EUROPEAN SYNCHROTRON RADIATION FACILITY

INSTALLATION EUROPEENNE DE RAYONNEMENT SYNCHROTRON

ESRF

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://wwws.esrf.fr/misapps/SMISWebClient/protected/welcome.do*

Deadlines for submission of Experimental Reports

Experimental reports must be submitted within the period of 3 months after the end of the experiment.

Experiment Report supporting a new proposal ("relevant report")

If you are submitting a proposal for a new project, or to continue a project for which you have previously been allocated beam time, you must submit a report on each of your previous measurement(s):

- even on those carried out close to the proposal submission deadline (it can be a *"preliminary report"),*
- even for experiments whose scientific area is different form the scientific area of the new proposal,
- carried out on CRG beamlines.

You must then register the report(s) as "relevant report(s)" in the new application form for beam time.

Deadlines for submitting a report supporting a new proposal

- 1st March Proposal Round - **5th March**
- 10th September Proposal Round - **13th September**

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.

Instructions for preparing your Report

- fill in a separate form for each project or series of measurements.
- type your report in English.
- include the experiment number 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:** **Highly siderophile partitioning during core formation of the Earth**	**Experiment number**: ES 1166
Beamline: ID16	**Date of experiment**: from: 03/06/2022 to: 07/06/2022	**Date of report**: 28/07/2022
Shifts: 12	**Local contact(s)**: Valentina Bonino	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

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Sylvain Petitgirard (ETH)

Report:

The context of our work is the differentiation of the planet into its two main reservoirs that are the mantle and the core. At that time, about 4.5 billion years ago, elements were partitioned between the two reservoirs depending on their chemical affinity for silicate (lithophile element) or iron (siderophile element). Most of the respective compositions of the mantle and the core were established once the differentiation ceased, about a hundred million years after the beginning of accretion. However, the abundance of Highly Siderophile Elements (HSEs) in the mantle is at odds with the generally accepted scenario, whereby siderophile elements segregated into the forming core. Indeed, they display a chondritic relative abundance in the mantle. One possible explanation for the overabundance of HSEs in the Earth's mantle could be that their core-mantle partitioning was affected by the extreme pressure and temperature of the Earth's differentiation, as it is the case for moderately siderophile elements (e.g. nickel, cobalt[1]). This has never been tested experimentally at the accurate conditions of the differentiation, and could potentially change our view of the accretion and differentiation of the planet.

We aim at measuring low concentrations of HSEs (namely rhenium, iridium, palladium and gold) dissolved in the silicate phase of high pressure and high temperature (HP–HT) runs in equilibrium with a metallic phase. Our experimental runs are synthetized at various P and T using laser heated diamond anvil cell technique (LH-DAC) in order to decipher these effects on the metal–silicate partitioning of HSEs during Earth's differentiation. Extrapolations of previous experiments performed at lower P–T suggest that the chondritic abundance of HSEs in the mantle could be controlled by metal-silicate equilibrium instead of calling for a late delivery of chondritic material[2,3]. We want to directly test this hypothesis at the conditions of core-mantle differentiation ($P > 40$ GPa and $T > 3000$ K). We expect very low amounts of HSEs in the silicate of our runs (ppm level), and due to the geometry of our samples (lamellae with silicate phases of about 2x2x3 microns, see Fig. 1) the use of nanobeam analyses is mandatory. During a first session in April 2021, we have established a procedure to efficiently measure diluted HSEs in different standards, and we highlighted the importance of the geometry of the runs in order to obtain satisfactory results. These results were recently published[4].

The goal of this second round of measurements was to analyze actual high P–T samples synthetized using LH-DAC and extracted by Focused Ion Beam (FIB), see Fig. 1a. We brought to the beamline fourteen HP–HT samples synthesized between 40–80 GPa and 3500–4900 K, covering the putative conditions of core–mantle differentiation. The starting material used to synthesize these samples consisted on synthetic silicate and iron alloys doped in Pd, Au, Re and Ir. They consisted on 3 microns-thick FIB lamellae on which two phases are visible: a quenched molten silicate and a quenched molten metal that represent a snapshot of the Earth's core–mantle differentiation (Fig. 1b). Along with the samples, we analyzed several standards that were already presented in the previous report for beamtime ES 998.

