The inevitable use of Raman spectroscopy to identify the major salt components in single fluid inclusions

Baumgartner, Miriam and Bakker, Ronald J.

Resource Mineralogy, Department of Applied Geosciences and Geophysics, University of Leoben, Peter-Tunner Str.5, Leoben, Austria

INTRODUCTION

The determination of fluid composition is one of the major tasks in fluid inclusions research. Microthermometry is the most common analytical technique and is the only non-destructive method, which can be applied to obtain directly qualitative and quantitative information on the salts dissolved in the fluid. Multi component salt systems show various complex phase assemblages at low temperatures (ice and salt-hydrates). The final melting of ice and salt hydrates can be used to determine the salinity, if the phase can be clearly identified. Nevertheless, various salt hydrates show similar optical properties and they are difficult to distinguish by purely optical means. In addition, optical observations cannot be applied to microcrystalline aggregates of hydrates and ice, which may regularly occur in frozen inclusions. Eutectic and peritectic reactions are additionally used to define the salt systems, as they occur at specific temperatures in dependence of the salt composition. Those temperatures are difficult to monitor accurately and the theoretic temperatures of phase transitions may occur in relatively small temperatures ranges (e.g. $CaCl_2$-H_2O eutectic at -49.8 °C and $CaCl_2$-KCl-H_2O eutectic at 50.5 °C; Borisenko, 1977). The approach presupposes the presence of stable phase assemblages and the availability of reliable data of phase transitions and relationships. Due to metastabilites, precipitation of stable phase assemblages in salt-H_2O fluid inclusions is often inhibited and expected phase transitions do not occur. Therefore, microthermometry cannot be adequately interpreted by optical means only. Raman spectroscopy has to be used to overcome the difficulties in identifying stable and metastable phase assemblages. The presence of brine, ice and salt-hydrates can be verified by specific Raman bands, which occur in the stretching region of water (e.g. Dubessy, 1992, Bakker 2004). In addition, Raman spectroscopy at selected temperatures is the only method which can be used to identify phase changes in inclusions of Raman active materials, e.g. melting of hydrates.

METASTABLITIES

Fluid inclusions containing a NaCl-$CaCl_2$-H_2O mixture (see Fig. 1) freeze to a glassy matrix during cooling to -90 °C. During heating the matrix re-crystallize into a microcrystalline aggregate. Optically the inclusions seem to be completely frozen and in theory the salt-hydrates hydrohalite ($NaCl \cdot 2H_2O$) and antarcticite ($CaCl_2 \cdot 6H_2O$) should be stable with ice below the eutectic point of -49.8 °C.

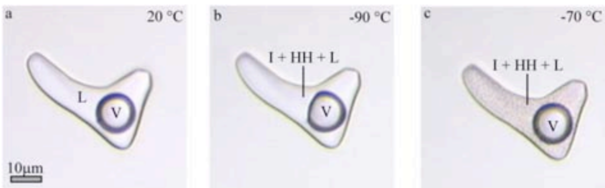

Fig. 1. Freezing of NaCl-$CaCl_2$-H_2O inclusions. V-vapour, L – liquid, I – Ice, HH – hydrohalite

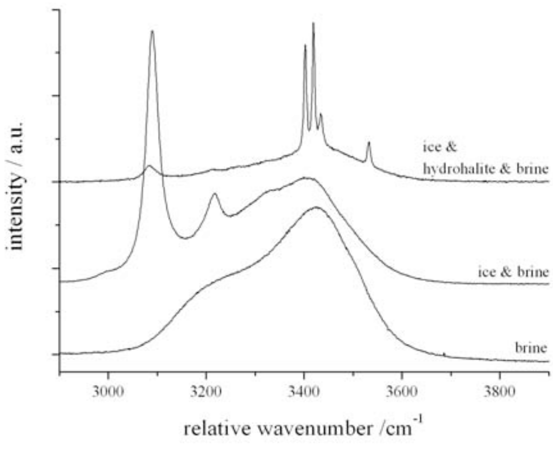

Fig. 2. Raman spectra of ice, hydrohalite, and brine at -190 °C.

Raman spectra (Fig. 2) taken from the inclusion, reveal the presence of ice, hydrohalite and brine at temperatures down to -190 °C. This inclusion contains a metastable phase assemblage at low temperature and the eutectic reaction cannot be observed in this inclusion.

