

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: Effect of halogens (F) and melt composition on the mobility and speciation of Zr in SiO₂-rich fluids: Implications for the recycling of HFSE in subduction zones.	Experiment number: EC-563
Beamline: BM30B	Date of experiment: from: 10 Nov 2009 to: 16 Nov 2009	Date of report: March 1 st 2010
Shifts:18	Local contact(s): J-L. Hazemann	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): C. Sanchez-Valle, M. Louvel, W.J. Malfait Institute for Mineralogy and Petrology, ETH Zurich, Switzerland. D. Testemale, J-L. Hazemann ESRF BM30B, CNRS Grenoble, France		

Report:

Subduction-related silicate melts and aqueous fluids play a critical role in the Earth's crust and mantle evolution, triggering significant mass and energy transfer from the slab to the crust and abundant volcanic activity on the surface. Subduction-related magmas exhibit a particular trace element signature mainly characterized by Large Ion Lithophile Element (LILE) enrichment and High Field Strength Element (HFSE) depletion. HFSE, like Zr, are therefore important tracers of sources of arc magmas and data on Zr solubility, speciation and partitioning between aqueous fluids and silicate melts are essential to constrain the geochemical cycle of HFSE and provide new insight on the genesis of arc magmas. In sight of recent studies reporting that HFSE could be efficiently mobilized by alkali-SiO₂ rich fluids or fluorine-rich melts [1,2], better constraints on the influence of fluid and melt compositions on HFSE behavior also need to be established.

During the allocated beamtime at BM30B, X-ray Absorption Fine Structure (XAFS) and X-Ray Fluorescence (SXRF) experiments were conducted in Hydrothermal Diamond-Anvil Cell (HDAC)[3] up to 800 °C and 1.5 GPa to investigate the speciation of Zr in subduction zone fluids (aqueous fluids, silicate melts and 'supercritical fluids') and its partitioning between alkali SiO₂-rich aqueous fluids and haplogranitic melt. In addition, the influence of fluorine on Zr speciation and partitioning was also determined.

The controlled implementation of the experiments critically depended on the ability to rapidly switch between the visual observation of the sample environment, the collection of the SXRF/XAFS signal from the sample and the acquisition of the X-ray diffraction pattern from the pressure marker (Au). Despite stringent spatial constraints, an optimal experimental configuration was achieved at BM30B that allowed us to rapidly switch between the different detectors (visual camera, Si drift detector, X-ray CCD) and facilitated, for the first time, simultaneous *in situ* XAFS and SXRF measurements in a HDAC at BM30B under well-constrained P-T conditions.

This set-up comprised a set of Kirpatrick-Baez mirrors that ensures the focusing of the monochromatic X-ray beam down to 10 x 15 (VxH) µm size with a flux of ~1.10¹² photons per second. X-ray fluorescence was excited with incident energy of 18.05 keV and SXRF spectra were collected using a Si drift detector set at 20° from the incoming beam in the horizontal plane. XAFS spectra at the K_α edge of Zr were collected in fluorescence mode using the same detector. During XAFS measurements, the monochromatic X-ray beam scanned across the Zr K-absorption edge between 17.8 and 18.37 keV at ≈ 5.0-eV intervals, with 1 second residence time per point. In addition, XAFS

measurements were collected in absorption mode on different Zr-bearing mineral and glass standards (zircon, baddaleyite, vlasovite, eudialyte and F-free and F-bearing $\text{Na}_2\text{Si}_2\text{O}_5$ and haplogranite glasses) outside the HDAC with a 300 x 100 (HxV) μm size beam. A Frelon2000 X-ray CCD detector set in transmission was used to collect angle-dispersive X-ray diffraction spectra during the experiments.

All experiments were carried out using a hydrothermal diamond-anvil cell. A gold chip was added to the experimental volume to be used as pressure sensor during the experiments. Pressure was determined from the variation of the lattice parameters of gold obtained from the X-ray diffraction patterns recorded at high P-T conditions during the experiments with an accuracy of ± 0.2 GPa. Temperature was monitored with an accuracy of ± 2 °C using K-type thermocouples attached to each of the diamond anvils very close to the compression chamber. A motorized camera allowed monitoring of the sample during heating stages.

Two different set of experiments were conducted during the allocated beamtime. The first one probed Zr partitioning between alkali- SiO_2 rich aqueous fluids and haplogranitic melt, while the second investigated the speciation of Zr over a wide range of compositions, including 5000 ppm Zr standard solutions (in 2.5 wt% HCl), $\text{Na}_2\text{Si}_2\text{O}_5$ (NS2) and haplogranite glasses and melts, and alkali- SiO_2 aqueous miscible fluids (20-30 wt% NS2). Preliminary results are summarized below.

