

Experiment Report Form

The double page inside this form is to be filled in by all users or groups of users who have had access to beam time for measurements at the ESRF.

Once completed, the report should be submitted electronically to the User Office using the **Electronic Report Submission Application:**

<http://193.49.43.2:8080/smis/servlet/UserUtils?start>

Reports supporting requests for additional beam time

Reports can now be submitted independently of new proposals – it is necessary simply to indicate the number of the report(s) supporting a new proposal on the proposal form.

The Review Committees reserve the right to reject new proposals from groups who have not reported on the use of beam time allocated previously.

Reports on experiments relating to long term projects

Proposers awarded beam time for a long term project are required to submit an interim report at the end of each year, irrespective of the number of shifts of beam time they have used.

Published papers

All users must give proper credit to ESRF staff members and proper mention to ESRF facilities which were essential for the results described in any ensuing publication. Further, they are obliged to send to the Joint ESRF/ ILL library the complete reference and the abstract of all papers appearing in print, and resulting from the use of the ESRF.

Should you wish to make more general comments on the experiment, please note them on the User Evaluation Form, and send both the Report and the Evaluation Form to the User Office.

Deadlines for submission of Experimental Reports

- 1st March for experiments carried out up until June of the previous year;
- 1st September for experiments carried out up until January of the same year.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report, in English.
- include the reference number of the proposal to which the report refers.
- make sure that the text, tables and figures fit into the space available.
- if your work is published or is in press, you may prefer to paste in the abstract, and add full reference details. If the abstract is in a language other than English, please include an English translation.

**Experiment title:**

XAS study of Mn(II)-chlorocomplexing under hydrothermal conditions: octahedral to tetrahedral transitions as a driver for metal fractionation in hydrothermal systems

Experiment**number:**

EC-747

Beamline:	Date of experiment: from: 17/11/2010 to: 23/11/2010	Date of report: 1/3/2011
Shifts: 18	Local contact(s): Denis Testemale	<i>Received at ESRF:</i>

Names and affiliations of applicants (* indicates experimentalists):***Prof Joël Brugger*****Dr. Denis Testemale*****Dr. Barbara Etschmann****Dr Weihua Liu*****Mr Yuan Tian****Report:**

Synchrotron XAS measurements at the manganese *k*-edge for Mn(II)-bearing chloride solutions have been successfully conducted at the FAME beamline (BM30B) at ESRF on 17-23 November 2010. The aim of this project was to i) determine the structure (coordination numbers and distances) of Mn(II) chloride complexes at temperatures up to ~500 °C at 600 bar, as a function of varying Mn(II)/Cl ratios; ii) derive the formation constants for aqueous Mn(II) chloride complexes; and iii) compare the coordination chemistry of Mn(II) in chloride brines under hydrothermal conditions to that of other divalent transition metals measured by our team (Co(II), Ni(II), Fe(II)) and other groups (Zn(II), Cd(II)).

Operations at the facility were incident free, and setup and data collection were performed without any significant issues. Mn *K*-edge EXAFS spectra were collected with NaCl concentrations ranging from 0 to 5 m, and temperatures ranging from 30 °C to 500 °C. In addition three Br-bearing solutions (0.054 m Mn + 0.108 m Br; 0.1 m Mn + 1.2 m Br; 0.063 m Mn + 2.12 m Br) were collected to compare the speciation in the chloride and bromide systems, and indentify unequivocally the stoichiometry of the end-member species, since Br is easily distinguished from O in EXAFS analysis, while Cl and O are difficult to differentiate.

Preliminary data analysis shows that Mn(II) displays a similar evolution with temperature and chloride concentration as the other divalent transition metals (Fig. 1). However, contrary to Fe(II), we did not observe the formation of the fully chlorinated complex $[\text{MnCl}_4]^{2-}$. We are very excited by this result, since a systematic pattern emerges among three geochemical 'twin' elements for which XAS data on chloride complexing to supercritical conditions exist: for Mn/Fe, Ni/Co, and Cd/Zn, the first member of the couple does not form high order complexes ($[\text{MCl}_3]^-$ appears to be stable in highly saline brines; Fig. 2), while the second forms fully chlorinated tetrahedral complexes $[\text{MCl}_4]^{2-}$ at relatively high salinity and high temperature. These differences can explain the strong fractionation between these metals observed in many hydrothermal systems.

