



## 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 via the User Portal:

<https://www.esrf.fr/misapps/SMISWebClient/protected/welcome.do>

### ***Reports supporting requests for additional beam time***

Reports can 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:</b> Fe <sup>2+</sup> /Fe <sup>3+</sup> ratio in iron-based minerals studied by x-ray Raman scattering	<b>Experiment number:</b> HE-3697
<b>Beamline:</b> ID16	<b>Date of experiment:</b> from: 19/10/2011 to: 25/10/2011	<b>Date of report:</b> 08/08/2012
<b>Shifts:</b> 18	<b>Local contact(s):</b> Dr. Laura Simonelli	<i>Received at ESRF:</i>

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**Report:**

Knowledge of the Earth's composition, structure and dynamics is essential for understanding of geological processes. Most physical properties of the Earth's interior have been extracted from seismological observations or structural laboratory studies of phases attendant in the Earth's body [1,2]. Here, iron is one of the most important components of the minerals which form the Earth's mantle and crust. Furthermore, iron contributes significantly to the core composition. Depending on pressure, temperature and oxygen fugacity, the coordination number, oxidation state and spin state of iron can change strongly which influences macroscopic properties of the iron containing minerals. Thus, experimental determination of the oxidation state and coordination is crucial for understanding the thermodynamic properties of the minerals at the conditions of the deep Earth.

Core-level spectroscopy provides a possibility to investigate physical properties of iron containing minerals by measuring iron absorption edges. Fe K-edge spectroscopy is known to be a feasible tool to determine the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio of a mineral under ambient conditions [3]. However, Fe K-edge studies under high pressure require an experimental energy resolution below 1 eV which reduces the count rate. Due to the strong absorption of the signal by the diamonds, high pressure studies of the Fe K-edge are difficult. Thus, bulk sensitive study of the Fe M<sub>2/3</sub>-edge is presented on differently coordinated iron oxides to show the feasibility of the M-edge as a tool to determine the Fe<sup>2+</sup>/Fe<sup>3+</sup> ratio of a mineral.

The experiment was performed at beamline ID16 [4]. The multi-analyzer spectrometer in Rowland geometry was used at an analyzer energy of 9.68 keV. The scattering angle was set to 35° and 135° resulting in momentum transfers of (3.22±0.81) Å<sup>-1</sup> and (9.13±0.53) Å<sup>-1</sup>, respectively, to study dipolar and non-dipolar excitation channels. XRS spectra of different polycrystalline powders were measured between 9.734 to 9.757 keV to cover the energy loss range from 46 to 69 eV in the vicinity of Fe M<sub>2/3</sub>-edge with an overall energy

resolution of 0.8 eV. The single spectra for each sample were summed up and a background was subtracted (Lorentzian function for low momentum transfer and linear background for high momentum transfer). Finally, the spectra were normalized to the integrated intensity between 702 eV and 728 eV.

The XRS spectra of different iron minerals ( $\text{FeAl}_2\text{O}_4$  (tetrahedral  $\text{Fe}^{2+}$ ),  $\text{Fe}_2\text{SiO}_4$  (octahedral  $\text{Fe}^{2+}$ ),  $\text{FePO}_4$  (tetrahedral  $\text{Fe}^{3+}$ ) and  $\text{Fe}_2\text{O}_3$  (octahedral  $\text{Fe}^{3+}$ )) are presented in figure 1. The shape of the Fe  $M_{2/3}$ -edge for  $q = (3.22 \pm 0.81) \text{ \AA}^{-1}$  shows significant differences for  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  including a shift of the white line of approximately 2.5 eV. Furthermore, an additional shift of 0.5 eV of the absorption edge can be observed for each oxidation state from octahedral to tetrahedral coordination which emphasizes the sensitivity of the dipolar contribution to the Fe  $M_{2/3}$ -edge to the oxidation state and symmetry of iron in a mineral. The high momentum transfer data at  $q = (9.13 \pm 0.53) \text{ \AA}^{-1}$  show significant differences compared to lower  $q$ . Here, slight dependence of the spectral shape related to the coordination can be observed but strong changes according to the oxidation state are clearly visible. The  $\text{Fe}^{2+}$  spectra show a twin-peak shape while only one line contributes to the spectra of  $\text{Fe}^{3+}$ . Furthermore, an energy shift of approximately 1 eV can be observed between the  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  spectra for the non-dipolar excitations ( $\Delta J = 0, \pm 1, \pm 2$ ).