1) Partitioning of Zr between aqueous fluids and haplogranitic melts at high P-T

For the partitioning experiments, the HDAC was loaded with a chip of synthetic haplogranite glass, doped with 1 wt% Zr (as determined by electron microprobe analysis), a flake of Au for pressure calibration and distilled H_2O . In addition, identical experiments were also conducted in F-bearing systems (2 wt% F in the haplogranite glass). For each P-T condition, transverse scans of the experimental chamber were collected after each heating stage to monitor the distribution of Zr between the the different phases (coexisting aqueous fluid and silicate melt or single miscible phase)(Fig1). Subsequently, 3 to 6 SXRF analyses were recorded in fluid and melt phases for 100s to determine Zr fluid-melt partition coefficients from the intensities of Zr emission lines (Fig2). Careful attention was given that collection point was located in a pure phase (bridging fluid or melt globule) in order to avoid any contamination of the signal.

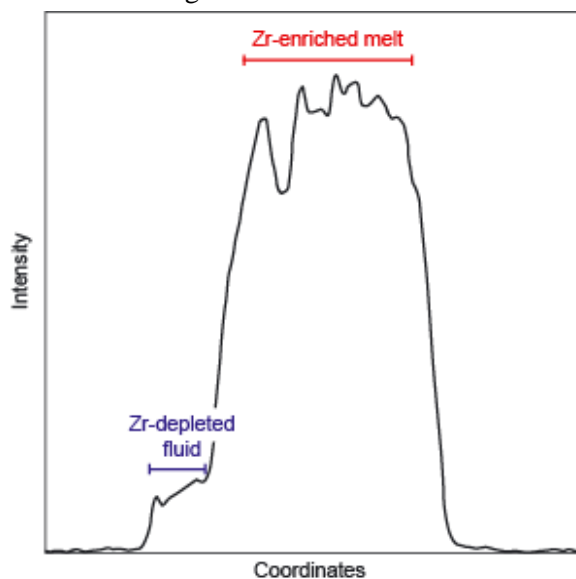


Fig1: Fluorescence scan mapping Zr distribution in the sample chamber at 745 ° and 1.5 GPa in H_2O -haplogranite. Two distinct phases are observed which correspond to coexisting fluid and melt. Zr preferentially partitions into the melt phase.

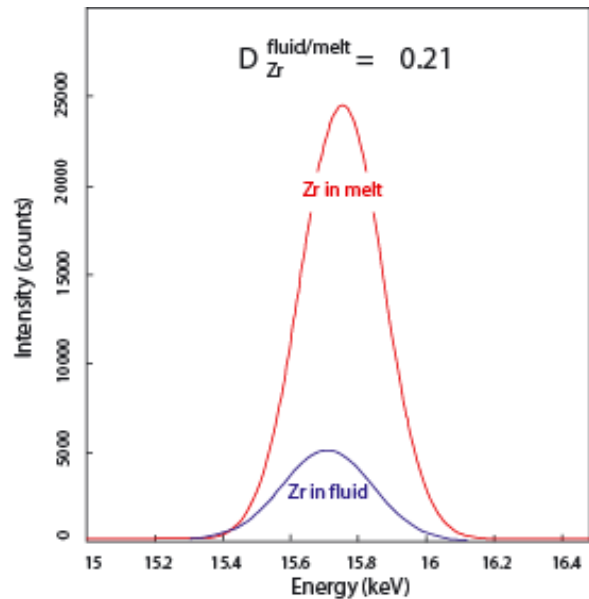


Fig2: X-ray fluorescence signal of Zr collected in coexisting fluid and melt phases at 745 °C and 1.5 GPa in H_2O -haplogranite system.

Determination of Zr fluid-melt partition coefficient is still under progress. However, preliminary results show that Zr preferentially partitions into the melt phase at any investigated P-T. Zr concentration in the melt appear to increase with increasing temperature and with the addition of fluorine, suggesting the efficient mobilization of Zr (and HFSE) by fluids enriched in alkali-Al-Si dissolved components and volatiles.

2) Zr speciation in subduction zone fluids

To determine Zr speciation, Zr standard solution and/or H₂O were loaded in the HDAC with Na₂Si₂O₅ or haplogranite glass pieces, together with a flake of Au for pressure calibration. XAFS analyses were performed at the K-edge of Zr in glasses, single miscible phase or melt phases. Representative XANES spectra collected during the experiments are reported in Fig. 4.