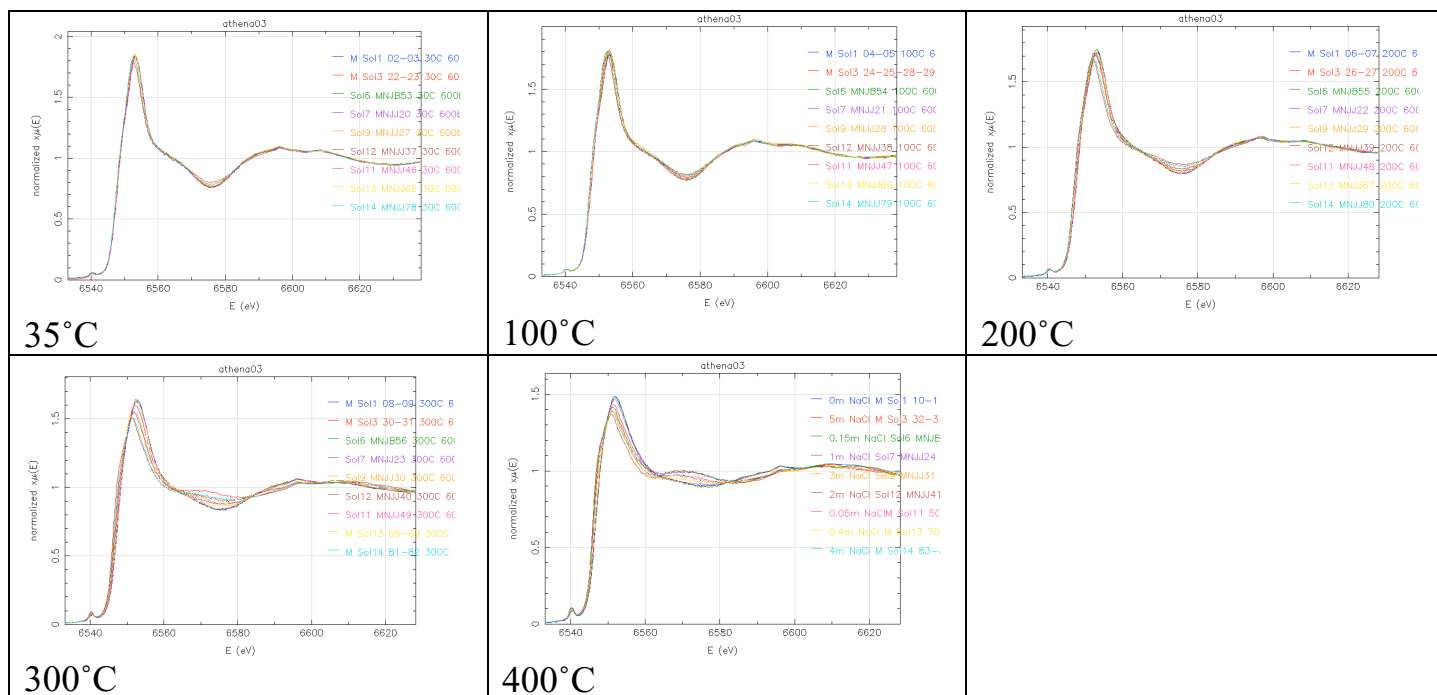


Figure 1. Summary of XANES data collected for solutions with Cl:Mn ratios varying from 2 to 78, as a function of temperature. The spectral evolution with increasing T and Cl:Mn ratio reflects a change in coordination of the Mn(II) complex from octahedral to tetrahedral.

