



	Experiment title: X-ray Absorption spectroscopy study of ferrous chloride complexes in hydrothermal solutions.	Experiment number: EC56
Beamline:	Date of experiment: from: 03/05/2006 to: 09/05/2006	Date of report: 01/06/2006
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Report:

Iron-chloride complexes play a major role in the transport and deposition of Fe-bearing minerals in both natural (e.g., ore deposits) and engineered environments. Despite this the nature and thermodynamic properties of the aqueous Fe(II) complexes in hydrothermal hypersaline brines are poorly understood. The purpose of this experiment is thus to provide the first *in situ* speciation and thermodynamic data for such complexes in elevated conditions of temperature and pressure. The idea is to complete the picture drawn from previous results (see ref. [1] and experimental report HS2628), by investigating a larger range of conditions ($T < 500^{\circ}\text{C}$, $P < 500$ bar, chloride concentration $< 12\text{M}$).

The experimental conditions investigated were the following: 50mM Fe solutions with 0.92M, 2M, 3M, 4M, 5M, and 12M total Cl concentration, at 500 bar. For each concentration, temperatures ranging from ambient up to 500°C were applied. At each temperature, at least 3 spectra were collected (either XANES or EXAFS).

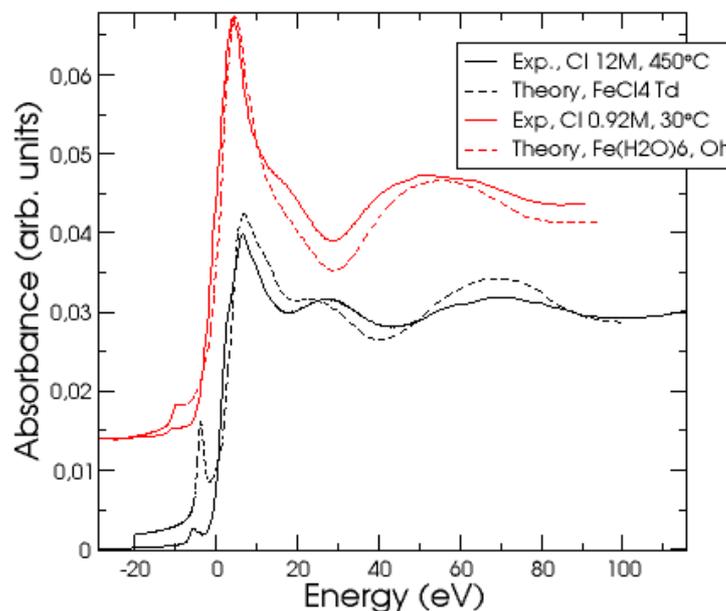
Our analysis strategy is to exploit both the XANES and the EXAFS parts of the spectra:

- Standard EXAFS analyses and novel ab initio XANES calculations (see [2]) will enable the derivation of the electronic and 3D structures of the iron chloride complexes (Fe^{2+} , FeCl^+ , FeCl_2 , FeCl_3^- , and FeCl_4^{2-}). XANES spectra were collected at all conditions, but high-quality EXAFS spectra were collected only at the extreme

temperatures (ambient and 450°C) for each concentration investigated. As can be seen in Figure 1, the ab initio calculations developed before the experiment, based on the results of experiment HS2628, are in good agreement with the experimental spectra.

- XANES spectra collected systematically with increasing chloride concentration can also be used in an original way to derive thermodynamic properties of the iron-chloride complexes [1]: based on Principal Component Analysis of the XANES spectra obtained at different temperature and concentration conditions, the formation constant and the speciation of each complex (either Fe^{2+} , FeCl^+ , FeCl_2 , FeCl_3^- , or FeCl_4^{2-}) can be derived. Preliminary work indicates that this technique is well suited for following the octahedral to tetrahedral transition between $\text{FeCl}_3(\text{H}_2\text{O})_3^-$ and FeCl_4^{2-} , but is not sensitive enough to provide accurate thermodynamic properties for the successive replacement of H_2O by Cl^- in the octahedral complexes.

The results from this study will aid in constraining the thermodynamic models used to determine the solubility and precipitation of Fe-bearing minerals in hydrothermal brines. It also contributes to our understanding of the role of coordination changes, driven by P,T and fluid composition, in controlling element mobility in the Earth's crust.



References:

- 1 W. Liu, B. Etschmann, G. Foran, M Shelley, and J. Brugger,, « Deriving formation constants for aqueous metal complexes from XANES spectra: Zn(II) and Fe(II) chloride complexes in hypersaline solutions», *American Mineralogist*, submitted.
- 2 D. Testemale, G. S. Pokrovski, J.-L. Hazemann, Y. Joly, J. Roux, R. Argoud and O. Geaymond, « Structural and electronic evolution of the $\text{As}(\text{OH})_3$ molecule in high temperature aqueous solutions: an x-ray absorption investigation », *J. Chem. Phys.*, 121, 8973 (2004).