Heavy halogen impact on Raman water bands at high pressure

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Abstract

Halogen complexes (e.g., in saline fluids, brines, or molten salts) are major agents for metal transport in ore-forming processes related to hydrothermal systems (Aiuppa et al., 2009). Samples of such fluids can be found entrapped as inclusions in minerals like quartz (Pankrushina et al., 2020) or olivine (Kawamoto et al., 2013) where they are often analyzed with Raman spectroscopy. The impact of dissolved chlorine on the water stretching bands in Raman spectra is studied since about 40 years and is frequently used to determine salinity in fluid inclusions (Georgiev et al., 1984; Mernagh and Wilde, 1989; Pankrushina et al., 2020; Sun et al., 2010). Less is known about the impact of the heavy halogens bromine and iodine, and about the pressure effect on Raman water bands.

We conducted experiments in a hydrothermal diamond anvil cell to study systematically the shift alteration of Raman water bands at different concentration of dissolved chlorine, bromine, and iodine. We conducted these experiments at ambient temperature and varying pressure from 0 to 1.4 GPa.

The strength of the shift change correlates with the ionic size of the halogens: Chlorine shows the smallest shift, iodine the largest shift, and bromine is in between for comparable concentrations. Increasing pressure diminishes the effect of halogen concentration and causes a shift change in opposing direction relative to the change caused by halogen concentration and ionic size.

In consequence, salinity determination in fluid inclusions with Raman spectroscopy can strongly underestimate the salinity in the inclusion, if the pressure effect is not considered.

References

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