtained from the LVS inclusion RL94-60-2-1 shows the typically intense, broad peak positioned at 3090 cm\(^{-1}\) (Fig. 21a). The spectrum, which was recorded after quickly freezing the inclusion to -185 °C, warming to -47 °C, followed by refreezing to -185 °C, also has intense, sharp peaks at 3403 and 3422 cm\(^{-1}\). The peaks at 3536 and 3220 cm\(^{-1}\) are less intense and a response centred at about 3435 cm\(^{-1}\) is very broad and ill-defined. Subsequently the inclusion was warmed to -54 °C and refrozen to -185 °C. The spectrum acquired after this cycle (Fig. 21b) shows a weak, broad peak at 3090 cm\(^{-1}\) along with a weak, narrower peak at 3422 cm\(^{-1}\).

**Mt. Pleasant Inclusions**

Three types of spectra have been obtained from Mt. Pleasant inclusions after the application of the freeze-thaw method described above. The first group of spectra (Figs. 22 and 23) show no distinct peaks (see also Appendix II, Figs. 4 and 5) and was obtained from both LV and LVHS inclusions. The inclusions were frozen quickly to -185 °C, warmed to between -64 to -29 °C, and then quickly refrozen to -185 °C.

The second group of spectra, obtained from LV inclusions (Figs. 24 and 25), show broad, intense peaks located at 3098 to as high as 3113 cm\(^{-1}\) and a broad, less intense peak, generally at around 3225 cm\(^{-1}\) (see also Appendix II, Figs. 6 and 7). In some cases these spectra may contain a weak response at about 3422 cm\(^{-1}\). These spectra were recorded after the inclusions had been frozen quickly to -185 °C, warmed to between -55 to -30 °C, and then quickly refrozen to -185 °C.

The third group of spectra were obtained from L, LV, and LVH inclusions (Figs. 26 to 28). These spectra again contain peaks at ~ 3090 and 3225 cm\(^{-1}\), but, in addition, show peaks in the region between 3400 to 3550 cm\(^{-1}\), generally located at 3405, 3422, 3438 and 3536 cm\(^{-1}\) (see also Appendix II, Figs. 1, 2, 8, 9 and 10).

**Wawa Inclusions**

The spectrum presented in Figure 28c was collected after quickly freezing an LVS inclusion from sample IS90-53b to -185 °C. The spectrum has a single peak at 3074 cm\(^{-1}\). After warming the inclusion to -40 °C, then refreezing it to -185 °C, the spectra shown in Figures 29a and b were acquired. One of these spectra (Fig. 29a) has four weak peaks
Fig. 21 Raman spectra of inclusion RL94-60-2-1 (inset). The spectra were collected after (a) freeze-thaw cycle warming to -47 °C and (b) after subsequent freeze-thaw cycle warming to -51 °C. (c) Raman spectrum, of the host quartz at low temperature(-185 °C). The elongate crystals visible are anhydrite (Levasseur, 1997).
Fig. 22 Raman spectra of inclusion B14-136A-3 (inset) collected after; (a) freeze-/thaw cycle warming to -58 °C , (b) and (c) subsequent freeze-thaw cycles, with warming to (b) -30 °C followed by warming to (c) -58 °C. (d) The low-temperature (-185 °C) spectrum of the host quartz.
Fig. 23  Raman spectrum of inclusion SYA83-19-4 after (a) freeze-thaw cycles warming to -30 °C and subsequent freeze-thaw cycles with warming to (b) -29 °C and again to (c) -29 °C. The low-temperature (-185 °C) host quartz spectrum.
Fig. 24  Raman spectra of inclusion SYA83-19-5 (inset) collected after; (a) freeze-thaw cycle, warming to -55 °C followed by quickly refreezing to -185 °C and (b and c) subsequent freeze-thaw cycles with warming to -30 °C.
Fig. 25  Raman spectra of inclusion SYA83-19-6 (inset) collected after (a) quickly freezing to -185 °C, (b) freeze-thaw cycle with warming to -55 °C and (c) subsequent warming to -30 °C. (d) The low-temperature(-185 °C) Raman spectrum of the host quartz.
Fig. 26 Raman spectrum of inclusion SYA83-19-2 (inset) after (a) quickly freezing to -185, followed by warming to -29 °C. (b) The low-temperature (-185 °C) Raman spectrum of the host quartz.
Fig. 27  Raman spectra of inclusion b10-1/4-6-2 (inset drawing) all collected after freeze-thaw cycle, warming to -32 °C. (a), (b) and (c) were obtained from the same spot in the inclusion using an increasing number of reads, namely: (a) 7 reads, (b) 15 reads, and (c) 40 reads. (d) The low-temperature (-185 °C) Raman spectrum of the host quartz.
Fig. 28  Raman spectrum of inclusion B10-174-6-4 (inset drawing) after (a) freeze-thaw cycle with warming to -32 °C and quick refreezing to -185 °C. (b) The low-temperature (-185 °C) spectrum of the host quartz.
at 3087, 3223, 3422 and 3485 cm\(^{-1}\). The spectrum shown in Figure 29b is similar except that the peak at 3485 cm\(^{-1}\) appears to be missing. A spectrum obtained from an adjacent inclusion (Fig. 30a) was collected after quick freezing to -185 °C, followed by warming to -33 °C, then quickly refreezing to -185 °C. This spectrum has only one definite weak peak at 3070 cm\(^{-1}\).

**Gallinas Mountains Inclusions**

Several spectra were acquired from complex gypsum-bearing LVS inclusions in fluorite from the Gallinas Mountains fluorite-REE deposits. Upon quickly freezing inclusion PIN2-1 to -185°C, then warming to -41 °C, two distinct areas of crystals formed. An area of clear crystals initially formed in the centre of the inclusion, followed by the formation of an area of darker crystals around the margin of the inclusion. The inclusion was held at -41°C for about 2-3 minutes to allow for the completion of the crystallization events, after which the inclusion was cooled to -185°C. The spectrum acquired from the area of clear crystals (Fig. 31a) shows only the distinct peaks of the host fluorite at 3454 and 3464 cm\(^{-1}\). The spectrum collected from the area of darker crystals (Fig. 31b) shows a broad, very weak peak at 3090 cm\(^{-1}\), weak peaks at 3404 and 3422 cm\(^{-1}\), and the peaks at from the host fluorite (Fig. 31c). Spectra from inclusion PIN2-2 (Fig. 32) were acquired during the same freeze-thaw cycle. A clear core of crystals surrounded by darker crystals was seen in this inclusions also. The spectra acquired from both the clear and dark areas of crystals (Figs. 32a and b) are very similar with a broad peak of moderate intensity at 3090 cm\(^{-1}\) along with weak peaks at 3404, 3422, 3436, and 3538 cm\(^{-1}\), in addition to peaks from the fluorite.

**Raman Spectra of Frozen Synthetic Solutions**

The spectra obtained from the inclusions in this study show similarities to those obtained by Walker (1994) from mixed solutions in the system NaCl-CaCl\(_2\)-H\(_2\)O. However, all of the spectra obtained by Walker (1994) contain broad peaks at around 3266 and 3500 cm\(^{-1}\) (Walker and Samson, 1995), which are absent from the inclusion spectra obtained in this study. In an attempt to reproduce these spectra, new solutions were prepared consisting of mixtures of 15 and 20 wt. % NaCl and CaCl\(_2\) solutions. The
Fig. 29 Raman spectra of inclusion IS90-53b IS2-1 (inset), after; (c) quickly freezing and (a and b) separate freeze-thaw cycles, both with warming to -40 °C. (d) The low-temperature (-185 °C) Raman spectrum of the host quartz.
Fig. 30. Raman spectra of inclusion 1590-53b IS2-2 (inset), after (a) freeze-thaw cycle with warming to -33 °C.
(b) The low-temperature (-185 °C) Raman spectrum of the host quartz.
Fig. 31 (a) and (b) Raman spectra of inclusion PIN 2-1 (inset) after application of a freeze-thaw cycle with warming to -41 °C. The spectra were collected from (a) an area of clear crystallization and (b) from an area of darker crystallization around the margin of the inclusion. (c) The low temperature (-185 °C) Raman spectrum of the host fluorite.
Fig. 32 (a) and (b) Raman spectra of inclusion PIN 2-2 (inset) after application of a freeze-thaw cycle, with warming to -41 °C. The spectra were collected from (a) an area of darker crystallization around the margin of the inclusion and (b) from an area of clearer crystallization in centre of inclusion. (c) The low-temperature (-185 °C) Raman spectrum of the host fluorite.
Fig. 33  Low-temperature Raman spectra acquired from synthetic solutions from the NaCl-CaCl₂-H₂O system. The spectra are acquired from solutions with atomic Na/Ca ratios of; 1.45 (a), 1.09 (b) and 0.82 (c).
atomic Na/Ca ratios of the mixed solutions ranged between 1.45 and 0.82. Low-
temperature Raman spectra have been obtained from these mixtures and are presented in
Figure 33.

These spectra are characterized by hydrate peaks in the region 3350 to 3550 cm\(^{-1}\)
and by the ice peaks at about 3090, 3220, 3405, 3422, 3433 and 3536 cm\(^{-1}\). The peaks at
3266 and 3500 cm\(^{-1}\) noted by Walker (1994) are missing and remain unexplained as they
could not be reproduced.

**WDS and EDS Analyses**

**Decrepitites**

Table 2 shows the results of the WDS analyses of fluid inclusion decrepitates from
two South Platte samples and one Mt. Pleasant sample. The analyses were performed on
an electron microprobe at the University of Western Ontario. The compositions are
presented as atomic percentages. Silicon and oxygen are not reported as the substrate to
the decrepitates was quartz. The decrepitates analyzed were similar to those seen in
Figure 2. The micrographs in Figure 2 show the various formations of the decrepitates
with diameters on the order of 10 to 20 \(\mu\)m.

**Table 2. Atomic concentrations of decrepitates from South Platte and Mt. Pleasant
inclusions (Atomic %)**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>host</th>
<th>Na</th>
<th>Ca</th>
<th>Cl</th>
<th>K</th>
<th>Al</th>
<th>S</th>
<th>Mg</th>
<th>Fe</th>
<th>Zn</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL94-60-4</td>
<td>1</td>
<td>quartz</td>
<td>10.91</td>
<td>3.13</td>
<td>18.19</td>
<td>1.87</td>
<td>0.06</td>
<td>0.03</td>
<td>0.42</td>
<td>0.22</td>
<td>0.04</td>
</tr>
<tr>
<td>RL94-60-4</td>
<td>2</td>
<td>quartz</td>
<td>7.36</td>
<td>1.96</td>
<td>9.06</td>
<td>0.28</td>
<td>0.10</td>
<td>0.01</td>
<td>0.09</td>
<td>0.02</td>
<td>0.01</td>
</tr>
<tr>
<td>RL94-60-4</td>
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<td>19.24</td>
<td>0.02</td>
<td>15.54</td>
<td>0.38</td>
<td>0.04</td>
<td>0.73</td>
<td>0.12</td>
<td>0.00</td>
<td>0.04</td>
</tr>
<tr>
<td>RL94-60-3</td>
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<td>0.00</td>
<td>0.83</td>
<td>0.00</td>
<td>0.02</td>
<td>0.00</td>
<td>0.01</td>
<td>0.00</td>
<td>0.00</td>
</tr>
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<td>29.24</td>
<td>0.40</td>
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<td>0.06</td>
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<td>1.06</td>
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<td>0.00</td>
<td>0.01</td>
</tr>
<tr>
<td>RL94-60-3</td>
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<td>quartz</td>
<td>8.33</td>
<td>0.79</td>
<td>7.85</td>
<td>0.29</td>
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<td>0.01</td>
<td>0.14</td>
<td>0.00</td>
<td>0.02</td>
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<tr>
<td>SYA83-19</td>
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<td>quartz</td>
<td>0.35</td>
<td>2.10</td>
<td>2.03</td>
<td>0.12</td>
<td>0.12</td>
<td>0.00</td>
<td>0.05</td>
<td>0.10</td>
<td>0.00</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>2</td>
<td>quartz</td>
<td>0.36</td>
<td>2.15</td>
<td>2.09</td>
<td>0.13</td>
<td>0.13</td>
<td>0.27</td>
<td>0.05</td>
<td>0.10</td>
<td>0.65</td>
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<td>SYA83-19</td>
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<td>quartz</td>
<td>0.53</td>
<td>0.69</td>
<td>0.02</td>
<td>0.14</td>
<td>0.35</td>
<td>0.02</td>
<td>0.17</td>
<td>0.01</td>
<td>0.13</td>
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<td>SYA83-19</td>
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<td>quartz</td>
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<td>0.59</td>
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<td>0.28</td>
<td>0.25</td>
<td>0.38</td>
</tr>
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<td>0.12</td>
<td>0.00</td>
<td>0.01</td>
<td>0.01</td>
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<td>2.90</td>
<td>12.02</td>
<td>0.10</td>
<td>0.06</td>
<td>0.09</td>
<td>0.00</td>
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</tr>
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<td>quartz</td>
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<td>0.02</td>
<td>0.13</td>
<td>0.06</td>
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</tbody>
</table>
In the decrepitates from Mt. Pleasant and South Platte the major elements present are Na, which ranges from 0.4 to 19.2 atomic %, and Cl, which ranges from 0 to 29.2 atomic %. Calcium is generally present in subordinate amounts, with concentrations of between 0 and 9.7 atomic %. In three analyses from Mt. Pleasant, Ca is present in greater concentrations than Na. Minor amounts (generally < 0.75 atomic %) of K, Al, S Mg, Fe and Zn were also detected.

