EUROPEAN **S**YNCHROTRON **R**ADIATION **F**ACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

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.

ESRF	**Experiment title:** Partitioning coefficients of Highly Siderophile Elements measured in situ between liquid silicate and iron rich liquid at pressure and temperature of the earth's mantle	**Experiment number**:
Beamline: ID27	**Date of experiment**: from: 10/02/2011 to: 15/02/2011	**Date of report**: 15/03/2011
Shifts: 15	**Local contact(s)**: Petitgirard S.	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

European synchrotron Radiation Facility Polygone Scientifique Louis Néel, 6 rue Jules Horowitz, 38000 GRENOBLE, France :

Dr. PETITGIRARD Sylvain* Email sylvain.petitgirard@esrf.fr (main proposer)

Laboratory Hasylab at DESY Notkestrasse 85 22607 HAMBURG GERMANY :

Dr. APPEL Karen* Phone +49-40-8998-2930 Email karen.appel@desy.de

Dr. LIERMANN Hanns-Peter* Email hanns-peter.liermann@desy.de

Dr. BORCHERT Manuela* Email manuela.borchert@desy.de

Laboratory Universite Blaise Pascal Laboratoire des Magmas & Volcans 5 rue Kessler 63038 CLERMONT-FERRAND FRANCE:

Prof. ANDRAULT Denis* Phone 33-4-73-34-67-81 Email d.andrault@opgc.univbpclermont.fr

Report: At the early stage of formation of the earth, highly siderophile elements (HSE) or "iron loving elements" were supposed to sink down with the iron in the Earth's core, thus depleting the upper part of the Earth of noble metals. However, they are found to be overabundant on Earth's surface and in the upper mantle. This inconsistency has remained one of the most outstanding problems for the interpretation of the geochemical signatures of the Earth's mantle and is still lively debated today. An explanation of this feature may originate from the equilibrium between iron-rich liquid and a molten silicate mantle during the early differentiation of the Earth. Thus, Righter *et al.* [1], postulated a differentiation model with a chemical equilibrium at the bottom of a silicate magma ocean while a metallic core forms at a depth of 1100km (40 GPa). It remains unclear if the chemical excess of the siderophile elements in the mantle can be attributed to a higher partitioning coefficient of the HSE in the silicate melt [2] or to a late chondritic veneer that enriched the mantle 100 ± 50 My after the Earth accretion [3], or a combination of both.
The above hypotheses were tested using experimental techniques in large volume press, and are limited by a maximum pressure of 15 GPa due to the temperature yield of the graphite furnace used in such apparatus. In addition all samples were analyzed ex-situ and no one used high spatial resolution probes.

During the allocated beamtime, we quantified in situ in a laser heated Diamond Anvil Cell (DAC) the concentration of some relevant trace elements (Pd, Ru, Zr) involved in the processes describe above. In order

to reach this goal, we use a special DAC (Figure 1a)[4] that allows to place a Vortex detector at 90° in the horizontal plan, where Compton scattering is minimized because of the polarisation of the synchrotron beam. Figure 1a) shows the internal design of the DAC using asymmetrical anvils, the lower one has a 1mm culet while the other one has a 300 microns culet and conical shape at the back side (left figure). Figure 1 also indicates the different paths of the X-Rays, with *i)* in yellow the incoming beam at 33 keV, *ii)* in blue the XRD cone going through the conical anvil and *iii)* in green the XRF path through the side of the large anvil. The YAG Lasers follows the red beam path through the diamond anvils. The set-up on the beamline is shown on Figure 1b) with the same colour code as in Figure 1a).