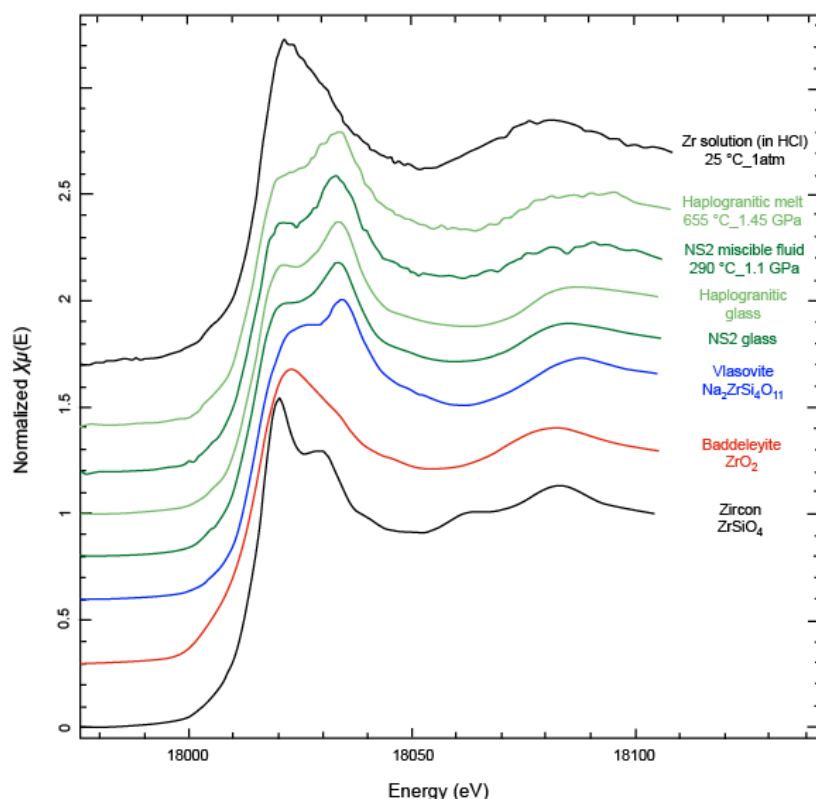


Fig4: XANES spectra collected at Zr K-edge in various subduction-related fluid compositions and related Zr-bearing mineral standard. Mineral standards (zircon, baddeleyite and vlasovite) and glass samples XANES were collected outside the HDAC with a 300 x 100 μm beam, whereas fluid and melt XANES were collected in the HDAC with a 10 x 15 μm beam.

XANES spectra of Zr in glasses, melts and alkali-SiO₂ fluids display distinct features compared to Zr in HCl, but bear a strong resemblance to spectra in solid-standard vlasovite (Na₂ZrSi₄O₁₁), providing evidence for octahedrally-coordinated Zr [4]. In addition, similarities observed between Zr XAFS spectra in F-free and F-bearing melts (not depicted) may indicate the absence of Zr-F complexation in hydrous silicate melts, in agreement with previous studies in Zr-F bearing silicate glasses [2]. Further modelling of XANES and EXAFS spectra with Athena-Artemis package [5] and FDMNES code [6] is in progress to better constrain the complexation of Zr in subduction zone fluids.

These experiments provide the first high-resolution *in situ* constraints on the speciation of Zr in silicate melts and alkali-SiO₂ rich fluids under well-constrained P-T conditions and give new insight on the nature of the mobile fluid-phase in subduction-related processes and on the geochemical cycle of Zr. These results of these experiments show that micro-SXRF and micro-XAFS can be conducted in aqueous systems at high temperature under well-constrained pressure conditions at BM30B FAME beamline. This results will be presented at geochemistry Goldschmidt conference (Knoxville, June 2010)[7]. An article presenting the results of Zr mobility and speciation in subduction zone fluids will be edited for publication during Spring 2010.

References:

- 1]Manning et al (2008). Earth Planet. Sci. Lett. 272, 730-737. [2]Farges (1996). Chem. Geol. 127, 253-268. [3]Bassett et al (1993). Rev. Sci. Inst. 64, 2340-2345. [4] Sokolova E. et al (2006). Can. Mineral. 44, 1349-1356. [5] Ravel B. & Newville M. (2005). J. Synch. Rad. 12, 537-541. [6]Joly Y. (2001). Phys. Rev. B63, 125120-125129. [7]Louvel M., Sanchez-Valle C., Malfait W.J., Testemale D., Hazemann J-L. (2010). Zr mobilization and speciation in subduction zone fluids. Abst. 2754, Goldschmidt conference Abstract volume.