**EDS Analysis of Precipitates formed within Inclusion Cavities**

As described in the methods section, in an attempt to characterize solids present within the inclusions, some samples were broken open and examined with an SEM. Upon inspection of inclusion cavities exposed in this manner it was discovered that in a few cases in the Mt. Pleasant inclusions, fine-grained precipitates had formed either within or adjacent to inclusion cavities. These were clearly not trapped or daughter minerals and presumably formed by precipitation from the evaporation of the fluid contents of the inclusion. Table 3 shows the compositions, expressed in atomic percentages, of these precipitates. The compositions are quite variable but, as was the case with the decrepitates, Na and Ca are the dominant cations present. However, K appears to be more abundant than in the decrepitates. Chlorine is abundant in three of the four analyses and was not detected in the fourth.

**Table 3. Atomic concentrations of precipitated cavity coatings**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>Na</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Fe</th>
<th>Cl</th>
<th>S</th>
</tr>
</thead>
<tbody>
<tr>
<td>B10-174</td>
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<td>35.06</td>
<td>0.00</td>
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<td>0.00</td>
<td>0.00</td>
<td>10.99</td>
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</tr>
<tr>
<td>B10-238</td>
<td>16</td>
<td>28.88</td>
<td>0.00</td>
<td>11.65</td>
<td>0.00</td>
<td>2.61</td>
<td>52.94</td>
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<tr>
<td>SYA83-40</td>
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</tr>
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<td>SYA83-40</td>
<td>22</td>
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<td>30.16</td>
<td>2.36</td>
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**EDS Analysis of Minerals within Inclusion Cavities**

Table 4 shows EDS analyses of solids within inclusions from Mt. Pleasant. Of the inclusion cavities observed after exposure, most contained at least one solid, with up to five solids present in some cavities. Solids observed included: sheet-like or tabular solids; equant, cubic solids; small, spheroidal solids; and solids of indeterminate shape (solids partially hidden within cavities). In some cases, the cavities also appeared to be coated with very fine-grained crystals (the precipitates described above). The analyses are
presented in groups that show similar chemical characteristics. Eight chemically distinct solids appear to be present within inclusion cavities.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Object*</th>
<th>Anal. Na</th>
<th>Ca</th>
<th>K</th>
<th>Al</th>
<th>Mg</th>
<th>Fe</th>
<th>Cl</th>
<th>S</th>
<th>Cr</th>
<th>Mn</th>
<th>W</th>
</tr>
</thead>
<tbody>
<tr>
<td>Type I</td>
<td>Na, Ca, Cl</td>
<td>B10-174</td>
<td>spheroid</td>
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<td>27.25</td>
<td>17.02</td>
<td>5.29</td>
<td>2.87</td>
<td>1.11</td>
<td>0.58</td>
<td>43.87</td>
<td>2.01</td>
</tr>
<tr>
<td></td>
<td></td>
<td>B10-238</td>
<td>spheroid</td>
<td>9</td>
<td>13.02</td>
<td>63.87</td>
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<td>0.90</td>
<td>0.00</td>
<td>0.86</td>
<td>20.45</td>
<td>0.00</td>
</tr>
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<td>cubic</td>
<td>14</td>
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<td>8.58</td>
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<tr>
<td></td>
<td></td>
<td>SYA83-40</td>
<td>cubic</td>
<td>20a</td>
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<td>10.64</td>
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<tr>
<td>Type VII</td>
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<td>B10-174</td>
<td>tabular</td>
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<td>14.41</td>
<td>0.00</td>
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<td>1.54</td>
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<td></td>
<td></td>
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<td>1.07</td>
<td>45.68</td>
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<tr>
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<td>0.00</td>
<td>-4.91</td>
<td>7.71</td>
<td>2.61</td>
<td>20.53</td>
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<td>28.80</td>
<td>29.42</td>
<td>0.00</td>
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</table>

* tabular = tabular or sheet-like solid, cubic = cubic, equant solid, spheroid = spheroidal solid, solid = solid of indeterminate shape (partially hidden in cavity).

**Type I Solids: Na, Ca, Cl**

In two analyses (7 and 9) Na, Ca and Cl are the dominant elements. Analysis 7 is complex; Na, Ca and Cl dominate but the analysis also shows the presence of minor amounts of K, Al, Mg, Fe and S. Analysis 9 also contains K, Al and Fe but these elements are present in lower concentrations than in analysis 7. The Na/Ca atomic ratio of the two analyses also differ, being 1.6 in analysis 7 and 0.2 in analysis 9.

**Type II Solids: Na, Cl**

Na and Cl dominate analysis 14, which is of a cubic solid within an inclusion cavity. Potassium is next most abundant at 8.6 % and there are lesser amounts of Al, Mg, Cr and Mn present. Analysis 20a is dominated by Na and Cl. The concentration of Na
and Cl in this analysis far outweighs those of the other elements present; K, Al, Fe and Cr, which range from 0.84 to 0.21 atomic % make up the remainder of the analysis.

**Type III Solid: K, Cl**

Analysis 13 stands out from the rest of the analyses as K and Cl are the only elements detected in significant concentrations. Minor amounts (< 3%) of Ca and Cr are also present.

**Type IV Solid: Fe, Cl**

Fe and Cl are the dominant elements in analysis 11 accounting for about 90% of the total. The other elements present are K, Al, and Cr.

**Type V Solid: S, K, Al**

Analysis 4 is of a small solid which produced a very bright backscattered image. The analysis of this solid stands out as the only one with a significant concentration of S (69.8 atomic %). Potassium and Al are also moderately abundant, with lesser Fe.

**Type VI Solid: W, Fe, S**

Analysis 15 is the only one to indicate the presence of W. Significant concentrations of Fe and S are also present. The analysis is dominated by Ca at 65.7 atomic %, whereas Al, Cl, S, Cr and Mn are present in minor proportions.

**Type VII Solids: K, Al, Mg, Fe ± Na, Cl**

Type VII solids are compositionally complex. This group includes analyses 2, 6, 10 and 17 (Table 4). These analyses were acquired from tabular and cubic solids in different cavities. The analyses are generally dominated by K, Al, Fe, ± Na and Cl, with lesser amounts (generally < 5 atomic %) of Mg, S, Cr and Mn. Analysis 2, 6 and 17 are similar in that Al dominates with concentrations of ≥ 50 atomic %. However, these analyses differ in that Na and Cl are present in analysis 2 but absent from analyses 6 and 17. Analyses 6 and 17 have similar, high concentrations of K and Al. Iron is present in analysis 6 while absent in 17, whereas minor concentrations of Ca, Mg, and Mn (< 3 atomic %) are present in analysis 17 and absent in 6. Analyses 10 is dominated by Na and Cl. Although concentrations of K, Al, and Mg are not as high as those in analyses 2, 6 and 17, these elements are present.
Type VIII Solids: Na, Cl, Fe, Al, K

Analyses 19 and 20b both show high concentrations of Fe, ranging from 20.5 to 28.8 atomic %. These analyses are very similar except with respect to the elements present in minor concentrations. Mg is present in analysis 19 but absent from analysis 20b, and Cr and Mn are seen in analysis 20b but are absent from analysis 19.
Chapter 4: DISCUSSION

General Nature of Raman Spectra and Peak Positions

The fundamental internal symmetric and anti-symmetric stretching vibrations of the water molecule produce the most intense lines in the Raman spectrum of crystalline hydrates in the wavenumber range between 3000 and 3600 cm\(^{-1}\) (Dubessy et al., 1982). It was the peaks, which represent these stretching vibrations, that were therefore selected as the probe in the characterization of the hydrates present in frozen fluid inclusions.

Low temperature spectra of hydrates produced from synthetic solutions in the systems NaCl-H\(_2\)O and CaCl\(_2\)-H\(_2\)O have been presented by Walker (1994) (Fig. 1). The broad, intense peak at around 3090 cm\(^{-1}\) and the less intense, broad peak at 3220 cm\(^{-1}\) seen in each of the spectra in Figure 1 are those of hexagonal ice (Dubessy et al., 1982). This is expected because ice is a stable subsolidus phase in both of these binary systems (Fig. 34).

![Fig. 34 Phase diagram for part of the ternary system NaCl-CaCl\(_2\)-H\(_2\)O. L = liquid, Ant = antarcticite, Hh = hydrohalite.](image)

The peaks at 3385, 3401, 3407 and 3433 cm\(^{-1}\) in Figure 1a are from antarcticite. However, the peaks have not been assigned to specific vibrational modes because of the small separation between the peaks. These lines are, however, sufficient for mineralogical
identification (Dubessy et al., 1982). The peaks at 3402, 3422, 3435 and 3536 cm\(^{-1}\) in Figure 1b indicate the presence of hydrohalite and have been assigned to the stretching of four OH\(^-\) groups in the structure of hydrohalite (Dubessy et al., 1982).

The spectra collected in the current study from natural fluid inclusions exhibit similar characteristics. Some spectra contain no peaks in the region 3000 to 3600 cm\(^{-1}\) which indicates that neither ice nor hydrates crystallized in these inclusions. Some spectra contain just the peaks for hexagonal ice at about 3090 cm\(^{-1}\) and, in some cases, at 3220 cm\(^{-1}\), and others, in addition, show hydrate peaks in the region between 3350 and 3550 cm\(^{-1}\). In general, peaks have been observed between 3401 to 3406 cm\(^{-1}\); at about 3422 cm\(^{-1}\); between 3433 to 3438 cm\(^{-1}\); and at about 3536 cm\(^{-1}\). Assignments of these peaks are presented in Table 5.

In all, peaks from hexagonal ice and the low-temperature hydrates, hydrohalite (NaCl\(\cdot\)2H\(_2\)O) and antarcticite (CaCl\(_2\)\(\cdot\)6H\(_2\)O) were identified from the low-temperature Raman spectroscopic investigations of the fluid inclusions in samples from the various deposits.