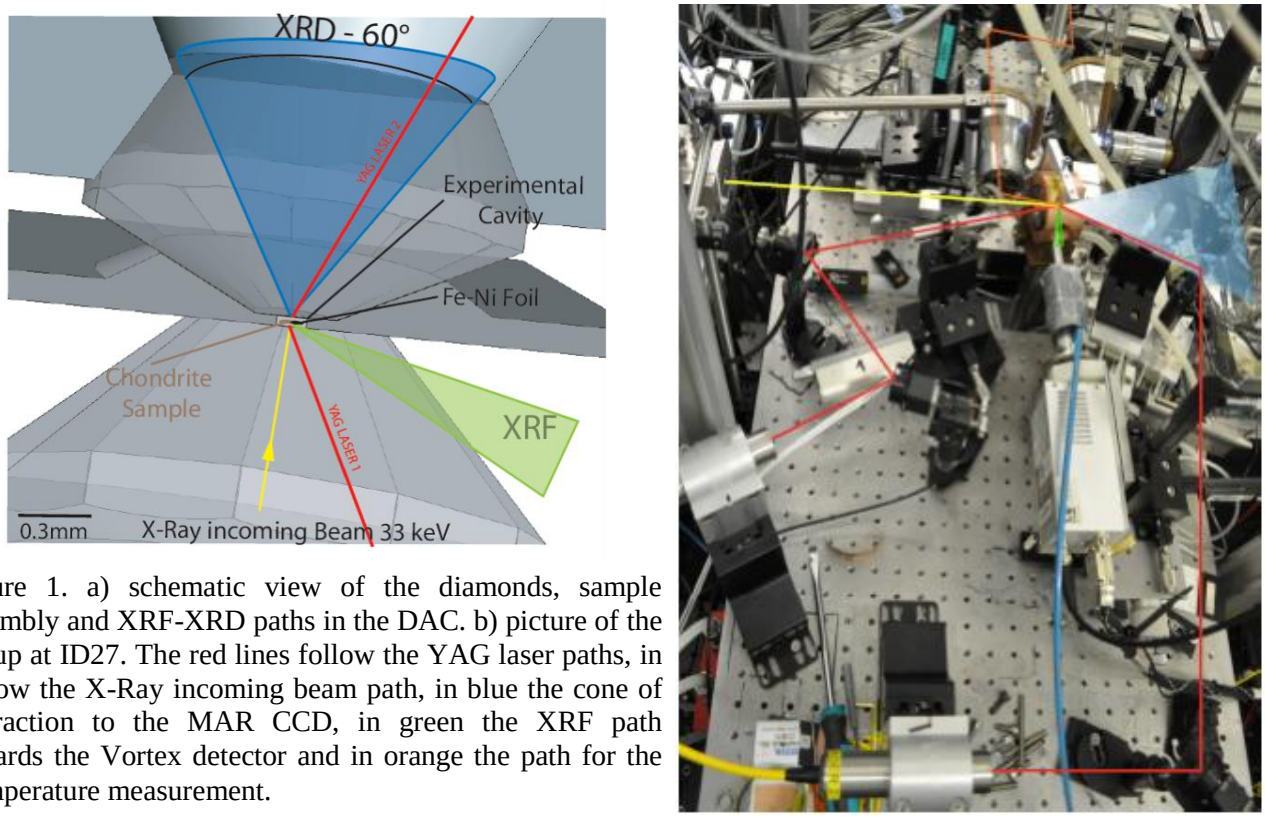

Figure 1. a) schematic view of the diamonds, sample assembly and XRF-XRD paths in the DAC. b) picture of the set-up at ID27. The red lines follow the YAG laser paths, in yellow the X-Ray incoming beam path, in blue the cone of diffraction to the MAR CCD, in green the XRF path towards the Vortex detector and in orange the path for the Temperature measurement.

The Vortex detector was equiped with a confocal capillary that enhances the signal to background ratio [5] and can provide detection limits of 1 to 2 ppm for Zr, Ru and Pd when measuring a standard solution. We tested the efficiency of the capillary compared to a classical collimator used on ID22. The results are shown on figure 2, and highlight the improvement on the signal to background using the capillary made for the DAC. With the conventional collimator the K-beta line of Palladium is practically undetectable while it becomes clearly resolved with the polycapillary in place. In addition, the whole background is considerably reduced, resulting in an order on magnitude higher signal intensity.

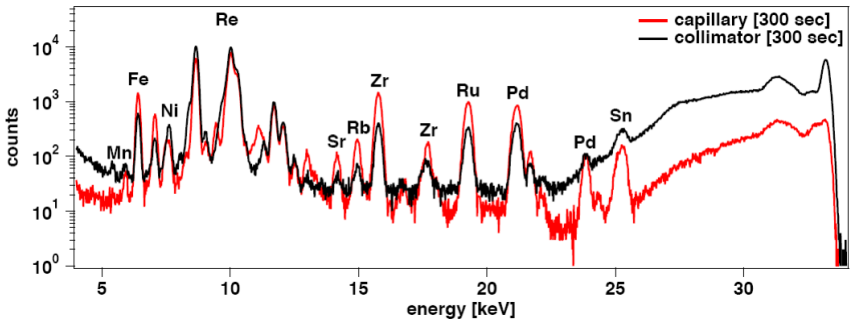

Figure 2. Spectrum acquired with the collimator in black in 300s and with the polycapillary in red in 300s.

