

An in situ Raman spectroscopic investigation of aqueous zinc(II) bromide speciation to 500 deg C and 900 MPa

Kenji Mibe[1]; I-Ming Chou[2]; Alan J. Anderson[3]; Robert A. Mayanovic[4]; William A. Bassett[5]

[1] ERI, Univ. Tokyo; [2] USGS; [3] Earth Sci., St. Francis Xavier Univ.; [4] Physics, Astronomy and Materials Sci., Missouri State Univ.; [5] Earth and Atmospheric Sci., Cornell Univ.

<http://www.eri.u-tokyo.ac.jp/mibe/index.html>

Knowledge of the speciation of metal ion complexes in water under high temperature and high pressure conditions is crucial for our understanding of the physical and chemical properties of crustal fluids. At hydrothermal conditions, it is known that the dissolved metals in aqueous fluids exist mainly as metal halide complexes. We therefore carried out in-situ Raman spectroscopic investigation on three aqueous solutions of various concentration and bromide/zinc ratios. Spectra were collected at eleven different temperature-pressure conditions ranging from ambient to 500 °C and up to 900 MPa. Raman band assignments for aqueous zinc bromide complex species reported in previous studies were used to determine the relative concentrations of ZnBr_4^{2-} , ZnBr_3^- , ZnBr_2 , and ZnBr^+ species at various temperatures and pressures. Our results are in close agreement with X-ray absorption spectroscopic (XAS) data [Mayanovic et al. (2001) Chem. Phys. Lett. 336, 212-218], and confirm that the tetrabromo zinc complex, ZnBr_4^{2-} , is the predominant species up to 500 °C in solutions having high zinc concentration (1 *m*) and high bromide/zinc molar ratio ($[\text{Br}]/[\text{Zn}] = 8$). This result is consistent with the observed predominance of the ZnCl_4^{2-} complex in chloride-rich fluid inclusion brines at high temperatures [Anderson et al. (1998) Can. Mineral. 36, 511-524]. In agreement with previous Raman spectroscopic experiments [Yang et al. (1988) J. Sol. Chem 17, 751-762], our measurements also indicate that species having fewer halide ligands and charge are favored in dilute solutions and in solutions with low bromine/zinc ratios ($[\text{Br}]/[\text{Zn}]$ smaller than 2.5). This study shows how Raman spectroscopy in combination with XAS analyses can provide a more complete depiction of the speciation and structure of transition-metal complexes in fluids at elevated temperatures and pressures. Such data are relevant to the study of reaction kinetics in fluid-rock interaction and to an understanding of the transport and deposition of ore metals.