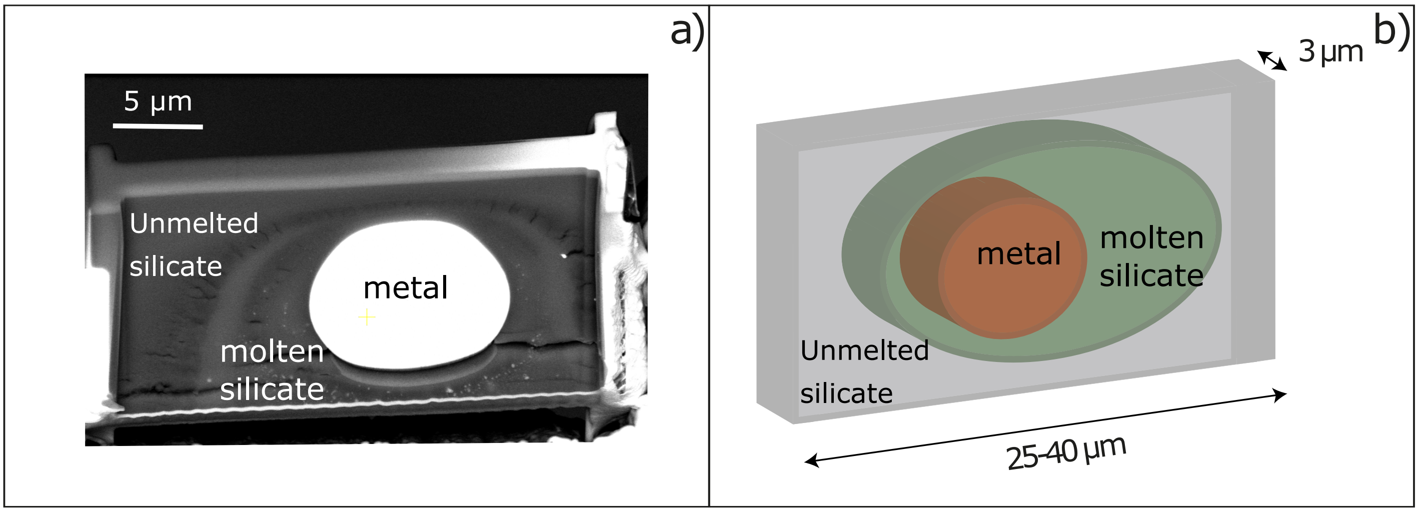

Figure 1: a) FIB lamella of a HP-HT sample synthesised using LH-DAC with both metallic and silicate phases visible. b) Schematic view of the sample to illustrate its geometry.

Nano XRF measurements were performed on ID16B at the European Synchrotron Radiation Facility (ESRF). The spatial resolution of the beam is about 60x60 nm and was combined with the high flux in the monochromatic (pink) beam mode. The X-ray beam was set at 29.5 keV, the brilliance was about 7.10^{10} photons.s^{-1}, and we used Si and Ge detectors. Using this technic, it is possible to map large area (up to 30 x 20 microns in our case) of our samples and standards with high sensitivity for heavy elements studied here. We could reach the K-lines of Pd and the L-lines of Re, Au and Ir. In terms of geometry, the samples and standards were mounted on Cu-grids during the FIB preparation, and grids were subsequently taped to a Si_3N_4 membranes using double sided tape. The membrane itself was attached to a PEEK holder using Kapton tape.
Using nano XRF, we acquired high precision chemical maps of the samples (500 to 1000 ms per pixel) from which we can extract Regions Of Interest (ROIs). With the nano XRF measurements, it is possible to retrieve the concentration of several siderophile elements diluted into the silicate melt. In order to do so, we have to use the software PyMCa developed by the ESRF[5]. To retrieve the concentration of HSEs, it is necessary to have the composition of the major elements present in our runs. Given the specific geometry and size of our samples, a FEG probe is needed, and the measurements will be done in September. Once we have the major elements composition of our runs, we can use one of them (such as Fe) as an internal standard in the PyMCa software, and determine the concentration of HSEs in the silicate phases. This will then allow us to calculate the partition coefficient of the HSEs between metal and silicate, and evaluate how it evolves with pressure and temperature. These results will be the first on of their kind on those elements, and will be a milestone in our comprehension of the history of Earth's formation and differentiation.

Bibliographie

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