



Experiment title: Partition and speciation of Zr between aqueous fluids and silicate melts at high P-T conditions: implications for the genesis of magmas in subduction zones.

Experiment number:
EC384

Beamline:
ID22

Date of experiment:
from: 7 Nov 2008 to:

Date of report:
1 March 09

Shifts:
16

Local contact(s): Jean Cauzid

Received at ESRF:

Names and affiliations of applicants (* indicates experimentalists):

C. Sanchez-Valle, M. Louvel, Davide Mantegazzi

Institute for Mineralogy and Petrology, ETH Zurich, CH.

S. Petitgirard, H. Cardon, I. Daniel

Laboratoire de Sciences de la Terre, ENS Lyon, France.

J. Cauzid

ESRF ID22, France.

Report:

Silicate melts and aqueous fluids are of major importance in the evolution of the Earth's crust and mantle. It is particularly evident in subduction zones where fluid/melt generation and interaction between aqueous fluids and silicate melts can trigger significant mass and energy transfer from the slab to the crust and abundant volcanic activity on the surface. Knowledge of the physical and chemical properties of these systems is essential for a better understanding subduction processes. Subduction-related magmas exhibit particular trace element signature mainly characterized by Large Ion Lithophile Elements (LILE) enrichment and High-Field Strength Elements (HFSE) depletion. HFSE, like Zr, are therefore important tracers of the sources of arc magmas and data on Zr solubility and partitioning between aqueous fluids and silicate melts is needed in order to constrain the geochemical cycle of Zr and provide new insight on the genesis of arc-magmas beneath volcanoes.

During the allocated beamtime at μ -FID22, Synchrotron X-ray micro-fluorescence spectroscopy (SXRF) and X-ray absorption Fine Structure (XAFS) measurements have been conducted simultaneously at high P-T conditions (up to 600°C and 2.5 GPa) using hydrothermal diamond anvil cells to investigate *in situ* the partitioning of Zr between aqueous fluid and alkali-silicate melts ($\text{Na}_2\text{Si}_2\text{O}_5$) and its speciation in SiO_2 -rich aqueous fluids.

The experimental setup for XAFS and XRF measurements at high P-T conditions in the HDAC comprised a set of Kirkpatrick-Baez mirrors that ensures the focusing of the monochromatic X-ray beam down to 3×5.5 (VxH) μm size with a flux of $\sim 1.10^{12}$ photons per second. The intensity of the transmitted beam was monitored by a silicon PIN-diode placed behind the HDAC and used to simplify sample alignment procedures during the measurements. X-ray fluorescence was excited with incident energy of 19.0 keV and SXRF spectra were collected using an energy dispersive single-element Si(Li)-detector set at 24° from the incoming beam in the horizontal plane. XAFS spectra at the K_α edge of Zr were collected at selected P-T conditions in fluorescence mode using the same detector. During XAFS measurements, the monochromatic X-ray beam scanned across the Zr K-absorption edge between 17.9 and 18.4 keV at ~ 1.0 -eV intervals, with 2 second residence time per point. A X-ray CCD detector set in transmission was used to collect angle-dispersive X-ray diffraction spectra during the experiments.

Two different sets of experiments were conducted: 1) Zr partitioning between aqueous fluids and alkali-silicate melts and 2) speciation experiments in SiO₂-rich fluids. The experimental details and preliminary results are summarized below.

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

For the partitioning experiments, the HDAC was loaded with a chip of synthetic Na₂Si₂O₅ glass, doped with 4000 ± 200 ppm of Zr (as determined by electron microprobe analysis), a flake of gold (Au) for pressure calibration and distilled H₂O. Pressure at high temperature was determined with an accuracy of ± 0.2 GPa from the variation of the lattice parameters of Au obtained from the X-ray diffraction patterns recorded during the experiments. A motorized camera allowed to observe the sample chamber during the heating stages (**Fig1a**). To monitor the composition of coexisting fluids and melts during the heating stages and also in the vicinity of the miscibility, Zr distribution and concentration were determined *in situ* during the experiment by SXRF. Repeated SXRF analyses were recorded in the fluid as a function of time until equilibration was reached. Acquisition times for single analysis range from 3 to 10 min. 2D scans of the sample chamber (**Fig1b**) were performed using a 10 s per step integration time to monitor the distribution of Zr between phases. Attempts to conduct XAFS analysis at the Zr K-edge in the aqueous phase at high P-T conditions were unfruitful due to the low concentration of Zr in the fluid (~10-20 ppm).

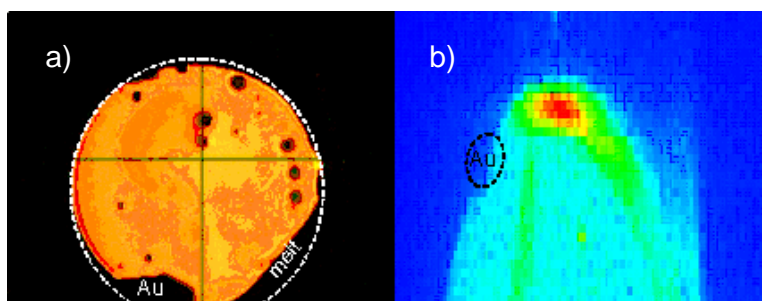


Fig1. a) Microphotograph of the experimental load at 600°C-1GPa. Na₂Si₂O₅ melt is concentrated on the lower edge of the gasket. Except from few small melt globules, the rest of the cell is an alkali silica-rich fluid. b) 2D fluorescence map of Zr in the cell at the same P-T condition (specular image). Zr-rich regions (from green to red) correspond to the melt phase.

