A synchrotron XAS study of speciation and thermodynamic properties for aqueous cobalt chloride complexes at 600 bar and 35-500°C

W. LIU[1], S. BORG[1,3], D. TESTEMALE[4,5], B. ETSCHMANN[2,], J-L HAZEMANN[4,5] AND JOËL BRUGGER[2]

[1]CSIRO Earth Science and Resource Engineering, Australia (*correspondence: weihua.liu@csiro.au)
[2]South Australian Museum and The University of Adelaide, Australia.
[3]CODES, The University of Tasmania, Australia
[4]Institut Néel, Département MCMF, France.
[5]ESRF, Polygone Scientifique, 6 rue Jules Horowitz, 38043 Grenoble, France

Aqueous Co (II) chloride complexes play a crucial role in cobalt transport and deposition in ore-forming hydrothermal systems, ore processing plants, and in corrosion of special Co-bearing alloys. Numerical modelling of reactive transport of cobalt in hydrothermal fluids relies on the availability of thermodynamic properties for Co complexes under wide range of T, P and salinity.

We used synchrotron X-ray absorption spectroscopy techniques to determine the speciation of cobalt (II) in 0-5 m chloride solutions at 35-440°C and 600 bar. The qualitative analysis of XANES spectra shows that octahedral species predominate in the solutions at 35°C, while tetrahedral species become increasingly important with increasing temperature, with the tetrahedral $CoCl_4^{2-}$ complex predominating at high chloride concentrations and high temperatures. *Ab initio* XANES calculations confirmed this structural evolution, and the EXAFS analysis reveals the structure parameter for these models. Finally, the XANES spectra have been used to derive the thermodynamic properties of the $CoCl_4^{2-}$ complex, which enable the thermodynamic modelling of cobalt transport in hydrothermal fluids. Solubility calculations show that tetrahedral $CoCl_4^{2-}$ is responsible for transport of cobalt in hydrothermal solutions with moderate Cl concentration (~2 m NaCl) at and above 250°C, and decreasing temperature and dilution can cause deposition of cobalt from hydrothermal fluids.

Application of laser ablation-ICP-MS in environmental fate and transport studies

X.G. LIU[1] AND Q.H. HU[2]*

[1]School of Environmental Studies, China University of Geosciences, Wuhan, 430074, P.R. China (xgliu@cug.edu.cn)
[2]Department of Earth and Environmental Science, The University of Texas at Arlington, Arlington, TX 76010, USA (*correspondence: maxhu@uta.edu)

In studies supporting environmental remediation, nuclear waste disposal, or the decontamination of radionuclides accidentally or deliberately dispersed in an urban environment, it may be necessary to determine the micro-scale contaminant distribution within solid samples, as a prerequisite to an understanding of the processes controlling contaminant transport. This paper discusses the utility of using a micro-scale sensitive analytical approach, laser ablation coupled with inductively-coupled plasma-mass spectrometry (ICP-MS), for profiling contaminant concentration directly on solids. The approach is discussed in the context of three cases or applications: (1) 3-D imaging of the uranium distribution in sediment grains from the Hanford site; (2) fracture-matrix interaction in unsaturated fractured rock in a potential high-level nuclear waste repository; and (3) cesium deposition and migration in concrete after a mock detonation of a radiological dispersal device. It is shown that the application of laser ablation-ICP-MS can help investigators understand and quantify interacting unsaturated transport processes (imbibition, diffusion, and sorption), as well as factors (water saturation, sample size, and pore connectivity) affecting contaminant transport in unsaturated geological media.