**Table 5. Hydrate Raman peaks observed after application of the freeze-thaw method**

<table>
<thead>
<tr>
<th>Location</th>
<th>Inclusion #</th>
<th>Incl. Type</th>
<th>Hh peaks (cm(^{-1}))</th>
<th>Ant peaks (cm(^{-1}))</th>
<th># of spectra</th>
</tr>
</thead>
<tbody>
<tr>
<td>South Platte</td>
<td>RL94-60-2-1</td>
<td>LV</td>
<td>3403(c), 3422, 3438(c), 3536</td>
<td>3433(c)</td>
<td>2</td>
</tr>
<tr>
<td>South Platte</td>
<td>RL94-60-3-2-1</td>
<td>LV</td>
<td>3403(c), 3420, 3438(c), 3536</td>
<td>3401(c), 3433</td>
<td>6</td>
</tr>
<tr>
<td>South Platte</td>
<td>RL94-60-3-2-2</td>
<td>LV</td>
<td>3403(c), 3420, 3437(c), 3536</td>
<td>3433(c), 3401(c)</td>
<td>3</td>
</tr>
<tr>
<td>South Platte</td>
<td>RL94-60-3-2-3</td>
<td>LV</td>
<td>3404(c), 3422, 3438, 3538(s)</td>
<td>3433(s)</td>
<td>2</td>
</tr>
<tr>
<td>South Platte</td>
<td>RL94-60-3-1-3</td>
<td>LV</td>
<td>3422(*)</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>South Platte</td>
<td>RL94-60-4-1</td>
<td>LVHS</td>
<td>3404(c), 3422, 3439(c), 3536</td>
<td>3434(c)</td>
<td>1</td>
</tr>
<tr>
<td>South Platte</td>
<td>RL94-60-4-3</td>
<td>LVHS</td>
<td>3404(c), 3422, 3438(c),3537</td>
<td>3433(c)</td>
<td>2</td>
</tr>
<tr>
<td>Mt. Pleasant</td>
<td>SYA83-19-2</td>
<td>LV</td>
<td>3405*, 3425*, 3537*</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Mt. Pleasant</td>
<td>SYA83-19-6</td>
<td>LV</td>
<td>3422, 3405*</td>
<td></td>
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<td>B14-136A</td>
<td>LV(H?)</td>
<td>3406(c), 3422</td>
<td>3402(c)</td>
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<tr>
<td>Mt. Pleasant</td>
<td>B10-174-6-1</td>
<td>LVHS</td>
<td>3423*</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Mt. Pleasant</td>
<td>B10-174-6-2</td>
<td>LVHS</td>
<td>3405, 3422, 3438, 3536</td>
<td></td>
<td>3</td>
</tr>
<tr>
<td>Mt. Pleasant</td>
<td>B10-174-6-3</td>
<td>LVHS</td>
<td>3422, 3405(*), 3538*</td>
<td></td>
<td>1</td>
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<td>B10-174-6-4</td>
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<td>1</td>
</tr>
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<td>LV</td>
<td>3422*</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Gallinas</td>
<td>PIN2-1</td>
<td>LV</td>
<td>3404, 3422</td>
<td></td>
<td>1</td>
</tr>
<tr>
<td>Gallinas</td>
<td>PIN2-2</td>
<td>LV</td>
<td>3404, 3422, 3436, 3538(c)</td>
<td>3433(c)</td>
<td>2</td>
</tr>
<tr>
<td>Wawa</td>
<td>IS90-53b IS2-1</td>
<td>LV</td>
<td>3422*</td>
<td>3433*</td>
<td>2</td>
</tr>
</tbody>
</table>

(c) - peak position which may be a component of a composite of multiple peaks
(s) - peak position is a component of a shoulder
* - peaks with very weak intensity. Hh = hydrohalite, Ant = antarcticite.
Two general types of spectra have been obtained in the current study, those with hydrate peaks present and those without. In most cases, the differences can be related to the freezing techniques employed. Spectra acquired from inclusions following quick freezing do not show distinct hydrate peaks. In some cases such spectra have a very weak, broad band centred at about 3440 cm\(^{-1}\) (the hydrate region), along with hexagonal ice peaks at about 3090 and 3220 cm\(^{-1}\) (Figures 9a to d and 10a). The very weak hexagonal ice peaks and broad band in the hydrate region (centred at 3440 cm\(^{-1}\)) of quickly frozen inclusions indicates that crystalline hydrates did not form. The broad band in this region however, suggests that a poorly ordered hydrate-like solid formed.

More complex spectra were obtained from inclusions which had subsequently been warmed to the point where some visible change, such as crystallization or recrystallization occurred, and then quickly refrozen to -185 °C (Fig. 10c) or inclusions which have been warmed, allowing partial melting to a few crystals and then slowly refrozen allowing for large crystal growth (Fig. 10b). Distinct peaks at 3424 and 3536 cm\(^{-1}\) can be unequivocally assigned to hydrohalite. A broad peak at 3403 cm\(^{-1}\) can be assigned to a mixture of hydrohalite (~ 3402 cm\(^{-1}\)) and antarcticite (~ 3401, 3407 cm\(^{-1}\)). Similarly, peaks between 3431 and 3437 cm\(^{-1}\) probably represent a mixture of hydrohalite (3435 cm\(^{-1}\)) and antarcticite (3433 cm\(^{-1}\)). The hexagonal ice peaks at about 3090 and, in some cases, 3220 cm\(^{-1}\) are also present (Fig 10c). These spectra clearly indicate more complete crystallization of the hydrates.

As would be expected, in spectra collected from large, single hydrate crystals, (e.g. Fig. 12) the hydrate peaks are more intense than the hexagonal ice peaks. Such spectra should not include much ice in the sample volume. In these particular analyses, the hydrate crystals were large enough that the entire laser spot can be positioned within a single crystal. The ice peaks presumably result from the interaction of the laser with ice in the sheath of fine-grained crystals surrounding these single large crystals. In the case of the spectra obtained from fine-grained aggregates, after the freeze-thaw method had been applied (e.g. Fig. 16), the main ice peak is much closer in intensity to the hydrate peaks or is more intense. This reflects the higher proportion of ice in the fine-grained aggregate within the sampling volume, which more accurately represents the bulk chemistry of the
inclusion. The relative intensity of the ice and hydrate peaks in a fine-grained mixture will reflect the salinity of the inclusion assuming that the relative amounts of ice and hydrate in the sample volume is close to that of the entire inclusion, i.e. the fine-grained mixture is homogeneous throughout the inclusion.

The spectra acquired from inclusions PIN 2-1 (Fig. 30) and PIN 2-2 (Fig. 31) also show some interesting solidification behaviour. The inclusions, upon warming from -185 °C, started crystallizing at about -41 °C. Crystallization occurred in two phases, the first saw a wave of crystallization move outwards from the centre of the inclusion. This was followed by the formation of a darker and somewhat coarser aggregate around the margin of the inclusions. The spectra in Figures 30a and 31b were collected from a spot near the centre of the inclusions which represents the first crystallization event and show no or very poor hydrate and ice peak development, suggesting that this portion of the inclusions contains either a glass or poorly crystallized aggregate. Spectra acquired from the outer, darker area of crystallization show either the presence of ice and hydrate peaks (Fig. 30b) or somewhat better defined hydrate and ice peaks (Fig. 31a). In the case of PIN2-1 (Fig. 30), these results may indicate a crystallization sequence in which a glassy ice initially formed at the centre of the inclusion followed by the crystallization of an ice-hydrate mixture around the margin of the inclusion. In PIN2-2 the darker, outer area yielded a spectrum in which the hydrate peaks are better defined than in the central area. Again, this presumably indicates more complete crystallization in the outer portion of the inclusion.

South Platte

Mathematical Modeling of Low-temperature Raman Spectra

As described above, spectra collected from frozen inclusions from the South Platte District, Colorado (see Table 5), generally show distinct lines of moderate to strong intensity between about 3350 and 3550 cm⁻¹. These peaks were variably assigned to hydrohalite or mixtures of hydrohalite and antarcticite. The hydrate lines are generally equal to slightly greater in intensity than the ice peaks (at about 3090 and 3220 cm⁻¹). The peak at 3422 cm⁻¹ is always the most intense, followed in intensity by the peaks at about 3405 and 3436 cm⁻¹. The peak at about 3536 cm⁻¹ shows considerable variation in intensity, being altogether absent in some spectra and as high as moderate in intensity in
other spectra. Broad bands or shoulders in these spectra probably result from the overlap of peaks in the region from hydrohalite and antarcticite. In an attempt to resolve these composite peaks, four spectra were selected for mathematical modeling.

The spectra were modeled using PeakFit™, a peak separation and analysis software package produced by Jandel Scientific Software. Based on the spectra described above, it was initially assumed that only peaks from hydrohalite and antarcticite were present. Modeling was therefore conducted using the six main hydrohalite (3402, 3422 and 3438 cm⁻¹) and antarcticite peaks (3401, 3407 and 3433 cm⁻¹). Although it was predicted that a Lorentzian function would best approximate the Raman peak shapes (R. Aroca, pers. comm., 1997) models involving Gaussian, Lorentzian, Voigt, and Pearson functions were run. As expected, the most satisfactory fits were obtained from the Lorentzian function. Initially, spectra were smoothed prior to fitting by employing a 3 point sliding window using the EasyPlot™ software package.

An arbitrary coefficient of determination ($r^2$) value of 0.95 was selected as the lower limit for an acceptable fit for the models (an $r^2$ value of 1.00 is a perfect fit, $r^2 = 0.00$ indicates a complete lack of fit). The quality of a fit may also be represented graphically using residual graphs, which show the difference in intensity between that of the actual spectrum and the sum of the component peaks of the mathematical model at a given wavenumber. The residuals for all of the models, with few exceptions, are small indicating that the fits are an accurate representation of the spectra.

In Figures 35 through 38, the top figure shows the original smoothed spectra (dots) along with the summation of the modeled peaks (solid line). The latter are shown in the central graph in these figures with the residuals shown in the bottom graph.

The spectrum shown in Figure 35 was obtained from a fine-grained aggregate of crystals produced after quickly freezing to -185°C, warming to -60°C, followed by again quickly freezing to -185°C. The spectrum shown in Figure 36 was collected from the same inclusion but from an area of fine-grained crystals surrounding large hydrate crystals grown by slow cooling. Spectra collected from these large hydrate crystals show
Fig. 35 Mathematical model of spectrum JA9723 of inclusion RL94-60-3-2-1, based on the peak positions of hydrohalite (Hh) and antarcticite (Ant). A plot of the residuals is seen below.

Fig. 36 Mathematical Model of spectrum SE9612 from inclusion RL94-60-3-2-1, based on the peak positions of hydrohalite (Hh) and antarcticite (Ant). A plot of the residuals is seen below.
Fig. 37 Mathematical Model for spectrum JA9741 of inclusion RL94-60-2-1 based on the peak positions of hydrohalite (Hh) and antarcticite (Ant). A plot of the residuals is seen below.

Fig. 38 Mathematical model of spectrum JA9731 of inclusion RL94-60-4-1, based on the peak positions of hydrohalite (Hh) and antarcticite (Ant). A plot of the residuals is seen below.
that they are hydrohalite (Fig. 12). In both models, the spectra can be accurately represented by the six hydrohalite and antarcticite peaks. The residuals in both models are on the order of a degree of magnitude lower in intensity than the weakest modeled peak present. These models confirm that the broad composite peaks do indeed result from the summation of closely spaced peaks from the respective hydrates.

In both cases, the peak at 3422 cm\(^{-1}\) is the most intense and can be modeled simply with the hydrohalite peak at 3422 cm\(^{-1}\). These spectra also contain a broad band centred at about 3435 cm\(^{-1}\). In the region between 3430 and 3440 cm\(^{-1}\) the residuals of both models are very small, indicating that this broad band can be accurately modeled using the hydrohalite 3438 cm\(^{-1}\) and antarcticite 3433 cm\(^{-1}\) peaks. The shapes of this band in the two spectra are different because the antarcticite peak is relatively more intense than the hydrohalite peak in Figure 36 than in Figure 35, as are the antarcticite peaks in the region between 3390 and 3410 cm\(^{-1}\). This reflects a greater relative abundance of antarcticite in the fine-grained mixture surrounding the large hydrohalite crystals caused by the depletion of Na in the fluid due to hydrohalite crystallization.

