

## 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.



	<b>Experiment title: The redox state of subduction zone fluids: insights from XANES studies in Fe-bearing fluids at high P-T conditions</b>	<b>Experiment number:</b> EC-258
<b>Beamline:</b> BM30B	<b>Date of experiment:</b> from: 10 June 2015 to: 16 June 2015	<b>Date of report:</b> Feb 21 <sup>th</sup> 2017
<b>Shifts:18</b>	<b>Local contact(s):</b> Isabelle Kieffer	<i>Received at ESRF:</i>
<b>Names and affiliations of applicants</b> (* indicates experimentalists): <b>C. Sanchez-Valle<sup>*</sup>, C. Kusebauch<sup>*</sup> and C. Plückthun<sup>*</sup></b> Institute for Mineralogy, WWU Münster, Germany <b>D. Testemale<sup>*</sup></b> ESRF BM30B, CNRS Grenoble, France		

#### Report:

Arc magmas, which are produced when cold hydrated oxidized oceanic crust is subducted below the mantle in subduction zones, are characterized by a higher oxidation degree compared to magmas from other locations. The oxidized signature is considered to be related to the influx of an oxidized fluid from the dehydrating subducted slab, but the nature of the oxidizing agent remains unclear. Although water may act as an efficient oxidizing agent in many terrestrial environments, this is not the case in the Earth's upper mantle. The oxidized signature may be thus transferred by chemical components mobilized by the slab-flux, namely Fe, S or C. The aim of this proposal was to investigate the oxidizing capacity of slab fluids that infiltrate the source of arc magmas by monitoring the speciation/redox state of Fe by XANES in aqueous fluids and hydrous silicate melts at high pressure (up to 2 GPa) and different redox conditions relevant for the present-day mantle wedge (FMQ to HM).

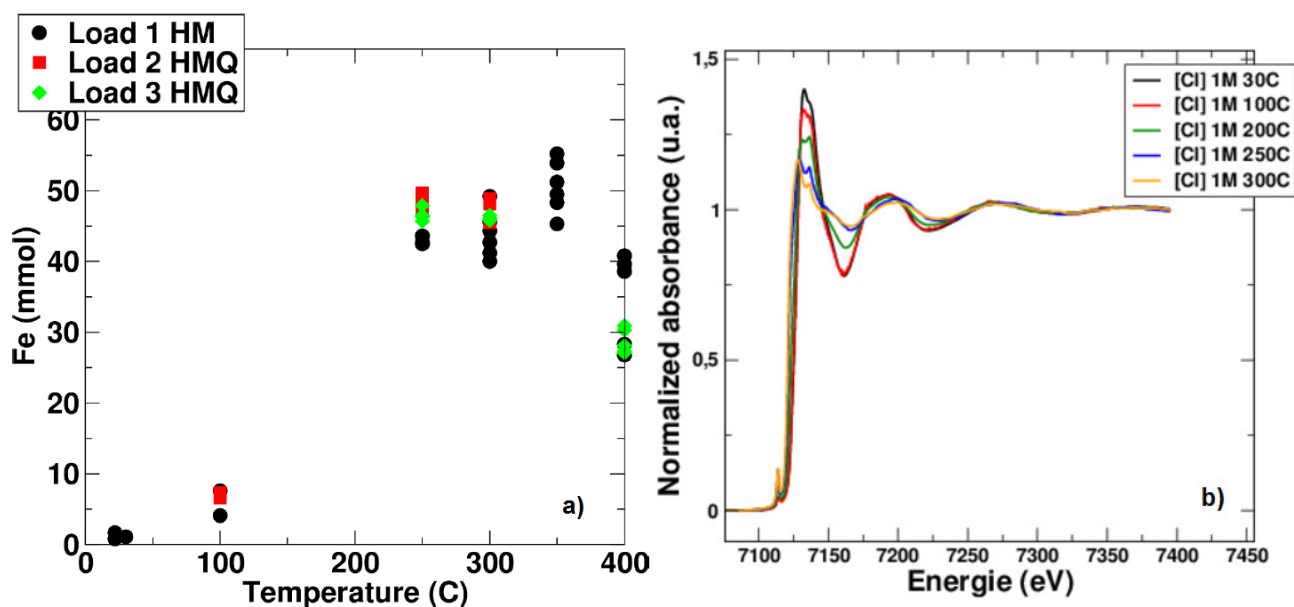
The original experimental plan involved XANES measurements in the diamond anvil cell (DAC) using the micro-focus station of FAME. Unfortunately, short before the experiments the KB mirror of FAME was damaged and experiments could not be conducted in the diamond anvil cell. Therefore, the experimental plan was modified to investigate the speciation and solubility of Fe in shallow crustal fluids (up to 400 °C and 0.1 GPa) using the autoclave developed at FAME for the study of hydrothermal fluids. X-ray absorption (XAS) measurements were conducted at the Fe K-edge using a X-ray beam of 100x200 µm and energy resolution of ~1.3 eV. The experimental setup included an inert glassy carbon cell and beryllium windows to reduce the attenuation of X-rays through the assembly. Fe signal in the fluid was monitored both in transmission and in fluorescence geometries by using ionization chambers and a 30-elements Ge detector, respectively.

