An XAS study of lead speciation in chloride solutions under hydrothermal conditions

ICHOLAS RAE[1]*, JOËL BRUGGER[2], BARBARA ETSCHMANN[2], WEIHUA IU[3] AND MEI YUAN[1]

[1]Australian Synchrotron, Clayton Vic, Australia
[2]Monash University Department of Earth Sciences, Australia
[3]CSIRO Exploration and Mining Clayton VIC, Australia

We measured the speciation of Pb(II) in chloride solutions (0.05-5 m NaCl, 0-1 m HCl, 0-10m LiCl) under hydrothermal conditions (600 bar, 0-500˚C) using *in-situ* XANES and EXAFS spectroscopy. The measurements were conducted at the Australian Synchrotron using the hydrothermal spectroscopic cell described by [1]. We use this data to map Pb(II) speciation as a function of temperature, pressure and solution composition, and test the key assumptions that underpin the predictions of recent modelling studies for mass transfer of metals in the crust (Lukanin *et al* 2013; Zhong *et al* 2015) .[2] [3]. *et al*This is the first *in-situ* XAS study of the nature and stability of Pb(II) chloride complexes under hydrothermal conditions. The experimental data shows that Pb forms mixed ligand complexes such as $Pb(H_2O)Cl_2^-$, with decreasing bond lengths with increasing temperature.that *Ab initio* molecular dynamic simulations were conducted to help interpret the experimental EXAFS data. The bond distance and the number of chloride ligands obtained from the MD simulations are broadly consistent with the experimental results. MD shows that the Pb(II) complexes share a predominantly trigonal pyramidal geometry with a stereochemically active lone electron pair. One specific question is whether or not $PbCl_4^{2-}$ exists in saline solutions, analogous to the highly stable $ZnCl_4^{2-}$ complex [3]; $PbCl_4^{2-}$ has only been hinted at experimentally [4]*et al*. Our data shows no evidence for this species. In Nature, Pb is associated closely with Zn in hydrothermal ore deposits, and understanding the factors that control the Pb/Zn ratio is a key question for mineral explorers. Our recent experimental and MD study of Zn(II) in chloride solutions over a wide range in P,T and solution composition (Mei *et al*, 2015) shows that ZnCl42- is stable up to high pressure and temperature in moderately saline solutions (1 m Cltot) ; The difference in stability of high order chloride complexes may explain the fractionation among Pb and Zn in chloride brines [3].

[1] Tian, Y., Etschmann, B., Testemale, D., Ngothai, Y. and Brugger, J., (2014) *Geochim. Cosmochim. Acta* **129C**, 77-95. [2] Lukanin, Ryzhenko, Kurovskaya. (2013) *Geochem. International*, **51**, 802-830 [3] Zhong, Brugger, Chen and Li, (2015) *Chemical Geology*, **395**, 154–164 [4] Powell, Brown, Byrne, Gajda, Hefter, Leuz, Sjöberg and Wanner. (2009) *Pure Appl. Chem.*, **81**, 2425-2476