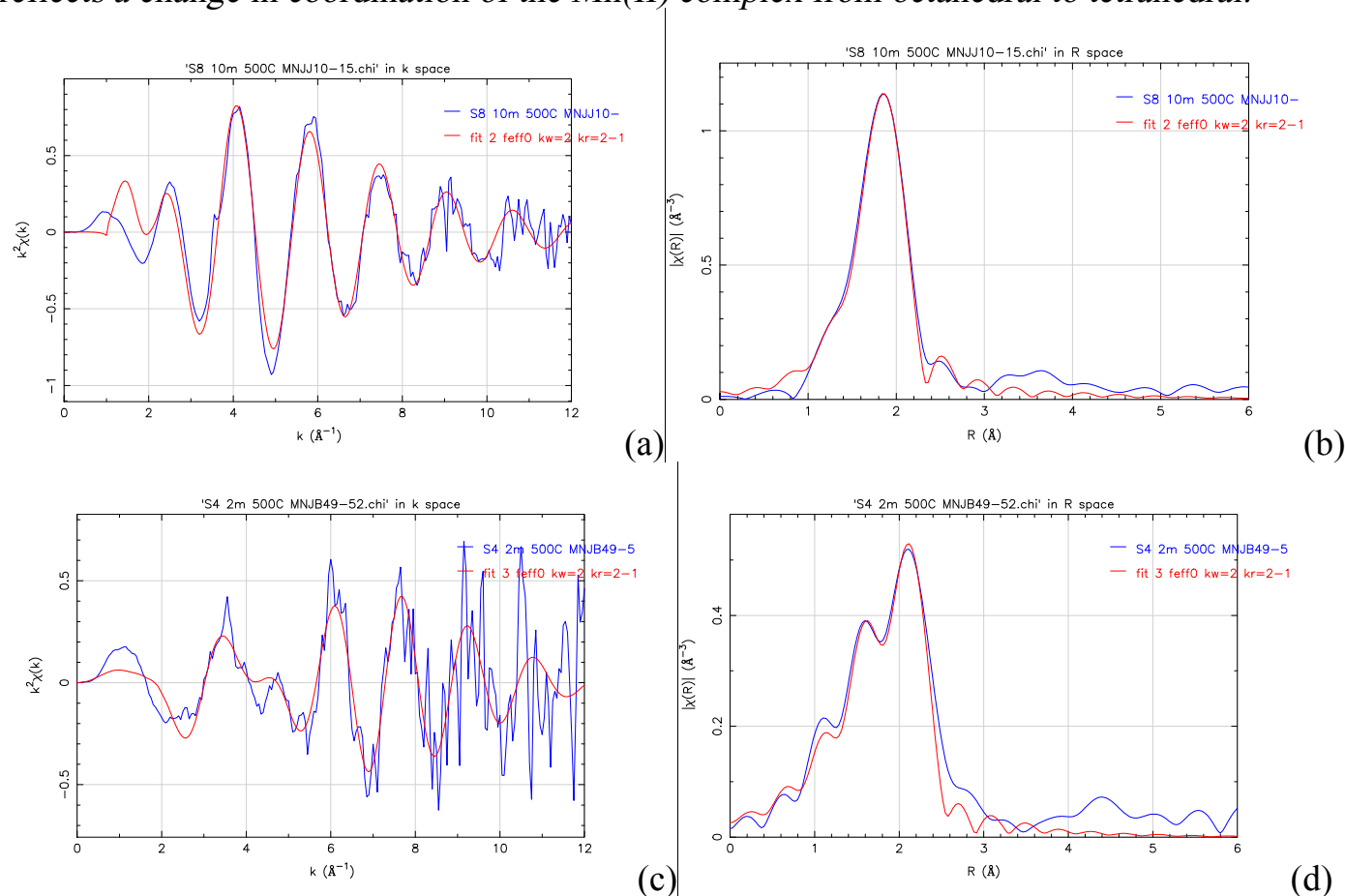


Figure 2. EXAFS refinements for 10 m Cl⁻ (a,b) and 2 m Br⁻ (c,d) solutions at 450 °C, 600 bar with experimental (blue line) and fitted spectra (red line) shown in both K -space and R -space, respectively. $\text{MnBr}_{3.2}\text{O}_{0.8}$ and $\text{MnCl}_{3.0}\text{O}_{1.0}$ are the best models to fit for these experimental data. Derived bond lengths of Mn-O and Mn-Cl are 2.24 Å and 2.36 Å, respectively for 10 m Cl⁻ solution; and the bond lengths of Mn-O and Mn-Br 2.13 Å and 2.44 Å for the 2 m Br⁻ solution. $\text{MnCl}_3(\text{H}_2\text{O})$ is the dominant species in highly saline brines at elevated T and P .