

Speciation and transport of transition metals in hydrothermal fluids: controls of temperature, pressure and salinity

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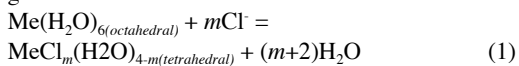
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Speciation of aqueous metal complexes is one of the fundamental controls of metal transport and mineral solubility in natural and industrial hydrothermal systems. In the past decade, we have used *in situ* X-Ray Absorption Spectroscopy (XAS) to investigate the speciation of aqueous chloride complexes of the first-row divalent transition metals (e.g. Mn(II), Fe(II), Co(II), Ni(II), Zn(II)). These studies complement the available speciation and solubility data by other experimental methods (e.g., solubility, UV-Vis, potentiometric). The EXAFS (Extended X-ray Absorption Fine Structure) data have been used to determine structural information of the predominant species, with their stability constants being regressed using the XANES (X-ray Absorption Near-edge Spectra) data.

In general, the structure of metal chloride complexes changes from octahedral to tetrahedral with increasing temperature and/or halide concentration, accompanied with dehydration and increased number of chloride ligands, with a general reaction of



where Me denotes metals, *m* refers the number of ligands.

In contrast, our recent XAS experimental studies of the pressure dependence of Ni(II) and Zn(II) chloride complexes reveal that pressure has a reverse impact on this octahedral-tetrahedral transition, i.e., increasing pressure at a given temperature and salinity drives the above reaction (1) towards the formation of octahedral complexes. The fundamental control of the octahedral-tetrahedral transition can be explained by the change of configurational enthalpy and/or change of fluid properties in particular dielectric constants. This transition of metal chloride complexes has an important impact on the metal transport and solubility of relevant minerals in hydrothermal systems.