Models were also created for the spectra collected from inclusions RL94-60-2-1 (Fig. 37) and RL94-60-4-1(Fig. 38). Spectrum JA9741 (Fig. 37) was collected from inclusion RL94-60-2-1 after quickly freezing to -185°C, then warming to -47°C, followed by quickly refreezing to -185 °C. The smoothed spectrum shows a broad, skewed band centred at about 3405 cm\(^{-1}\), with another broader band at about 3435 cm\(^{-1}\). The broad band at about 3405 cm\(^{-1}\) has been modeled with peaks placed at 3401 and 3407 cm\(^{-1}\), representing antarcticite, along with a hydrohalite peak at about 3404 cm\(^{-1}\). The residuals in the region between 3400 and 3410 cm\(^{-1}\) are again very small, suggesting that the proposed peaks model the data well. Two peaks are evident in the smoothed data in the region between 3430 and 3445 cm\(^{-1}\) in spectrum JA9741. Peaks placed at 3433 (Ant) and 3438 (Hh) cm\(^{-1}\) model this region of the spectrum well, producing very minor residuals. The use of hydrohalite and antarcticite peaks to model spectrum JA9741 has produced a model which fits the data well, implying that the broad peaks observed may indeed result from multiple, closely-spaced hydrohalite and antarcticite peaks. A region of relatively large residuals exists between 3410 and 3430 cm\(^{-1}\). The large residuals (i.e. poor fit) over
this region could indicate the presence of an unknown hydrate peak, however, no known hydrate peaks occur in this region. It is perhaps more likely that this poor fit is an artifact of the smoothing of a noisy spectrum. Overall, this spectrum from an LVH inclusion is rather similar to that obtained from the LV inclusion described above (Fig. 35) and indicates that the two inclusions have similar Na/Ca ratios.

Spectrum JA9731 (Fig. 38) was acquired from inclusion RL94-60-4-1 after quickly freezing to -185 °C, then warming to -60°C followed by quickly refreezing to -185°C. To model spectrum JA9731 peaks have been positioned as in the model for spectrum JA9741. The residuals resulting from this model, in the areas of the multiple peaks, are much smaller than the weakest peak employed in the models, once again suggesting a good fit to the data. Spectrum JA9731 is similar to JA9741 with a broad, skewed band centred at about 3405 cm⁻¹ with a less intense broad band between 3430 and 3445 cm⁻¹, again showing peaks superimposed at about 3433 and 3438 cm⁻¹. One obvious difference in the model for spectrum JA9731 is the additional broad peak positioned between 3422 and 3433 cm⁻¹ in the model. This broad peak is required to model a 'raised' area immediately adjacent to the hydrohalite peak at 3422 cm⁻¹. The original spectrum has relatively few data points in this region due to the removal of numerous spikes. Thus, the smoothed spectrum probably does not accurately represent the original spectral features, resulting in the poor fit. In addition, there are no known hydrate peaks in this wavenumber region.

In all models, the intense peak at 3422 cm⁻¹ can be fitted with a single hydrohalite peak positioned at 3422 cm⁻¹. A single peak is employed here as hydrohalite is the only hydrate to have a line at this position. This is the most intense peak in all the spectra, as is the case in the synthetic H₂O-NaCl solutions (Fig. 1b). In synthetic solutions of H₂O-CaCl₂ (Fig. 1a) the peak at 3433 cm⁻¹ is by far the most intense. In the inclusion spectra this peak is much less intense than the hydrohalite peak, typically between ½ and ¼ of its intensity. In the mixed-component spectra (Fig. 32), in only the most Na-rich solution, is the hydrohalite (3422 cm⁻¹) peak significantly more intense than the antarcticite (3433 cm⁻¹) peak. Even in solutions where Na is more abundant on an atomic basis (those where the wt. percentage of NaCl equals that of CaCl₂), the antarcticite peak is subequal in intensity.
to the hydrohalite peak. This clearly indicates that the concentration of NaCl is significantly greater than CaCl₂ in the inclusions analyzed. Quantification of the relative abundance of NaCl and CaCl₂ will require more extensive analyses of synthetic solutions in the system H₂O-NaCl-CaCl₂.

The above models have been created employing the known OH-stretching region peak positions for hydrohalite and antarcticite only. The use of peaks from these two hydrates only can be justified by considering the known peak positions, in the same wavenumber region (3000-3600 cm⁻¹), of other salt hydrates. Other salt hydrates that may commonly form in frozen fluid inclusions were studied by Dubessy et al. (1982) and include FeCl₃•6H₂O, MgCl₂•6H₂O, MgCl₂•12H₂O and KCl•MgCl₂•6H₂O. The Raman spectra of these hydrates show their most intense lines at 3533, 3345, 3511 and 3448 cm⁻¹, respectively. Intense peaks in these positions should be distinct from the hydrohalite and antarcticite peaks and easily identifiable assuming the component are present in sufficient concentrations. There is no evidence of such peaks in these positions in the spectra collected in this study.

**WDS data**

An indication of the quality of the WDS and EDS data can be obtained by calculating a charge balance, which is expressed in Tables 6 and 10 as the percentage difference between the sums of the negative and positive charges. Haynes (1988) suggests an acceptance/rejection cutoff of around 10%. Such a cutoff would eliminate 3 of the 7 South Platte analyses two of which have charge imbalances of between 12 and 13%. Given this, and the nature of the Mt. Pleasant analyses (see below), a cutoff of about 20% is used. Such analyses must obviously be considered semi-quantitative but are nonetheless very useful for comparison with the Raman spectra. The WDS analyses of decrepitate products from South Platte inclusions (Table 6) indicate that Na and Cl are the dominant elements present, along with lesser Ca. Potassium was detected in subordinate amounts in one analysis.
Table 6. Major element composition (Atomic %) and Charge Balance of South Platte Deprecitates. (bd = below detection limits)

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>Host</th>
<th>Na</th>
<th>Ca</th>
<th>K</th>
<th>Cl</th>
<th>S</th>
<th>∑+</th>
<th>∑-</th>
<th>diff</th>
<th>diff%</th>
</tr>
</thead>
<tbody>
<tr>
<td>RL94-60-4</td>
<td>1</td>
<td>quartz</td>
<td>10.91</td>
<td>3.13</td>
<td>1.87</td>
<td>18.19</td>
<td>bd</td>
<td>19.04</td>
<td>18.19</td>
<td>0.85</td>
<td>2.28</td>
</tr>
<tr>
<td>RL94-60-4</td>
<td>2</td>
<td>quartz</td>
<td>7.36</td>
<td>1.96</td>
<td>0.28</td>
<td>9.06</td>
<td>bd</td>
<td>11.56</td>
<td>9.06</td>
<td>2.50</td>
<td>12.12</td>
</tr>
<tr>
<td>RL94-60-4</td>
<td>3</td>
<td>quartz</td>
<td>19.24</td>
<td>bd</td>
<td>0.38</td>
<td>15.54</td>
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<tr>
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<td>1.15</td>
<td>bd</td>
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<td>bd</td>
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<td>14.00</td>
<td>9.69</td>
<td>0.40</td>
<td>29.24</td>
<td>bd</td>
<td>33.78</td>
<td>29.24</td>
<td>4.54</td>
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<tr>
<td>RL94-60-3</td>
<td>3</td>
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<td>8.97</td>
<td>1.06</td>
<td>0.74</td>
<td>11.49</td>
<td>bd</td>
<td>11.83</td>
<td>11.49</td>
<td>0.34</td>
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<td>4</td>
<td>quartz</td>
<td>8.33</td>
<td>0.79</td>
<td>0.29</td>
<td>7.85</td>
<td>bd</td>
<td>10.20</td>
<td>7.85</td>
<td>2.35</td>
<td>13.02</td>
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</table>

Na/Na+Ca+K mostly ranges from 0.69 to 1.00, with one value at 0.58. Ca/Na+Ca+K ranges from 0.08 to 0.40 and K/Na+Ca+K from 0.02 to 0.11. Chloride is clearly the dominant anion as it was the only one detected in all but one analysis, in which Cl/Cl+S is 0.96 (Table 7).

Table 7. Atomic ratios in South Platte deprecitates.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>Na/Na+Ca+K</th>
<th>K/Na+Ca+K</th>
<th>Ca/Na+Ca+K</th>
<th>Cl/Cl+S</th>
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<tr>
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<td>-</td>
<td>-</td>
<td>1.00</td>
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<tr>
<td>RL94-60-3</td>
<td>2</td>
<td>0.58</td>
<td>0.02</td>
<td>0.40</td>
<td>1.00</td>
</tr>
<tr>
<td>RL94-60-3</td>
<td>3</td>
<td>0.83</td>
<td>0.07</td>
<td>0.10</td>
<td>1.00</td>
</tr>
<tr>
<td>RL94-60-3</td>
<td>4</td>
<td>0.89</td>
<td>0.03</td>
<td>0.08</td>
<td>1.00</td>
</tr>
</tbody>
</table>

Raman Spectra of Solid Phases

The most obvious feature of the spectrum from the high relief, faint green, rectangular solid phase in inclusion RL94-60-2-1 (Fig. 8) is the intense peak at 1019 cm⁻¹, which, along with those at 417, 628, 678, and 1131 cm⁻¹ identify the solid as anhydrite (CaSO₄) (Griffith, 1975). The existence of anhydrite is consistent with the presence of Ca in the fluid, but also implies the presence of SO₄²⁻, which was neither indicated from the Raman spectra nor from the WDS and EDS data. This can be explained by the fact that the solubility of anhydrite (0.05 mols/kg ~ 0.6 wt. % at 25°C) (I. Samson, pers. comm., 1997) is low enough that the concentrations of SO₄²⁻ in the enclosing fluid would be below the detection limits for both methods.
Implications for Microthermometry

Raman spectra obtained from frozen South Platte fluid inclusions have been shown to exhibit peaks which may be assigned to both hydrohalite and antarcticite. As discussed above, these spectra indicate that NaCl is significantly more abundant than CaCl$_2$. This conclusion is borne out by EDS data, which indicates a fluid chemistry in which Na$>$Ca$>$K, and Cl$^-$ is the dominant anion. All of this lends credence to the use of the NaCl-CaCl$_2$-H$_2$O system in modelling microthermometric measurements of the South Platte inclusions (Levasseur, 1997).

Mt. Pleasant

Characteristics of Low-Temperature Raman Spectra

As was the case with the spectra obtained from frozen South Platte inclusions, spectra collected from Mt. Pleasant (LV, LVS and LVHS) inclusions show hydrate peaks between 3350 and 3550 cm$^{-1}$. In general, the Mt. Pleasant spectra are noisier, however, distinct hydrate peaks can still be resolved. The Mt. Pleasant spectra generally show four distinct peaks at about 3405, 3422, 3438 and 3536 cm$^{-1}$ (Fig. 26a, b and c). These peaks are generally more intense and narrower than the hexagonal ice peaks at about 3092 and 3225 cm$^{-1}$. The relative intensity of the peaks in the spectra from the two suites of samples are similar. In each, the peak at 3422 cm$^{-1}$ is always the most intense of the hydrate peaks, followed by the peaks at about 3405 and 3436 cm$^{-1}$. The intensity of the peak at about 3536 cm$^{-1}$ shows similar variability in the spectra from each of the deposits. The intensity of this peak ranges from absent to moderate intensity, and it is generally the weakest of the hydrate peaks present.