In the presented study we show the high sensitivity of the Fe  $M_{2/3}$ -edge on the oxidation state and coordination of iron in different minerals. Changes of the spectral shape were observed for dipolar excitations for low momentum transfer and non-dipolar excitations for high momentum transfer, which are a special feature of XRS and are not accessible by other techniques. Due to this fact XRS becomes a very promising tool to investigate changes of the  $\text{Fe}^{2+}/\text{Fe}^{3+}$  ratio and spin state in situ even using highly absorbing sample environments by measuring Fe  $M_{2/3}$ -edge. Furthermore, atomic multiplet and charge transfer effects can be investigated in future using different theoretical models [5].

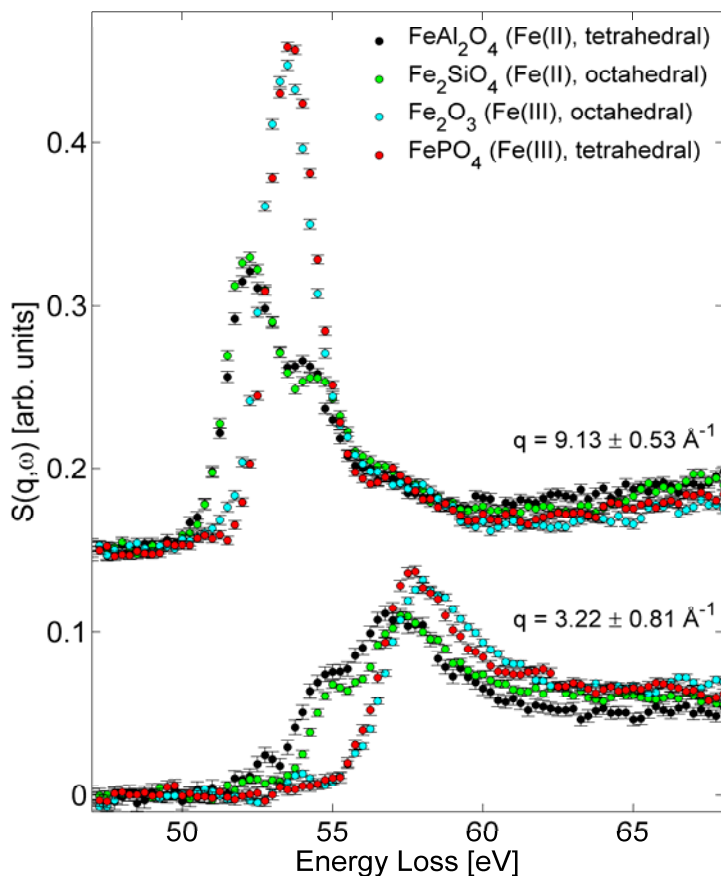


Figure 1: XRS spectra of the Fe  $M_{2/3}$ -edge of differently coordinated  $\text{Fe}^{2+}$  and  $\text{Fe}^{3+}$  for low and high momentum transfer.

- [1] A.M. Dziewonski and D.L. Anderson, *Phys. Earth. Planet. Int.* **25**, 297 (1981).
- [2] S. Speziale, A. Milner, V.E. Lee, S.M. Clark et al., *Proced. Nat. Acad. Sci.* **102**, 17918 (2005).
- [3] M. Wilke, F. Farges, P.E. Petit et al., *Amer. Mineral Soc.* **86**, 714 (2001)
- [4] R. Verbeni et al., *J. Synch. Rad.* **16**, 469 (2009).
- [5] E. Stavitski, F. M. F. de Groot, *Micron* **41**(7), 687 (2010).