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RAMAN SPECTRA OF AQUEOUS FLUID INCLUSIONS: EFFECT OF MINERAL BIREFRINGENCE AND METASTABILITY ON SALINITY MEASUREMENT. M.-C. Caumon¹ and A. Tarantola¹, ¹Université de Lorraine, CNRS, CREGU, GeoRessources lab., BP 70239, F-54506 Vandœuvre-lès-Nancy, France.

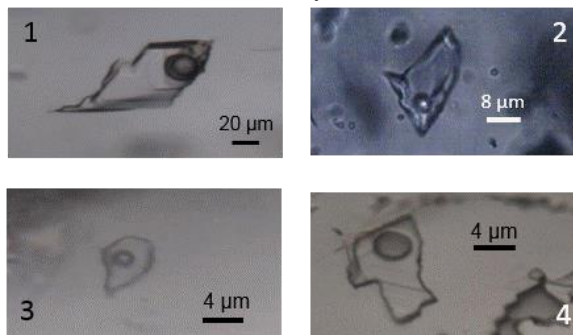
Introduction: Crustal fluids play a major role in ore deposits, basin diagenesis and metamorphic reactions, among others. The knowledge of the chemical composition of individual fluid inclusions is essential for the understanding of past fluid transport and circulations. Microthermometry, by the observation of specific phase transitions as a function of temperature, is the general approach to determine salinity in aqueous fluid inclusions [1]. However in some cases, this method cannot be carried out because of, for instance, difficulties encountered in carrying optical observations, metastability, or if the thermodynamic system is not enough constraint. Besides, some minerals are highly cleavable, particularly carbonates, and consequently fluid inclusions might easily stretch, leak or decrepitate during freezing or heating on the heating-cooling stage, because of the volume expansion of the content with temperature.

In replacement of microthermometry, salinity can be determined by Raman spectroscopy using a method based on the change of the shape of the water stretching vibration band with salinity. This change is due to the decrease of the strength of the hydrogen bonds in water by dissolved anions, often chloride [2,3]. An increase of the chloride concentration results in a decrease of the intensity of the OH stretching vibration band of water around 3200 cm^{-1} . Different methods of treatment of the raw spectrum correlate the deformation of the OH stretching vibration band of water to chlorinity [4-9].

The Raman signal of water is also sensitive to the fluid density and the birefringence of the host crystal. Birefringence is critical in quartz and carbonates, and more generally in all highly birefringent minerals. Depending on the crystallographic orientation of the sample, the value obtained for salinity in quartz samples displayed variations higher than 50 % [5,7-9]. It has been observed that the “true” value is measured when the crystal is at its extinction position [6-9]. However, the optical phenomena behind the effect observed on the Raman spectra are not elucidated. Moreover, only the case of quartz was studied. Consequently, there is no general method at this time to determine salinity from the Raman signal of water in birefringent minerals. Metastability may also affect the OH stretching vibration band of liquid water, the decrease of the fluid density affecting the strength of hydrogen bonds.

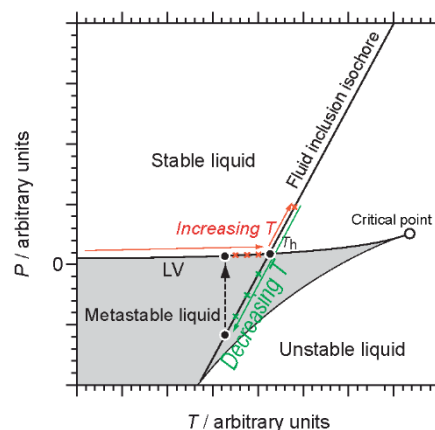
Objectives: The purpose of the present study is to measure the effect of (i) metastability and (ii) mineral birefringence on the Raman spectra of water in aqueous

fluid inclusions, in order to define a protocol to obtain accurate salinity measurement in any minerals, as an alternative to microthermometry.



Some examples of fluid inclusions in 1. Kyanite (Zambia [10]), 2. Calcite [11], 3. Celestite, 4. Siderite [12].

Material and methods: Several minerals (quartz, calcite, siderite, barite, kyanite, celestite, and sphalerite) with various birefringence properties are selected. The Raman spectra of water in fluid inclusions are acquired as a function of the orientation of the optical axis toward laser polarization direction (Ar⁺ laser) using a LabRAM or LabRAM HR microspectrometer (Horiba Jobin-Yvon). The salinity is compared to the one determined by microthermometry.



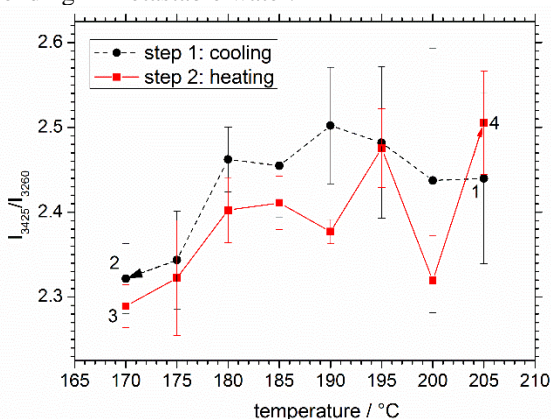
Phase diagram of water in the metastability range.

The effect of metastability on the Raman signal of water is measured during a heating-cooling cycle below homogenization temperature of a fluid inclusion in a quartz sample (Alpes, 2.0 mass% NaCl). The aqueous fluid inclusion is first heated up to T_h (207°C). The Raman spectra of metastable water in the OH stretching vibration region are recorded by step of 5°C decreasing

temperature down to bubble nucleation (165°C). The fluid inclusion is then heating up to T_h recording the spectra of water at equilibrium by step of 5°C. The spectra of metastable and equilibrated water are compared by measuring the intensities ratio between 3260 and 3425 cm^{-1} to determine the variations in hydrogen bonding [9].

Results: Birefringence. By elucidating the roles of the polarization properties of the grating, of the birefringence and optical system of the mineral, and of the polarization of the OH stretching vibrations of liquid water, a method is proposed to ensure reliable measurements of salinity by Raman spectroscopy not only in quartz but in any minerals. The experimental results help to define a protocol for the determination of salinity in aqueous fluid inclusions by Raman spectroscopy in case of birefringence of the host mineral.

Metastability. The Raman spectrum of water shows small differences when liquid water is metastable or at equilibrium with vapor (Fig. below). The intensity ratio is higher in metastable water between 170 and ~190°C, in agreement with a decrease of the strength of hydrogen bonding in metastable water.



Intensity ratio in the Raman spectrum of water as a function of temperature and heating-cooling cycle. (1) Metastable water is cooled down to 170°C. (2) Bubble nucleates at 165°C. (3) Water at equilibrium with vapor heated up to 205°C. $T_h=207^\circ\text{C}$, 2.0 mass% NaCl.

Conclusion: In some cases, microthermometry cannot be used to determine salinity in aqueous fluid inclusions. Raman microspectrometry is a good alternative technique if properly used. In case of birefringence of the host mineral, the section must be properly oriented in relation to the polarization direction of the laser. If the fluid inclusion is metastable, the effect of the physical state of the fluid must be considered in order to avoid overestimation of salinity.

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