A notable difference does exist between the spectra collected from Mt. Pleasant and those from South Platte. As described above, the spectra collected from frozen South Platte inclusions show lines at about 3422 and 3536 cm$^{-1}$ (Hh) (Fig. 39c and d) and closely spaced lines or broad bands/shoulders in the regions between 3395 to 3410 cm$^{-1}$ and 3430 to 3445 cm$^{-1}$. In the case of the region between 3430 to 3445 cm$^{-1}$, the band appears as a broad shoulder on the flank of the 3422 cm$^{-1}$ hydrohalite peak (Fig. 39c and d). Between 3395 to 3410 cm$^{-1}$ the spectra show a weak, broad band. These broad bands
Fig. 39 Comparison of low-temperature Raman spectra from (a) and (b) Mt. Pleasant and (c) and (d) South Platte inclusions.
and shoulder result from the overlap of closely spaced hydrohalite and antarcticite peaks (see Mathematical modelling). The spectra collected from frozen Mt. Pleasant inclusions show hydrohalite peaks at 3422 cm\(^{-1}\) and about 3405 and 3438 cm\(^{-1}\) (Fig. 39a and b). As can be seen from Figure 39, the broad peak at about 3435 cm\(^{-1}\) seen in the South Platte spectra is not present in the Mt. Pleasant spectra. Based on the mathematical modelling of the South Platte spectra, this difference almost certainly indicates the absence of an antarcticite component in the Mt. Pleasant spectra.

**Mathematical Modelling of Low-temperature Raman Spectra**

Although distinct peaks are present in the spectra collected from frozen Mt. Pleasant inclusions, modeling of the spectra proved to be unsuccessful. Because of the noisy nature of these spectra, smoothing (in preparation for modelling) resulted in the generation of ‘peaks’ that were not present in the spectra before smoothing. This resulted in very poor fits for models which utilized only the known hydrohalite and antarcticite peaks.

**Raman Spectroscopic Investigation of Solid Phases within Fluid Inclusions**

**Solid 4**

Raman spectra obtained from birefringent, prismatic (six-sided) crystals (solid 4) contain peaks at 618, 1024, 3551, 3558 and 3627 cm\(^{-1}\) (Figs. 2 and 3). Similar spectra have been obtained from the same mineral in inclusions from the Madeleine copper deposit, Quebec (I. Samson, pers. comm., 1997). The peaks in the range 3000-3600 cm\(^{-1}\) are consistent with OH\(^-\) stretching vibrations in silicate minerals (White, 1975). Hydroxyl stretching vibrations in salt hydrates occur at lower wavenumbers in the region 3080 to 3540 cm\(^{-1}\) (Dubessy et. al., 1982). Relatively few Raman spectroscopic studies of OH\(^-\) stretching in silicates are available. Comparisons with available spectra in the OH\(^-\) stretching region indicate that the peaks observed from solid 4 are closest in wavenumber value to those of tourmaline (Peng et al., 1989), which shows lines at 3551, 3557 and 3636 cm\(^{-1}\). This could indicate that solid 4 is tourmaline or simply that the OH\(^-\) groups occur in a similar molecular environment to the OH\(^-\) groups in tourmaline. The latter is perhaps indicated by the fact that the 618 and 1024 cm\(^{-1}\) peaks do not coincide with the
reported values for tourmaline in this region, the strongest of which occur at 255, 342, 
404 and 737 cm\(^{-1}\) (Peng et al., 1989).

Table 8 lists minerals which have peaks within 25 cm\(^{-1}\) of both the 618 and 1024 
\(\) cm\(^{-1}\) peaks seen in the spectra of solid 4. Given the presence of the peaks between 3400 
and 3600 cm\(^{-1}\), anhydrous minerals can immediately be eliminated as possibilities. 
Unfortunately, with the exception of tourmaline, the spectra reported for the various 
minerals do not cover wavenumbers above 2000 cm\(^{-1}\). The remaining hydrous minerals, 
gypsum, hydroxyapatite, margarite and tourmaline, remain as possible candidates.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Source</th>
<th>Peak Positions (cm(^{-1}))</th>
<th>Strongest Peak</th>
<th>Habit</th>
<th>Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Solid 4</td>
<td>618</td>
<td>1024 3551 3578 3628</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Anhydrite</td>
<td>1</td>
<td>608(m), 628(m)</td>
<td></td>
<td>orth.</td>
<td>CaSO(_4)</td>
</tr>
<tr>
<td>Anorthite</td>
<td>2</td>
<td>620(vw)</td>
<td>1044(sh) na na na 506(vs), 556(vs)</td>
<td>triclinic</td>
<td>Ca(_2)Al(_2)Si(_2)O(_9)</td>
</tr>
<tr>
<td>Celestite</td>
<td>1</td>
<td>624(m)</td>
<td>1000(vs) na na na 1000(vs)</td>
<td>orth.</td>
<td>SrSO(_4)</td>
</tr>
<tr>
<td>Fluorapatite</td>
<td>1</td>
<td>609(m)</td>
<td>1041(w) na na na 966(vs)</td>
<td>hexagonal</td>
<td>Ca(_5)(PO(_4))(_3)F</td>
</tr>
<tr>
<td>Gehlinite</td>
<td>3</td>
<td>626(vw)</td>
<td>1005(vw) na na na 626(vs)</td>
<td>tetrahedral</td>
<td>Ca(_2)Al(AlSi)O(_7)</td>
</tr>
<tr>
<td>Gypsum</td>
<td>1</td>
<td>620(w)</td>
<td>1007(vs) na na na 1007(vs)</td>
<td>monoclinic</td>
<td>CaSO(_4)•2H(_2)O</td>
</tr>
<tr>
<td>Hydroxyapatite</td>
<td>1</td>
<td>612(w)</td>
<td>1034(w) na na na 966(s)</td>
<td>hexagonal</td>
<td>Ca(_5)(PO(_4))(_3)(OH)</td>
</tr>
<tr>
<td>Margarite</td>
<td>4</td>
<td>622(w)</td>
<td>1039(w) na na na 265(m)</td>
<td>monoclinic</td>
<td>Ca(_2)Al(_2)Si(_2)O(_6)(OH)(_2)</td>
</tr>
<tr>
<td>Tourmaline</td>
<td>5</td>
<td>636(?)</td>
<td>1016 3551 3577 3636 353, 464</td>
<td>trigonal</td>
<td>W(_2)Y(_2)(BO(_3))Si(_2)O(_8)(O, OH,F)</td>
</tr>
</tbody>
</table>

(m) moderate intensity, (s) strong, (vw) very weak, (vs) very strong, (w) weak, (?) unknown intensity, (aa) not available

In the spectra of gypsum, the peak at 1007 cm\(^{-1}\) is always, by far, the strongest, 
including those obtained from variably oriented gypsum crystals within fluid inclusions (I. 
Samson, pers. comm., 1997). Furthermore, this peak shows little variation in position 
because of the chemical uniformity of gypsum. Given these arguments and the fact that 
the 618 cm\(^{-1}\) peak is stronger than the 1024 cm\(^{-1}\) peak, it is unlikely that solid 4 is gypsum. 
If solid 4 was hydroxyapatite, a very strong peak at 966 cm\(^{-1}\) should be present. There is 
no suggestion of such a peak in the spectra of solid 4, eliminating apatite as a possibility. 
In margarite spectra, the strongest peak occurs at 265 cm\(^{-1}\) and the peaks at 622 and 1039 
\(\) cm\(^{-1}\) are weak. Unfortunately, quartz also has a peak at around 265 cm\(^{-1}\), however, in the 
solid 4 spectra, this peak is invariably weaker or of equal intensity to the 618 cm\(^{-1}\) peak.
making it less likely that solid 4 is margarite. The differences in peak position could be an
indication of chemical variation in solid 4 relative to the reference spectrum. A similar
situation exists when comparing the solid 4 spectra to tourmaline. The strongest peaks in
reported tourmaline spectra occur at 353 and 464 cm\(^{-1}\), both of which coincide with quartz
peaks. These values are from polarized spectra so that relative intensities cannot be
directly compared to the non-polarized spectra collected here. As tourmaline is an
extremely chemically complex mineral group, variations in peak position can easily be
accounted for. Given the crystallography of tourmaline and margarite, the crystal forms
seen in the inclusions (prismatic and hexagonal) could represent either mineral, although
the high birefringence favours tourmaline. In summary, tourmaline seems the more likely
candidate, particularly as it is a common mineral at Mt. Pleasant (Table 9), although
maragarite cannot be ruled out at present. Data on the OH stretching vibrations of
margarite would help resolve this question.

<table>
<thead>
<tr>
<th>Mineral</th>
<th>Formula</th>
<th>Colour</th>
<th>System</th>
<th>Occurrence</th>
</tr>
</thead>
<tbody>
<tr>
<td>Fccrimolybdite</td>
<td>Fe(_2) (MoO(_4))(_3) \cdot 8\H(_2)O</td>
<td>yellow</td>
<td>ortho.*</td>
<td>frequent</td>
</tr>
<tr>
<td>Goethite</td>
<td>FeO(OH)</td>
<td>brown</td>
<td>ortho.</td>
<td>rare</td>
</tr>
<tr>
<td>Malachite</td>
<td>Cu(_2)(CO(_3))(_2)(OH)(_2)</td>
<td>green</td>
<td>mono.*</td>
<td>rare</td>
</tr>
<tr>
<td>Arsenobismite</td>
<td>Bi(_2)(AsO(_4))(_3)(OH)(_3)</td>
<td>pale green</td>
<td></td>
<td>rare</td>
</tr>
<tr>
<td>Scorodite</td>
<td>FeAsO(_4) \cdot 2\H(_2)O</td>
<td>green</td>
<td>ortho</td>
<td>rare</td>
</tr>
<tr>
<td>Dickite</td>
<td>Al(_2)Si(_2)O(_5)(OH)(_4)</td>
<td>white</td>
<td>mono.</td>
<td>frequent</td>
</tr>
<tr>
<td>Epidote</td>
<td>Ca(_3)(Fe,Al(_2))(SiO(_4))(_3)(OH)</td>
<td>green</td>
<td>mono.</td>
<td>frequent</td>
</tr>
<tr>
<td>Kaolinite</td>
<td>Al(_2)Si(_2)O(_5)(OH)(_4)</td>
<td>yellow-green</td>
<td>ortho.</td>
<td>common</td>
</tr>
<tr>
<td>Serpentine</td>
<td>(Mg,Fe,Ni(_2))(_2)Si(_2)O(_5)(OH)(_4)</td>
<td>green</td>
<td>mono.+orth.</td>
<td>frequent</td>
</tr>
<tr>
<td>Topaz</td>
<td>Al(_2)Si(_2)O(_5)(F,OH)(_2)</td>
<td>grey-yellow</td>
<td>ortho.</td>
<td>abundant</td>
</tr>
<tr>
<td>Hornblende (hydromica)</td>
<td>Ca(_3)(Mg,Fe(_2),Al(AlSi(_3)O(_2))(_2)(OH)(_2)</td>
<td>dark green</td>
<td>mono.</td>
<td>rare</td>
</tr>
<tr>
<td>Chlorite</td>
<td>(Mg,Al,Fe,Cr,Mn)(_4)(Si,Al(_2))O(_10)(OH)(_8)</td>
<td>green</td>
<td>mono.</td>
<td>abundant</td>
</tr>
<tr>
<td>Illite (hydr.)</td>
<td>(K,(_2)O)(Al, Mg, Fe(_2))(_2)(Si,Al(_2))O(_10)[(OH)(_2),H(_2)O]</td>
<td>-</td>
<td>mono.</td>
<td>?</td>
</tr>
</tbody>
</table>

ortho. = orthorhombic, mono. = monoclinic
**WDS-Decrepitate data**

In comparison to the South Platte inclusions, WDS analyses of inclusions from Mt. Pleasant are of lower quality. Only two of the analyses pass the rejection criteria based on charge balance (<20% difference). Even the two which pass have values close to 20%. These data suggest that some anionic components are missing from the analyses. The presence of carbonate minerals in some of the Mt. Pleasant inclusions (Samson, 1990) indicates that a carbonate species may be the missing species. The low concentrations of elements in these analyses (near detection limits) may also have contributed to the large charge imbalances (Table 10), as even small differences in the relative concentrations of cations and anions will be amplified. The two 'acceptable' analyses along with analysis 5 (charge imbalance of 21%) (Table 11) indicate that Na and Cl are the dominant ions present. Calcium is present in subordinate amounts, with minor K and S.