The aim of the experiment was to measure in situ, i.e. during the melting, partitioning of Pd, Zr and Ru between a silicate and iron melt. The samples consist of a chip of Chondrite (meteorite) doped with Pd, Zr,

and Ru at a level of 1000 ppm and sintered in the Paris-Edinburgh press prior to the experiment, in contact with a piece of FeNi alloy foil. The samples were loaded side by side with a slightly overlapping of about 5 microns in the DAC sandwiched between two layers of MgO, used as transmitting medium and temperature insulator for the diamond.

During the 15 shifts we manage to collect data at 5 different pressures points (each pressure point represented a separate loading) from 10 to 56 GPa and up to 4200 K. During some of the experiments we manage to monitor the X-ray diffraction (XRD) pattern at the same time as the X-ray fluorescence (XRF) spectra in situ in the laser spot. We were able to monitor the evolution of the XRF through time, for about 40 min and also as well as during temperature increase to ensure a proper melting of the sample interface. After each melting event we paid close attention to map the sample chamber in order to qualify the distribution of the trace elements with respect to iron. The recovered samples will be analyzed ex situ with more accurate probes available at ID21 and ID22NI.
Preliminary results from the 5 samples are shown on figure 3 that illustrates maps obtained after laser heating *in situ* in the DAC (ID27) and ex-situ using the recovered sample anaylzed at ID21.

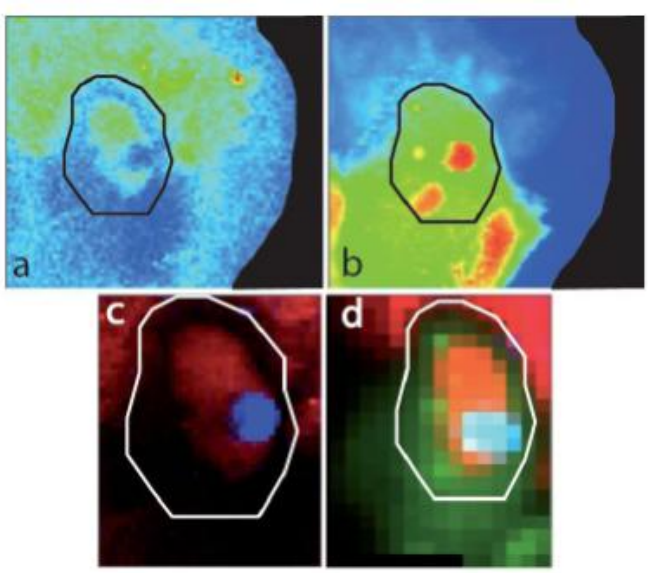

Figure 3. a) and b), partition maps of Ca and Fe carried out at the Fe K-edge at ID21. The black line shows the outline of the laser heated area. c) repartition map of Ca in red, and Palladium in blue below Fe K-edge carried out at ID21. Pd has been identified in one spot. d) repartition map of Zr (in red), Fe (in green) and Pd (in blue) carried out at 13 GPa in the DAC at ID27 at I K-edge.

The maps obtain ex situ at ID21 cotain complementary information on calcium partition in iron, while the in situ map allows tracking the repartition of Zr. The signal obtained for Pd is also much higher at ID27 than at ID21 and Ru, which has exactly the same repartition than Pd, was only detected on ID27. Nevertheless, both maps show that iron loving elements are highly concentrated in the enriched Iron zones. More analysis and processing of the data has to be undertaken espcially on the molten samples in orider to quantify the fractionation of the trace elements and its dependance on pressure.

References:

[1] Holzheid, A., P. Sylvester, et al. (2000). "Evidence for a late chondritic veneer in the Earth's mantle from high-pressure partitioning of palladium and platinum." Nature **406**(6794): 396-399.
[2] Righter, K. and M. J. Drake (1997). "Metal-silicate equilibrium in a homogeneously accreting earth: New results for Re." Earth and Planetary Science Letters **146**(3-4): 541-553.
[3] Righter, K., M. Humayun, et al. (2008). "Partitioning of palladium at high pressures and temperatures during core formation." Nature Geoscience **1**(5): 321-323.
[4] Petitgirard S. *et al.* 2009 "A diamond anvil cell for x-ray fluorescence measurements of trace elements in fluids at high pressure and high temperature." Review of Scientific Instruments **80**, 033906
[5] Wilke M. *et al.* 2010 "A confocal set-up for micro-XRF and XAFS experiments using diamond-anvil cells." Journal of Synchrotron Radiation Vol. 17 Pages 669-675