The determination of Zr partition coefficient between the aqueous fluids and the silicate melt at high P-T conditions corresponding to the upper mantle in subduction zones is currently in progress. The preliminary qualitative results indicate that Zr preferentially partitions into the melt phase at every investigated P-T conditions (Fig1)

2) Zr speciation in SiO₂-rich aqueous fluids at high P-T

The second set of experiments investigate the speciation of Zr in SiO₂-rich aqueous fluids at high P-T by XAFS. For the experiments, chips of gem quartz (SiO₂), a flake of Au for pressure calibration and Zr standard solutions (1000 ppm Zr) were loaded in the cell. XAFS analysis was performed at the K-edge of Zr in the aqueous phase as a function of P, T and the amount of dissolved silica up to 600 °C and 2.5(2) GPa. Representative XAFS spectra collected during the experiments are reported in Fig2a and Fourier transforms of the EXAFS spectra are reported in Fig2b. Preliminary analysis of the data suggest two shells that may be associated to O (Feature A, Fig2a) and Si (Feature B, Fig2b) next nearest neighbors around Zr. No dramatic changes in the structural environment of Zr were identified up to 600 °C and 2.5(2) GPa. Modeling of different local structural environments around Zr using *ab initio* calculations is currently in progress.

These studies provide the first *in situ* constraints on the speciation and partitioning behavior of Zr at high P-T fluids and shed new light on the nature of the mobile fluid phases in subduction-related processes and on the geochemical cycle of Zr. The results will be presented at the Goldschmidt conference held in Davos (Switzerland) in June 2009 [1]. However, additional constraints on the effect of melt (e.g., aluminum content, polymerization) and fluid composition on the behavior of Zr are required to explain the enrichment in HFSE (Zr, Ti, Nb) in ultra-high pressure rock exhumed in subduction zones [2].

Given the interesting results already obtained during this first series of measurements and the probed feasibility of XAFS and SXRF measurements in the DAC under well-constrained P-T conditions, we would request a continuation of EC384.

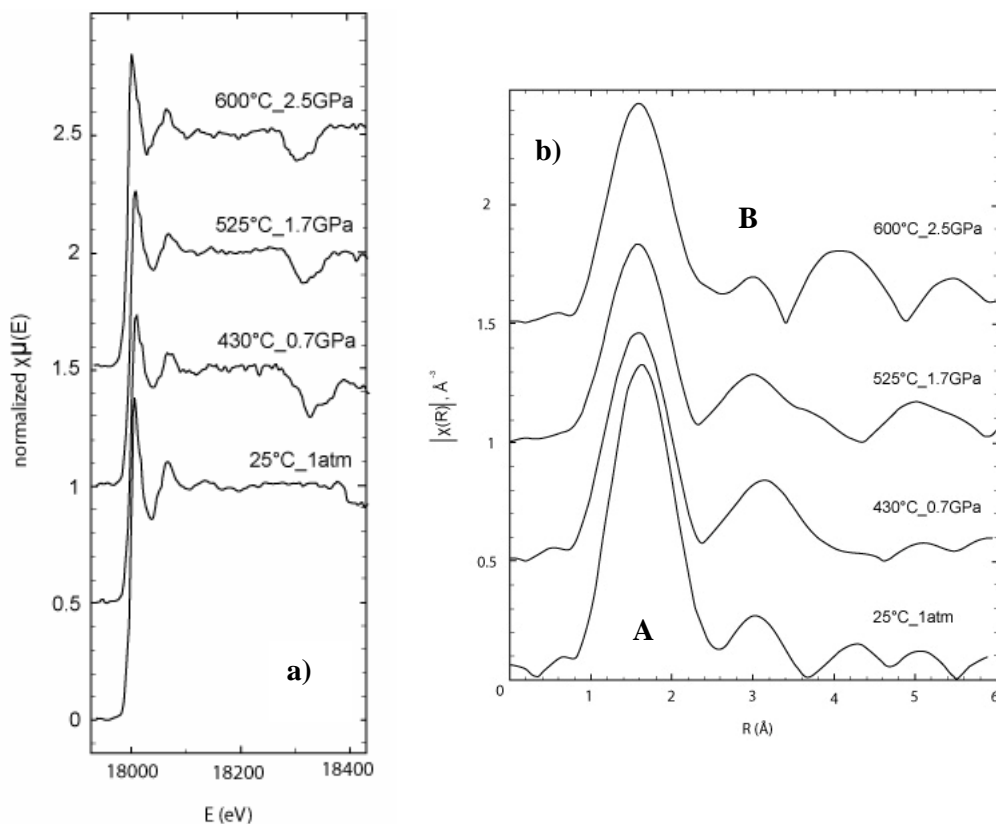


Fig3. a) XAFS spectra collected at the Zr K-edge (17.998keV) in the SiO₂-rich fluid at various P-T conditions. b) Fourier transforms of the spectra in Fig3a. Features A and B may arise from O and Si next nearest neighbors around Zr in the SiO₂-rich aqueous fluid.

References:

- [1] Louvel, M., Sanchez-Valle, C., Petitgirard, S., Cardon, S., Daniel, I., and Cauzid, J. (2009) In situ investigations of Zr speciation and partitioning in high-pressure in high-pressure SiO₂-rich aqueous fluids and silicate melts. Goldschmidt conference Abstract volume.
- [2] Rubatto, D., and Hermann, J. (2003) *Geochim. Cosmochim. Acta* 67, 2173-2187.