**Table 10. Major element composition and charge balance of Mt. Pleasant decrepitates (Atomic %).**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>host</th>
<th>Na</th>
<th>Ca</th>
<th>K</th>
<th>Cl</th>
<th>S</th>
<th>Σ+</th>
<th>Σ-</th>
<th>diff.</th>
<th>diff%</th>
<th>reject</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYA83-19</td>
<td>1</td>
<td>quartz</td>
<td>0.35</td>
<td>2.10</td>
<td>0.12</td>
<td>2.03</td>
<td>bd</td>
<td>4.67</td>
<td>2.03</td>
<td>2.64</td>
<td>39.40</td>
<td>x</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>2</td>
<td>quartz</td>
<td>0.36</td>
<td>2.15</td>
<td>0.13</td>
<td>2.09</td>
<td>0.27</td>
<td>4.79</td>
<td>2.63</td>
<td>2.16</td>
<td>29.11</td>
<td>x</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>3</td>
<td>quartz</td>
<td>0.53</td>
<td>0.69</td>
<td>0.14</td>
<td>bd</td>
<td>bd</td>
<td>2.05</td>
<td>bd</td>
<td>2.05</td>
<td>na</td>
<td>x</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>4</td>
<td>quartz</td>
<td>1.82</td>
<td>0.99</td>
<td>0.46</td>
<td>0.80</td>
<td>0.36</td>
<td>4.26</td>
<td>1.52</td>
<td>2.74</td>
<td>47.40</td>
<td>x</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>5</td>
<td>quartz</td>
<td>8.48</td>
<td>3.42</td>
<td>0.19</td>
<td>9.86</td>
<td>0.12</td>
<td>15.51</td>
<td>10.10</td>
<td>5.41</td>
<td>21.12</td>
<td>x</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>6</td>
<td>quartz</td>
<td>11.25</td>
<td>2.90</td>
<td>0.10</td>
<td>12.02</td>
<td>bd</td>
<td>17.15</td>
<td>12.20</td>
<td>5.13</td>
<td>17.59</td>
<td></td>
</tr>
<tr>
<td>SYA83-19</td>
<td>7</td>
<td>quartz</td>
<td>3.47</td>
<td>bd</td>
<td>bd</td>
<td>2.36</td>
<td>bd</td>
<td>3.47</td>
<td>2.36</td>
<td>1.11</td>
<td>19.04</td>
<td></td>
</tr>
</tbody>
</table>

The atomic ratios for these three analyses are similar (Table 11); Na/Na+Ca+K ranges from 0.70 to 1.00, Ca/Na+Ca+K from 0.20 to 0.28 and K/Na+Ca+K ranges from 0.01 to 0.02. Chloride is the dominant anion with Cl/Cl+S ratios ranging from 0.50 to 0.89.

**Table 11. Atomic ratios in 'acceptable' Mt. Pleasant decrepitate analyses**

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>Na/Na+Ca+K</th>
<th>K/Na+Ca+K</th>
<th>Ca/Na+Ca+K</th>
<th>Cl/Cl+S</th>
</tr>
</thead>
<tbody>
<tr>
<td>SYA83-19</td>
<td>5</td>
<td>0.70</td>
<td>0.02</td>
<td>0.28</td>
<td>0.89</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>6</td>
<td>0.79</td>
<td>0.01</td>
<td>0.20</td>
<td>0.50</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>7</td>
<td>1.00</td>
<td>-</td>
<td>-</td>
<td>0.69</td>
</tr>
</tbody>
</table>

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Precipitates

EDS analyses (Table 12) of the fluid residue precipitated onto inclusion walls were again subjected to charge balance calculations as described above. Two of the four analyses are deemed acceptable. Of these two, Na and Cl are the dominant ions present with K, Fe and S present in subordinate amounts.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>Na</th>
<th>Ca</th>
<th>K</th>
<th>Mg</th>
<th>Fe</th>
<th>Cl</th>
<th>S</th>
<th>Σ+</th>
<th>Σ-</th>
<th>% diff</th>
<th>reject</th>
</tr>
</thead>
<tbody>
<tr>
<td>B10-174</td>
<td>1</td>
<td>35.06</td>
<td>bd</td>
<td>5.72</td>
<td>bd</td>
<td>bd</td>
<td>10.99</td>
<td>bd</td>
<td>40.78</td>
<td>10.99</td>
<td>57.54</td>
<td>x</td>
</tr>
<tr>
<td>B10-238</td>
<td>16</td>
<td>28.88</td>
<td>bd</td>
<td>11.65</td>
<td>bd</td>
<td>2.61</td>
<td>52.94</td>
<td>bd</td>
<td>45.75</td>
<td>52.94</td>
<td>-7.29</td>
<td>x</td>
</tr>
<tr>
<td>SYA83-40</td>
<td>21</td>
<td>0.00</td>
<td>54.34</td>
<td>0.00</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
<td>bd</td>
<td>108.68</td>
<td>0.00</td>
<td>100.00</td>
<td>x</td>
</tr>
<tr>
<td>SYA83-40</td>
<td>22</td>
<td>37.66</td>
<td>bd</td>
<td>3.89</td>
<td>bd</td>
<td>bd</td>
<td>50.16</td>
<td>bd</td>
<td>41.55</td>
<td>54.88</td>
<td>-13.82</td>
<td></td>
</tr>
</tbody>
</table>

The Na/Na+Ca+K ratio for the two acceptable analyses are 0.71 and 0.91 (Table 13), values which are in the same range as those from the decrepitates. However, these analyses have significantly higher proportions of K, and Ca was not detected. This may be because the decrepitates and precipitates were analyzed in different samples and that they represent different generations of fluid.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>Na/Na+Ca+K</th>
<th>K/Na+Ca+K</th>
<th>Ca+K</th>
<th>Ca/Na+Ca+K</th>
<th>Cl/Cl+S</th>
</tr>
</thead>
<tbody>
<tr>
<td>B10-238</td>
<td>16</td>
<td>0.71</td>
<td>0.29</td>
<td>-</td>
<td>1</td>
<td></td>
</tr>
<tr>
<td>SYA83-40</td>
<td>22</td>
<td>0.91</td>
<td>0.09</td>
<td>-</td>
<td>0.96</td>
<td></td>
</tr>
</tbody>
</table>

ESD analyses of Minerals within Inclusion Cavities

Table 14 shows the compositions, as atomic percentages and atomic ratios, of the analyzed solids. As described in the results section, the analyses have been placed into eight group based upon the dominant elements present. As can be seen from Table 14, a number of the analyses show some similarity to the precipitate and decrepitate analyses in that they have significant proportions of Na, Ca, K and Cl. Figure 40 compares the relative proportions of Na, Ca and K in analyses which contain these elements to the
decrepitates and precipitates. A number of the solid analyses have very similar proportions of these elements to those in the decrepitates and precipitates in particular analyses 10, 14, 19, 20a and 20b.

Fig. 40 Relative atomic proportions of Na, Ca and K in the fluid residues from Mt. Pleasant and South Platte fluid inclusions.

Analyses 2 and 7 have relatively more K and Ca, respectively than the decrepitates and precipitates and analysis 9 is extremely Ca-enriched. Given that there are no known mixed Na-K or Na-K-Ca chloride minerals, those analyses that contain Cl and mixtures of Na, K and Ca have, at least in part, a contribution from precipitates on the mineral surface (cf. Anthony et al., 1984). This is supported by the reasonably good positive correlation between Na+K+Ca and Cl in many of these analyses (Fig. 41).
<table>
<thead>
<tr>
<th>Sample</th>
<th>Anal. #</th>
<th>Na</th>
<th>Ca</th>
<th>K</th>
<th>Al</th>
<th>Mg</th>
<th>Fe</th>
<th>Cl</th>
<th>S</th>
<th>Cr</th>
<th>Mn</th>
<th>W</th>
<th>K/Al</th>
<th>Mg+Fe/Al</th>
<th>Na/Cl</th>
<th>Possible Identification</th>
</tr>
</thead>
<tbody>
<tr>
<td>B10-174</td>
<td>7</td>
<td>27.25</td>
<td>17.02</td>
<td>5.29</td>
<td>2.87</td>
<td>1.11</td>
<td>0.58</td>
<td>43.87</td>
<td>2.01</td>
<td>0.00</td>
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<td>3.37</td>
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<td>0.00</td>
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<td>0.05</td>
<td>n/a</td>
<td>K-felspar</td>
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<td>0.00</td>
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<td>0.64</td>
<td>3.00</td>
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<td>SYA83-40</td>
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<td>3.15</td>
<td>0.91</td>
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</table>
Fig. 41 Na+K+2Ca versus Cl concentrations in WDS analyses of solids within inclusion cavities.

**Type I Solids: Na, Ca and Cl**

Type I solids are represented by analyses 7 and 9 and are both dominated by Na, Ca and Cl. However, as can be seen from Figure 40 the relative proportions of Na and Ca are quite different in the two analyses.

As noted above, it is possible that analysis 7 represents a precipitate rather than a daughter mineral, a suggestion that is supported by the spheroidal shape of the solid. However, the charge balance between Na+Ca+K and Cl shows a significant cation excess which may either reflect a poor analysis or that a substrate is present which contains alkali or alkaline earth elements. This is almost certainly the case for analysis 9 which may represent a Na-Cl-rich precipitate coating a Ca-rich phase, most likely either calcite or a calcium silicate. This is supported by the reasonably good charge balance between Na and Cl (Fig. 42). Calcite is more likely as it has been identified in some Mt. Pleasant inclusions (Samson, 1990).
Type II Solids: Na, Cl

The cubic shape of type II solids makes it likely that they are either halite or sylvite. As Na and Cl are the only elements detected in analysis 20a this solid is almost certainly halite. Analysis 14 is dominated by Na and Cl but also contains K and Mg. The presence of the latter probably reflect the presence of a coating on a halite crystal. Such a coating may of course also contain Na and Cl.

Type III Solid: K, Cl

Potassium and Cl are the main elements present in analysis 13, which is a cubic solid, making sylvite a likely candidate. Minor concentrations (~2 wt.%) of Cr and Ca are also present. As fluids in granitic environments are not known to contain even trace concentrations of Cr (I. Samson, pers. comm., 1997) it is almost certain that the 2.2 wt. % Cr is meaningless and represents a baseline value in the EDS spectrum.

Type IV Solid: Fe, Cl

Analysis 11, of a tabular solid, has high concentrations of Fe and Cl. Minor amounts of K, Al and Cr are also present. The dominance of Fe and Cl in the analysis indicates an iron chloride.
Type V: K, Al, S

Analysis 4 stands out from the rest of the analyses as S is the dominant anion at 69.8 atomic %. Potassium and Al are also present in lower concentrations. The major concentration of sulphur tends to imply the presence of either a sulphide or sulphate, with alunite (K$_2$Al$_8$(SO$_4$)$_4$(OH)$_{12}$) as the most likely candidate.

