Cryogenic Raman Spectroscopy of NaCl-H_2O Synthetic Fluid Inclusions and Deconvolution of Raman spectra with Gauss-Lorentzian Functions

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Knowledge of the salinity of fluid inclusions, including type of salts and amount, is of major importance for the interpretation of formation conditions of rocks. Synthetic fluid inclusions of NaCl brines have been investigated by cryogenic Raman Spectroscopy in combination with low temperature microthermometry from –180°C to 400°C. The fluid inclusions are synthesized with a known composition and density, in thermal shock–fractures in natural Brazilian quartz according to the method of Bodnar and Sterner (1987). The partially fractured quartz cores with a length of 2 cm and a diameter of 4 mm are placed in gold capsules, with a few microliters of NaCl brine of a known composition (varying from 2 up to 24 mass%) and small amounts of silica, to promote silica saturation of the solution and thereby fracture healing. Once loaded, the capsules are placed into cold-seal pressure vessels and taken to experimental conditions. The synthetic NaCl-H_2O inclusions are produced at 600°C and at pressures varying between 1300 and 2300 bar depending on the specific salt concentration. After synthesis, the quartz cores are cut into 1 mm slices and polished. Subsequently, Raman Spectroscopy is used to detect the presence of salt in the solution and the water spectra itself. The dissolved ions cannot be detected by Raman, however the specific shape of the water spectra (3000 to 3600 cm^{-1}) are influenced by them. At low temperatures dissolved salt ions form solid chemical compounds with covalent bonds, which are detectable with Raman Spectroscopy. Therefore spectroscopic measurements were performed at low temperatures (down to –180°C). In the case of a NaCl-solution, the ions form a solid salt-hydrate called hydrohalite ($NaCl \cdot 2H_2O$). Raman spectra of NaCl-brine, glass, hydrohalite and ice are measured at different temperatures. In order to analyse the systematics with temperature changes, a deconvolution with combined Gauss-Lorentzian functions was applied to each spectrum. Because of lacks in physical knowledge of vibrational properties of liquids there are great numbers of free parameters to fit Raman spectra. There is no consistent physical interpretation in literature, which makes a critical review necessary. At low temperatures the peaks of ice, glass and hydrohalite are well defined (relative narrow half-width), whereas at higher temperatures the spectra become more undefined (smeared over a broad wavenumber interval). In addition a shift in main peak positions is also observed. The best criteria for deconvolution of Raman spectra are purely geometrical constraints, which are applied in this study.

Bodnar R.J., Sterner S.M. (1987) Synthetic fluid inclusions: In: Hydrothermal Experimental Techniques (eds. G.C. Ulmer, H.L. Barnes), John Wiley & sons, New York, pp. 423-457