



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: The role of fluorine in the formation of giant Iron Oxide Copper Gold (U, REE) deposits		Experiment number: ES-254
Beamline: 30-BM-B	Date of experiment: from: 22 July 15 to: 29 July 15	Date of report: 23 Aug 15 <i>Received at ESRF:</i>
Shifts: 18	Local contact(s): Denis Testemale	

Names and affiliations of applicants (* indicates experimentalists):

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Barbara Etschmann*, Monash University

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Report: Aim

This proposal aimed to investigate the potential role of fluorine in the transport of iron, and compare ligand competition among halide ligands for iron in geosystems.

Experimental

Data were collected at the Fe K-edge (7112 eV) at the BM-30B (FAME) beam line, using the high T-P autoclave developed by the CNRS.

Sample	Conditions	Sample	Conditions
FeBr ₂	Pellet		
FeF ₂	Pellet		
FeF ₃	Pellet		
		Sol11: FeBr ₂ in 4.5 m NaBr	35-400 °C, 600 bar
Sol1: FeCl ₂ in 2.6 m NaBr	35-100 °C, 600 bar	Sol12: FeF ₃ in 0.1 m HCl	35-400 °C, 600 bar
Sol2: FeCl ₂ in 4.5 m NaCl	35-400 °C, 600 bar	Sol13: FeBr ₂ in 0.002m HBr	35-400 °C, 600 bar
Sol3: FeCl ₂ in 4.5 m NaBr	35, 300-400 °C, 600 bar	Sol14: FeF ₂ in 0.1 m HClO ₄	35-200 °C, 600 bar
Sol4: FeCl ₂ in 5 m NaBr + 1m NaF	35 °C, 600 bar	Sol15: FeF ₂ in 0.8 m NaF + 0.1m HClO ₄	35-100 °C, 600 bar
Sol7: FeCl ₂ in 0.01 m HBr	35-400 °C, 600 bar	Sol16: FeBr ₂ in 10 m LiBr	200-450 °C, 600 bar
Sol9: FeF ₃ in 0.1 m HClO ₄	35-400 °C, 600 bar	Sol18: FeBr ₂ in 1 m NaBr	35-450 °C, 600 bar
Sol10: FeF ₂ solubility	35-400 °C, 600 bar	Sol M: magnetite in 0.2 m HCl + 0.23 m NaF	400-100 °C, 600 bar

General observations/preliminary fits

1. The data provide the first in-situ spectroscopic characterisation of the structure of F-complexes of Fe(II) and Fe(III) at low T; these data confirm the existing thermodynamic models.
2. F is not a good ligand to transport Fe! At high temperatures (~200 °C), F induced Fe precipitation; this has important repercussions for ore deposit formation, as it invalidates the most widely accepted paradigm explaining the high F content in some IOCG deposits. Detail reactive transport is underway to revisit the causes of the association at the light of the new XAS data.
3. Fe reduces to Fe(II) at high temperature, no matter what!
4. **Preliminary fits** indicate that Fe(II) is best fitted with 4 Br in the highest salinity (10 m LiBr) solution. This confirms the high stability of tetrahedral Fe(II) complexes up to high T, in contrast to Mn(II) which favors lower numbers of halide ligands.