Type VI Solid: Ca, W, Fe, S

Analysis 15 is characterized by high concentrations of Ca, W and Fe, with lower concentrations of S and Cl. Calcium dominates this analysis at over 60 atomic %. The presence of Ca, W, Fe and Mn in the analysis may indicate that the solid is scheelite (CaWO$_4$) or wolframite ((Fe,Mn)WO$_4$), the only two common hydrothermal tungsten minerals. The Ca/W ratio of 5.51 is much greater than that of scheelite (CaWO$_4$). With an Mn+Fe/W ratio of 0.91 the solid is probably wolframite ((Fe,Mn)WO$_4$). The Fe/Mn ratio of 6.82 indicates that the wolframite is Fe-rich and is therefore probably ferberite. This agrees with the results of mineral cataloging by Parrish (1977), in which all wolframite at Mt. Pleasant is Fe-rich (ferberite) with Fe/Mn = ~10. The very high Ca concentration and near 1:1 ratio of Mn+Fe/W, may imply that Ca is from another phase, such as CaCO$_3$.

Type VII: K, Al, Mg, Fe, ±Na, Cl

The type VII solids are distinguished by their very high Al contents. As discussed previously, the Na, K and Cl in analyses 2 and 10 probably represent a precipitate on the mineral surface. In both analyses the Na and Cl concentration closely match, which implies that the K, in addition to the Al and Mg, represents analysis of the substrate. The relative proportions of K, Al and Mg suggest that these are biotite crystals. Analysis 6b does not have a precipitate component and comprises Al, K and Fe and is also likely to be biotite. The presence of biotite is not unexpected as this is a common mineral at Mt. Pleasant.

In analysis 17, of a cubic solid, K and Al are the dominant elements present. The only other elements indicated are Ca and Mg, in very low concentrations relative to K and Al. The dominance of K and Al and the K/Al ratio of 0.92 suggest that this solid is a
potassium feldspar (KAlSi$_3$O$_8$), which has an ideal K/Al ratio of 1.00. As with biotite potassium feldspar is a common mineral at Mt. Pleasant.

**Type VIII Solids: Na, Cl, Fe, Al, K**

Analyses 19 and 20b are similar in that they are dominated by large concentrations of Na and Cl with moderate to significant Fe, Al and K. The Na and Cl almost certainly represent a precipitate. The remaining elements indicate that biotite is the substrate. Micas such as biotite and celadonite contain the elements indicated in the analyses. The tabular solids in analyses 19 and 20b have K/Al ratios of about 0.6 and Fe/Al ratio of about 3.00. These ratios are close to those of biotite (KFe$_3$AlSi$_3$O$_{10}$(OH,F)$_2$) at 1.00 and 3.00. This may imply that the solid analyzed in analysis 20b is again biotite. Analysis 19 is similar to that of 20b with the addition of Mg. The analysis has a K/Al ratio of 0.64 and a Mg+Fe/Al ratio of 3.00. The values of these ratios are very close to those of an ideal biotite (K(Mg, Fe)$_3$(AlSi$_3$)O$_{10}$(OH,F)$_2$), which has a K/Al ratio of 1.00 and Mg+Fe/Al of 3.00. These ratios indicate that the solid analyzed in analysis 19 may indeed be biotite.

**Implications for Fluid Chemistry**

The Raman spectra collected from frozen Mt. Pleasant inclusions have peaks at about 3405, 3422, 3438 and 3538 cm$^{-1}$ and indicate the presence of hydrohalite and that Na$^+$ and Cl$^-$ are the major ions present in the fluid portion of the inclusions analyzed. WDS analyses of decrepitation products of Mt. Pleasant fluid inclusions echo this result, with Na and Cl again being shown to be the dominant ions present in the decrepitates and precipitates. Minor amounts of Ca, K and S are also seen in the decrepitate and precipitate analyses. Potassium would not be detected by Raman spectroscopy as it does not form a hydrate and sylvite does not give a first order Raman spectrum. The lack of evidence for Ca from the Raman data is consistent with the precipitate data but not with the decrepitate data. The two Raman spectra obtained from the sample from which the decrepitate data was acquired (SYA83-19; Table 5) are very poor and it is therefore possible that the antarcticite peaks were present but unresolvable. Alternatively, because the decrepitate method is non-inclusion specific, the two sets of data may represent different generations of inclusions. WDS analyses indicate that a fluid with Na$>>$Ca$>K$ and Cl$>>$S is present in the LVS inclusions analyzed from Mt. Pleasant. This data
supports the use of the NaCl-H2O system as a model for microthermometric analyses of high salinity LVS inclusions from Mt. Pleasant (Samson, 1990). Samson (1990) interpreted low salinity LV inclusions (< 10 equiv. wt %) using the H2O-NaCl-CaCl2 system. In the current study spectra obtained from inclusions of this type (SYA83-19 inclusions 2 to 6) have, at best, very weak peaks for hydrohalite, with no clear indication of antarcticite. However, the decrepitate data does indicate the presence of Ca. This suggests that Samson (1990) was probably justified in using this model system and that LV inclusions with the size and salinity characteristics of those analyzed are at the limits of the capabilities of the low-temperature Raman method.

**Wawa**

Low-temperature Raman spectra acquired from inclusions IS90-53b IS2-1 and IS90-53b IS2-2 (Figures 28 and 29, respectively) are similar. The spectra have weak, low intensity ice peaks centred at about 3074 to 3087 cm⁻¹. A very weak peak at 3422 cm⁻¹ indicates the presence of hydrohalite, and thus Na⁺ and Cl⁻ in the fluid. Although the spectra are of poor quality, the data is consistent with the decision by Samson et al. (1997) to interpret these inclusions in the H2O-NaCl system.

**Gallinas Mountains**

The spectra collected from the Gallinas Mountains inclusions (Fig. 30 and 31) have lines at 3404, 3422 and 3538 cm⁻¹ from hydrohalite (NaCl·2H2O), thus implying the presence of at least Na and Cl in the fluid of the two inclusions analyzed. This result compares well with SEM/EDS analyses of the decrepitate products from Gallinas Mountains inclusions, which indicate that NaCl is the main constituent of the decrepitates analyzed (Samson et al., 1997; Williams-Jones et al., 1997). The ability to acquire spectra from the inclusions in these samples is important, as it shows that Raman lines from hydrates within inclusions can be detected despite being hosted by fluorite, which has fluorescence emission peaks in the OH-stretching region.
Low-Temperature Raman Spectroscopic Investigation of Fluid Inclusions: Capabilities and Limitations

Inclusion Salinity

Most of the inclusions analyzed by the low-temperature Raman method were LVH, halite-bearing inclusions. These LVH inclusions were chosen because the presence of a halite cube at room temperature implies that the fluid portion of the inclusion is saturated with respect to NaCl at room temperature. High salinity inclusions were initially selected for analysis to increase the likelihood that hydrate peaks would be visible in the spectra. In addition, a group of low salinity (< 5 wt. % eq. NaCl+CaCl2) (Table 15) LV (liquid-vapour) inclusions was investigated. The inclusions in Mt. Pleasant sample SYA83-19 are large (tens of μm in length) LV inclusions hosted by a large, euhedral crystal of vug filling quartz. Spectra were collected from five large, shallow inclusions after quickly freezing to -185 °C, followed by warming to between -28 to -55°C, followed by quickly refreezing to -185 °C. Spectra collected from inclusions SYA83-19-6 and SYA83-19-2 from this group are the only two to show any signs of hydrate peaks and these are very weak in intensity.

<table>
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<th>Sample</th>
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</thead>
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<td>-2.65</td>
<td>4.75</td>
</tr>
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<td>6</td>
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<td>4.34</td>
</tr>
<tr>
<td>SYA83-19</td>
<td>7</td>
<td>-1.8</td>
<td>3.34</td>
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</table>

Very weak, hydrohalite bands are seen at 3422 cm⁻¹ in the spectra collected from inclusion SYA83-19-6 (Fig. 24b and c). Slightly more obvious, but still very weak hydrohalite lines at 3405 and 3425 and 3537 cm⁻¹, are present in a spectrum from inclusion SYA83-19-2 (Fig. 25a). The low intensity of these peaks indicates that the salinity (< 5 wt. % eq. NaCl+CaCl2) of these inclusions are nearing the lower detection limits of the freeze-thaw, low-temperature Raman method, given the instrumentation and acquisition parameters used.
Dubessy et al., (1982) report a 'good' spectrum from a solution with as little as 6 wt. % NaCl. The spectrum obtained by Dubessy et al. was acquired from a large hydrate crystal formed by cyclical and slow freezing of the inclusion, whereas the spectra presented in this study were collected from fine-grained aggregates of ice and hydrate produced upon warming a quickly frozen inclusion.

**Inclusion size**

The lower detection limits of a particular species is controlled by the species itself, the background from the host material, the geometry of the inclusion, spectral interference from other species and the ability of the species to withstand the intense irradiance required (Rosasco, 1975). The theoretically predicted minimum inclusion size that can be analyzed as determined by diffraction limitations is about 0.7 μm (Rosasco, 1980).

Inclusions analyzed in this study range in diameter from 5 to about 300 μm, with some solids as small as a few μm in length. The smallest inclusion chosen for low-temperature Raman spectroscopic investigation was inclusion B14-136A-1 which measures 2.5 × 2.5 μm (Appendix II, Fig. 1 inset). Spectra were collected after quickly freezing the inclusion to -185 °C, warming to -46°C, followed by refreezing to -185 °C, warming again to -32 °C and lastly refreezing to -185 °C (Appendix II, Figures 1 and 2). The spectra have definite peaks at about 3403 and 3421 cm⁻¹ from hydrohalite. It is therefore possible to obtain hydrate spectra from extremely small inclusions. Unfortunately, the salinity of this inclusion is not known. A proper analysis of the detection limits of this method requires a more comprehensive study of inclusions with variable salinities and sizes, as both parameters play a role in determining whether or not hydrate spectra can be obtained.

**Comparison of Raman and WDS/EDS Methods**

WDS and EDS analyses of the decrepitate products from South Platte and Mt. Pleasant fluid inclusions show that Na⁺ and Cl⁻ are the main elements present with lesser amounts of Ca and K (Table 16). In the case of the South Platte inclusions, Ca²⁺ is generally more abundant than K⁺. The presence of large concentrations of Na⁺, Ca²⁺ and Cl⁻ in the fluid portion of South Platte inclusions is also indicated from low-temperature Raman spectra. The low temperature spectra show distinct, moderate-intensity Raman
lines from hydrohalite (NaCl•2H₂O) along with less intense, composite peaks which have been shown to be attributable to the closely spaced lines of hydrohalite (NaCl•2H₂O) and antarcticite (CaCl₂•6H₂O). In contrast, spectra from Mt. Pleasant inclusions do not show lines from antarcticite, despite the indication of at least minor concentrations of Ca from some WDS analyses.

<table>
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<tr>
<th>Method</th>
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<td>Low-T Raman</td>
<td>low-temperature hydrates in fluid inclusions</td>
<td>Na, Ca, Cl</td>
<td>?</td>
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<td>K</td>
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<td>Low-T Raman</td>
<td>low-temperature hydrates in fluid inclusions</td>
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<tr>
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<td>Na, Cl</td>
<td>K</td>
</tr>
<tr>
<td>EDS</td>
<td>evaporation residue coating solids in cavities</td>
<td>Na, Cl</td>
<td>Ca</td>
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</table>

Both techniques used have advantages over one another. Although WDS analysis has the capability of detecting elements that do not form hydrates (and therefore cannot be detected using LRS) and has lower detection limits, it is very difficult to analyze specific inclusions with this method which, in addition, is destructive. LRS has the advantage that carefully chosen inclusions can be analyzed non-destructive, allowing unambiguous interpretation of the data with respect to the origin of the inclusions and to microthermometric data. In addition, it provides information on the phase behaviour of individual inclusions and potentially on the identity of daughter minerals and gases. It has the disadvantage of not being able to identify K or other elements that do not form hydrates. LRS also has the advantage that sample preparation is much simpler and the results are not susceptible to artifacts related to sample preparation.
Chapter 5: CONCLUSIONS

1. Low-temperature Raman spectra, containing intense and distinct hydrate peaks, have been obtained from fine-grained, frozen inclusions. These spectra provide a representation of the bulk chemistry of the inclusion, which is not the case where spectra are obtained from large, single crystals (e.g. Dubessy et al., 1982).