EUTECTIC REACTIONS

The volume fraction of salt-hydrates in inclusions may be very small and nucleation and melting may not be observed accurately. For example, inclusions containing 16 mass% $MgCl_2$ and 5 mass% NaCl freeze to a mixture of fine grained mass. At temperatures below the eutectic of -35 °C (see Fig. 3a) it is not obvious if the inclusion is completely solidificated, respectively single hydrate crystals are difficult to identify. Raman spectroscopy allows to detect already small amounts of the hydrate phase (see Fig. 4) and offers the possibility for an exact estimation of the eutectic point, with measuring the phase assemblage simultaneously during heating the inclusion (see Fig 3b and 3c).

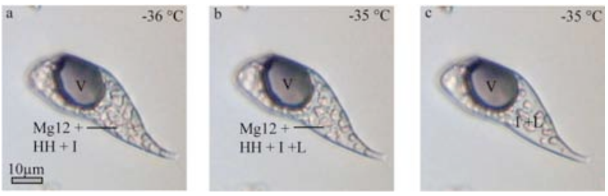

Fig. 3. Eutectic melting of NaCl-$MgCl_2$-H_2O inclusions. V – vapour, L – liquid, I – ice, Mg12 – $MgCl_2$.12H_2O, HH - hydrohalite

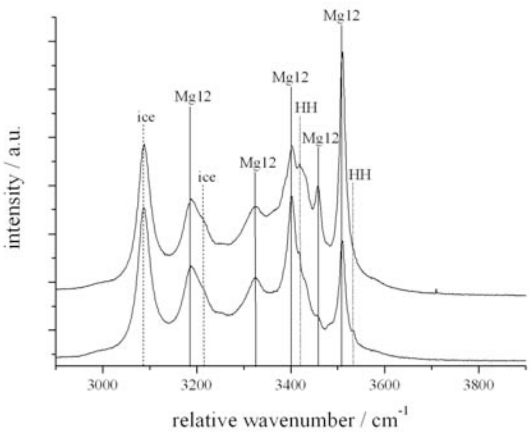

Fig. 4. Raman spectra of ice, $MgCl2 \cdot 12H_2O$ (Mg12) and hydrohalite (HH) at -190°C.

PHASE TRANSITIONS

Not only the change of state, e.g. melting of phases, also solid-solid transitions may occur in fluid inclusions and may be easily overseen by microthermometry. For example, the transition of sinjarite ($CaCl_2 \cdot 2H_2O$) into α-tetrahydrate ($CaCl_2 \cdot 4H_2O$) is only evident by a change in the Raman spectrum of the hydrate phase (Fig. 5 and 6; see Baumgartner and Bakker, 2010).

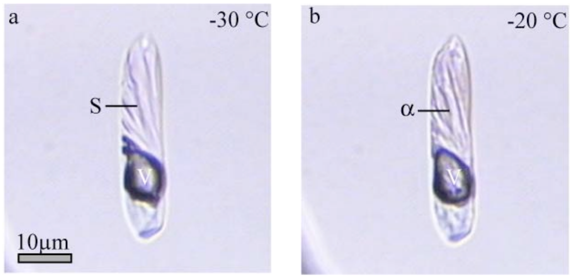

Fig. 5. Inclusion containing sinjarite (S) at -34 °C, which react between -29 to -25 °C into α-tetrahydrate (α).

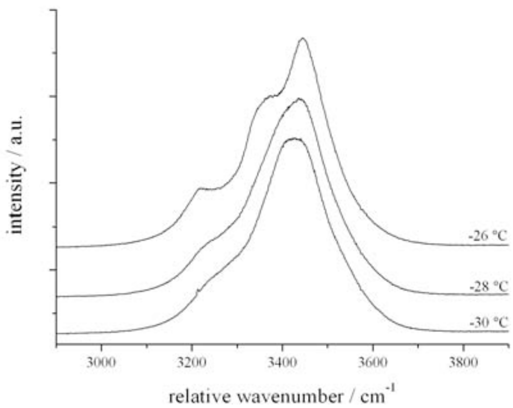

Fig. 6. Raman spectra of the phase transition sinjarite (spectrum at -30 °C) into α-tetrahydrate (spectrum at -28 °C).

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