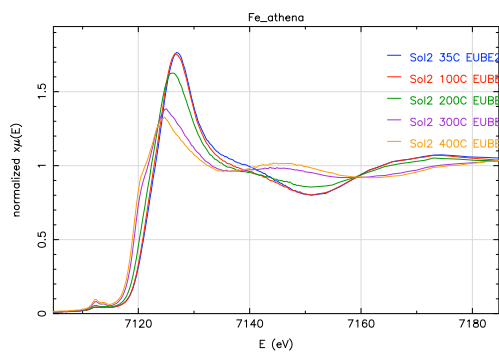


Fig. 1 Sol2=FeCl₂ in 4.5 m NaCl

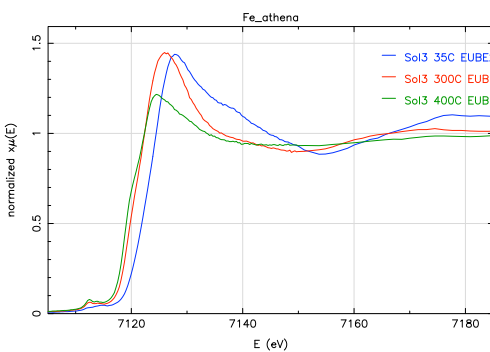


Fig. 2 Sol3=FeCl₂ in 4.5 m NaBr

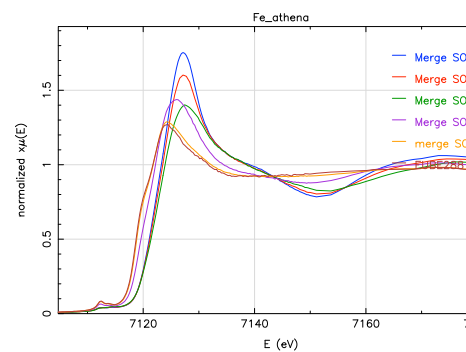


Fig. 3 Sol11=FeBr₂ in 4.5 m NaBr

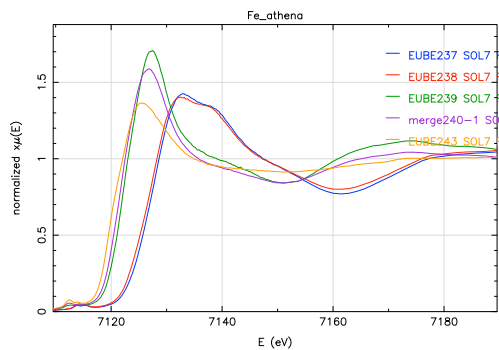


Fig. 4 Sol7=FeCl₂ in 0.01 m HBr

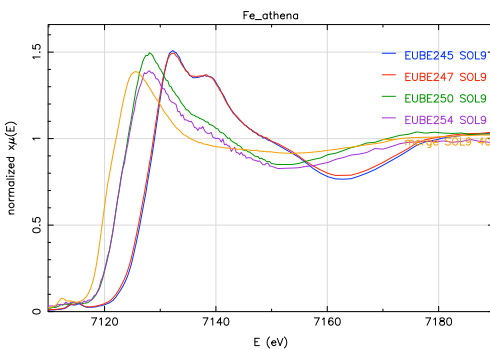


Fig. 5 Sol9=FeF₃ in 0.1 m HClO₄

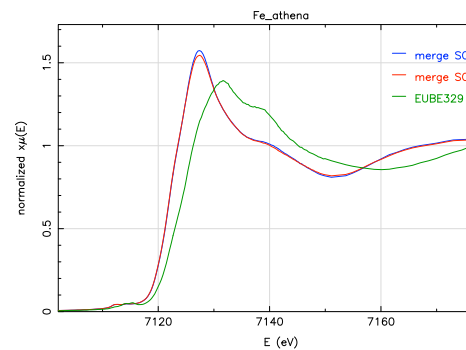


Fig. 6 Sol14=FeF₂ in 0.1 m HClO₄

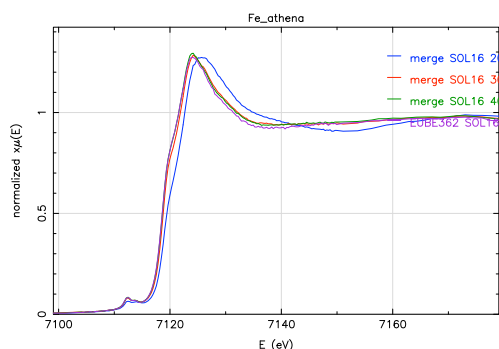


Fig. 7 Sol16=FeBr₂ in 10 m LiBr

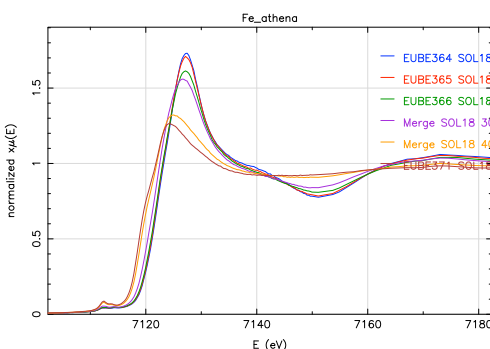


Fig. 8 Sol18=FeBr₂ in 1 m NaBr

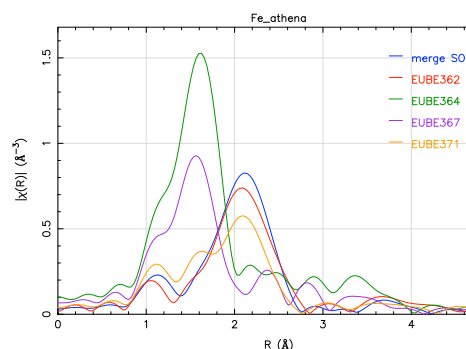


Fig. 9 Compare Sol16 & 18 in R-space

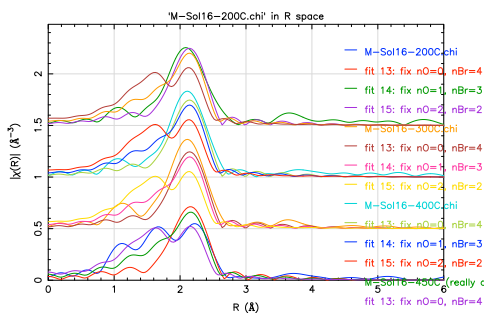


Fig. 10 Fit Sol16, fixed n

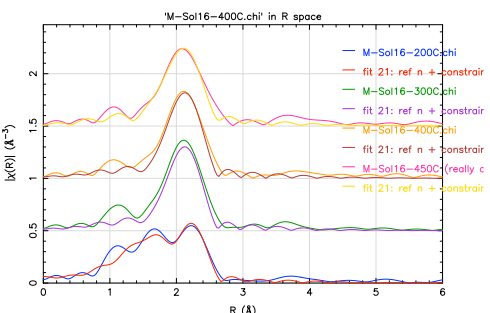


Fig. 11 Fit Sol16, refine n

Compare Figs. 1, 2 & 3: The trend for FeCl₂ in NaCl and FeBr₂ in NaBr are similar, namely a smooth change from octahedral to tetrahedral structures. FeCl₂ in NaBr has a much broader spectrum at low T, indicative of mixed Br/Cl/O.

Compare Figs. 4 & 6: Sort of comparing Cl vs. F. The main difference is data could be collected to higher T with no F in the system. With F, we observed precipitation at 200 °C (green line, Fig. 6).

Compare Figs. 5 & 6: Comparing Fe(II) vs Fe(III). The FeF₃ system was interesting – we believe we could measure to higher temperatures as the perchlorate broke down and we ended up with Fe-Cl complexing.

Compare Figs. 7, 8 & 9: Investigating the effect of salt with T. The more concentrated 10 m salt solution becomes tetrahedral faster than the 1 m salt (200 °C, whereas the 1 m solution becomes tetrahedral more around 400 °C).

Figs. 10 & 11: to get an idea re. ligand numbers, the number of O and Br was fixed in the fit and changed manually from nO=0, nBr=4 to nO=2, nBr=2 (Fig. 10). Ligand numbers were then refined to nO=1.7(3), nBr=3.0(4) (200 °C, structure still has a fraction of the octahedral component) to nBr=4.0(4) for all the other temperatures (Fig. 11).