2. Low-temperature Raman spectra obtained from quickly frozen fluid inclusions have provided some insight into fluid inclusion phase behaviour, in that the spectra demonstrate that hydrates do not form upon initial freezing as is commonly thought.

3. The freeze-thaw method is essential in allowing hydrate formation in quickly frozen inclusions. In inclusions which were initially frozen quickly, hydrate formation did not occur, resulting in Raman spectra that lacked hydrate and, in many cases, hexagonal ice peaks.

4. Ice, hydrohalite and antarcticite have been detected by the low-temperature Raman method in inclusions from South Platte, but only ice and hydrohalite were confirmed in inclusions from Mt. Pleasant, Wawa and Gallinas.

5. Even small, low salinity fluid inclusions have yielded low-temperature Raman spectra with recognizable hydrate peaks, although the peaks present in the spectra of such inclusions are of very low intensity.

6. Results from EDS/WDS generally agree with Raman results but indicate the presence of small concentrations of K in some cases.

7. Raman spectroscopic investigation of daughter minerals in Mt. Pleasant fluid inclusions has indicated the presence of a solid which is most likely tourmaline, although margarite is a possible alternative.

8. EDS analyses of solid phases in Mt. Pleasant inclusions indicate the presence of the minerals halite, sylvite, alunite, biotite, wolframite/scheelite and potassium-feldspar.

9. Raman spectroscopic investigation of daughter minerals in South Platte inclusions has indicated the presence of anhydrite.

10. Comparison with synthetic mixtures in the NaCl-CaCl₂-H₂O system allows for semi-quantitative estimates of the relative abundance of NaCl and CaCl₂.
11. These data confirm that the phase behaviour of fluid inclusions in the deposits studied can be modeled using the H_2O-NaCl and H_2O-NaCl-CaCl_2 systems.

**Recommendations for Further Study**

The results of the current study have shown that Raman spectra of salt hydrates formed at low-temperatures can be obtained from naturally occurring fluid inclusion which have been quickly frozen to liquid nitrogen temperatures (about -185 °C), followed by warming (to between -67 to -20 °C) and quickly refreezing to liquid nitrogen temperatures. This freezing technique prohibits the growth of large crystals of ice and hydrate, allowing only for a fine-grained ice-hydrate mixture.

In order to more accurately characterize inclusion composition with the low-temperature Raman spectroscopic method, further investigation of more complex synthetic solutions is required. This should include ternary and more complex systems such as: H_2O-NaCl-CaCl_2-FeCl_3, H_2O-NaCl-CaCl_2-MgCl_2 and H_2O-NaCl-CaCl_2-FeCl_3-MgCl_2, among others. Investigation of the lower salinity detection limits for single, binary and complex solutions would also be an asset to further development of the method. Quantification of, for example, Na/Ca ratios using relative peak intensities and synthetic solutions of appropriate compositions, would extend the usefulness of the method.

Further application of Raman spectroscopy to the analysis of fluid inclusions, particularly their daughter minerals, would be greatly enhanced by the development of a comprehensive library of mineral, including hydrate, spectra.

The nondestructive nature of Raman spectroscopic studies of fluid inclusions allows for subsequent analyses, either destructive or nondestructive. This characteristic of Raman spectroscopy alone is impelling enough to justify further refinement of the technique.
REFERENCES


Winnipeg, 27-29 May, 1996


APPENDIX I

Raman Spectra of Solid Phases within Fluid Inclusions
Fig. A1-1 (a) Raman spectrum of solid (a), an anhedral, high relief solid in inclusion B10-174-1-1 (inset). (b) The spectrum of the host quartz is seen below.

Fig. A1-2 (a) Raman spectrum of solid (a) an anhedral, high relief solid in inclusion B10-174-1-1 (inset).
Fig. A1-3  (a) Raman spectrum of solid (f) in inclusion B10-174-1-1, (b) the spectrum of the host quartz is seen above.

Fig. A1-4  (a) Raman spectrum of solid (d) in inclusion B10-174-1-1 (inset). (b) The host quartz spectrum is seen below.
Fig. A1-5 Raman spectra (a) of solid (b), an elongate, birefringent crystal in inclusion B10-174-2-1 (inset sketch). (b) The host quartz spectrum is shown below.

Fig. A1-6 Raman spectra (a) of solid (b), an elongate, birefringent crystal in inclusion B10-174-2-1 (inset image). (b) The host quartz spectrum is also shown below.
Fig. A1-7  Raman spectra of solid (b), a prismatic, birefringent crystal in inclusion B10-174-1-2 (inset sketch). Spectrum (a) (b) and (c) were acquired with ten reads, from various spots on the solid. (d) The host quartz spectrum is shown below.

Fig. A1-8  Raman spectra (a) of solid(b), an elongate, birefringent crystal in inclusion B10-174-1-9 (inset sketch). (b) The host quartz spectrum is also shown below.
Fig. A1-9 (b) Raman spectrum of the fibrous crystal(s) in inclusion B10-45-1-3. (a) The spectrum of the host quartz is shown above.

Fig. A1-10 (a) Raman spectrum of the fibrous crystal(s) in inclusion B10-45-1-3. (b) The spectrum of the host quartz is also shown.
Fig. A1-11 Raman spectrum (a) of the birefringent lathe-like solid in inclusion B10-45-1-4 (inset). (b) The spectrum of the host replacement quartz is also shown.

Fig. A1-12 Raman spectrum (a) of the birefringent lathe-like solid in inclusion B10-45-1-4 (see inset Fig. A1-11). (b) The spectrum of the host replacement quartz is also shown.
Fig. A1-13 Raman spectrum (a) of solid (b), a birefringent, lathe-like solid in inclusion B10-238-1-1 (inset). (b) The Raman spectrum of the host quartz is shown below.

Fig. A1-14 Raman spectrum of solid (b), a birefringent, lathe-like solid in inclusion B10-238-1-1 (inset) over the wavenumber range 3432 to 3665 cm\(^{-1}\).
Fig. A1-15 Raman spectrum (a) of solid (c), (the bright spot above solid b) in inclusion B10-238-1-1 (inset). (b) The host quartz Raman spectrum is shown below.

Fig. A1-16 Raman spectrum (a) of solid (c) in inclusion B10-238-1-1 (see inset in Fig A1-15). (b) The host quartz Raman spectrum is shown below.
Fig. A1-17  Raman spectrum (a) of solid (d), in inclusion B10-238-1-1 (inset). (b) The Raman spectrum of the host quartz is shown below.

Fig. A1-18  Raman spectrum (a) of solid (d), in inclusion B10-238-1-1 (inset). (b) The Raman spectrum of the host quartz is shown below.
Fig. A1-19  Raman spectrum (a) of solid (a) in inclusion B10-238-1-1 (inset). (b) The Raman spectrum of the host quartz is shown below.

Fig. A1-20  Raman spectra of solid (a) in inclusion B10-238-1-1 (inset). The spectra were acquired using (a) five and (b) ten reads. (c) The Raman spectrum of the host quartz is shown below.
Fig. A1-21  Raman spectrum (a) of solid (d), an elongate, blade-like solid in inclusion B10-45-1-1 (inset). (b) The Raman spectrum of the host replacement quartz is shown above.

Fig. A1-22  Raman spectrum (a) of an elongate, blade-like solid (d) in inclusion B10-45-1-1 (inset). (b) The spectrum of the host quartz is shown below.
Fig. A1-23  Raman spectrum (a) of solid (b) in inclusion B10-45-1-1 (inset). (b) The spectrum of the host replacement quartz is shown above.

Fig. A1-24  Raman spectrum(a) of solid (b) in inclusion B10-45-1-1 (inset). (b) The spectrum of the host quartz is shown below.
Fig. A1-25  Raman spectrum (a) of solid (a) in inclusion B10-238-1-4 (inset). (b) The Raman spectrum of the host quartz is shown below.

Fig. A1-26  Raman spectrum (a) of solid (a) in inclusion B10-238-1-4 (see inset in Fig A1-25). (b) The Raman spectrum of the host quartz is shown below.
Fig. A1-27  Raman spectrum of solid (a) in inclusion B10-238-1-4 (inset) over the wavenumber range 3432 to 3665 cm\(^{-1}\).

Fig. A1-28  Raman spectra (a); of solid (b), an elongate, birefringent crystal in inclusion B10-174(e)-23 (inset 1) and (b) in inclusion B10-174(e)-22 (inset 2). (c) The host quartz spectrum is also shown below.
Fig. A1-29 Raman spectrum (a) of the birefringent lathe-like solid in inclusion B10-45-1-4 (inset). (b) The spectrum of the host replacement quartz is also shown.

Fig. A1-30 Raman spectrum (a) of the birefringent lathe-like solid in inclusion B10-45-1-4 (inset). (b) The spectrum of the host quartz is also shown.
APPENDIX II

Low-temperature Raman Spectra of Fluid Inclusions
Fig. A2-1 Low-temperature Raman spectra of inclusion B14-136A-1 (inset), (a) after freeze-thaw cycle, warming to -46 °C (as in MR9712), followed by warming again to -32 °C ("zoom in" on the wavenumber region in which salt-hydrate lines may appear). (b) The low-temperature (-190 °C) spectrum of the host quartz is also shown.

Fig. A2-2 Low-temperature Raman spectra of inclusion B14-136A-1 (inset) after: (a) freeze-thaw cycle, warming to -46 °C (as in MR9712), followed by warming again to -32 °C. (b) The low-temperature (-190 °C) spectrum of the host quartz is shown below.
Fig. A2-3  Low-temperature Raman spectra of inclusion B14-136A-2 (inset image) after freeze-thaw cycle, warming to -64 °C (a). The inset spectrum (b) is a "zoom in" on the wavenumber region in which any salt-hydrate lines may appear. (c) The low-temperature (-190 °C) spectrum of the host quartz is also shown.

Fig. A2-4  Low-temperature Raman spectra of inclusion B14-136A-2 (inset image) after (a) freeze-thaw cycle, warming to -30 °C. (b) The low-temperature (-190 °C) spectrum of the host quartz is shown below. (c) The inset spectrum is a "zoom in" on the wavenumber region in which any salt-hydrate lines may appear.
Fig. A2-5  Low-temperature Raman spectra of inclusion SYA83-19-1 (inset) after: (a) freeze-thaw cycle, warming to -30 °C and (b) host quartz, low temperature spectrum.

Fig. A2-6  Low-temperature Raman spectra of inclusion SYA83-19-5 (inset) after (a) freeze-thaw, melting to a few ice crystals and refreezing quickly and (b) after freeze-thaw cycle warming to -53 °C.
Fig. A2-7  Low-temperature Raman spectra of inclusion SYA83-19-6 (inset) after: (a) quickly freezing, (b) freeze-thaw cycle warming to -55 °C followed by warming again to (c) -30 °C. (d) The low-temperature (-190 °C) spectrum of the host quartz is also shown.

Fig. A2-8  Low-temperature Raman spectrum of inclusion B10-174-6-1 (inset drawing) after freeze-thaw cycle, warming to -32 °C (a) (this inclusion is the deepest in below the surface of the wafer of group 6). The low-temperature (-190 °C) spectrum of the host quartz is also shown (b).
Fig. A2-9  Low-temperature Raman spectrum of inclusion B10-174-6-3 (inset drawing) after freeze-thaw cycle, warming to -32 °C (a). The low-temperature (-190 °C) spectrum of the host quartz is also shown (b).

Fig. A2-10  Low-temperature Raman spectrum of inclusions B10-174-6-5 (inset drawing) after (a) freeze-thaw cycle, warming to -32 °C. (b) The low-temperature (-190 °C) spectrum of the host quartz is also shown.
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