A total of 8 solubility/speciation experiments at 1 kbar and temperatures between 30 and 400 °C were conducted during the allocated beamtime. Typically, the cell was loaded with the Fe-bearing mineral assembly, either Hematite-Magnetite (HM), with or without Quartz (HMQ), or Fayalite-Magnetite-Quartz (FMQ), and an aqueous solution with various chlorine concentrations and acidity (0.5M NaCl and 0.1- 0.5M HCl). After reaching the desired P-T conditions, the dissolution of the Fe-bearing minerals was monitored by the fluorescence signal of Fe in the fluid until equilibration (~45-60 min at 250 – 400 °C). Once chemical equilibrium is reached, XAS spectra were recorded in 1) transmission mode to determine the absorption edge

height that is proportional to the total Fe dissolved, and in 2) fluorescence mode to extract the structural information from the near- and after-edge spectrum. In some experiments, a 0.5 M  $\text{FeCl}_3$  aqueous solution was equilibrated with the HM buffer (with or without quartz) to investigate the stability of  $\text{Fe}^{3+}$  in hydrothermal fluids.

Figure 1 highlights the most important results obtained from this study. Fig.1a shows the evolution of the total dissolved Fe in acidic chlorinated fluids in equilibrium with HM or HMQ between 30 and 400 °C. The concentration of Fe in the fluid decreases above 350 °C and the decrease is more pronounced as the oxygen fugacity in the system decreases (i.e., from HM to HMQ assembly). The changes in Fe solubility are most likely related to a change in the redox state of Fe in the fluid, from  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$  as temperature increases. This interpretation is consistent with the limited stability of  $\text{Fe}^{3+}$  in the fluid as temperature increases demonstrated by the XANES/EXAFS spectra recorded in  $\text{FeCl}_3$ -NaCl-HCl aqueous solutions (total chlorine content 1M) in equilibrium with the HMQ assembly (Fig.1b). The speciation is dominated by  $\text{Fe}^{3+}$  at low temperatures but an important fraction of  $\text{Fe}^{2+}$  is identified in the fluid at the highest temperature investigated here, 300 °C. The deconvolution of the spectra to determine the exact proportions of  $\text{Fe}^{3+}$  and  $\text{Fe}^{2+}$  in the fluid is currently in progress. Together with the total concentration of Fe in the fluid, it will allow to evaluate the redox state of hydrothermal fluids at crustal conditions, a key parameter to understand the formation of Fe and other metal ore deposits. Nevertheless, our results already demonstrate that even though hydrothermal fluids can transport significant amounts of Fe, the capacity to transport  $\text{Fe}^{3+}$  at high temperature may be very limited, even at redox conditions relevant for the present-day crust/mantle. These preliminary results have been presented as an invited contribution at the Goldschmidt Conference 2016 held in Yokohama, Japan (*Testemale et al.*, 2016).

A manuscript presenting the results and the implications for redox state of crustal fluids and their role in the formation of metal ore deposits will be prepared during Spring 2017.



**Fig1.a)** Fe concentration in 0.1 M HCl aqueous fluids in equilibrium with Hematite-Magnetite (HM) and Hematite-Magnetite-Quartz (HMQ) assemblies as a function of temperature at 1 kbar. **b)** Evolution with temperature of Fe speciation in chlorinated fluids (1 m total Cl, NaCl+ HCl) in equilibrium with HMQ at 1 kbar. Note the changes in speciation from  $\text{Fe}^{3+}$  towards dominating  $\text{Fe}^{2+}$  with temperature.

#### Issued publication(s):

Testemale D., Sanchez-Valle, C., Goujon, G., Pokrovski, G.S., and Guyot, F. (2016) The speciation of Fe (III) in hydrothermal solutions. Invited abstract Goldschmidt 2016, Yokohama (Japan).