EUROPEAN SYNCHROTRON RADIATION FACILITY

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 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:** **Incorporation of noble gases into Earth's lower mantle phases**	**Experiment number:** ES 694
Beamline: ID24 BM23	**Date of experiment:** from: 21.11.2017 to: 28.11.2017 from: 25.02.2018 to: 28.02.2018	**Date of report:** 17/02/2020
Shifts: **18**	**Local contact(s):** Angelika D. Rosa	*Received at ESRF:* *19/02/2020*

Names and affiliations of applicants (* indicates experimentalists):

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Report:

Noble gases and their isotopes are important traces for the formation and evolution of the Earth and its atmosphere [**1**]. However, their storage at depth are still debated [**2**]. The solubility of noble gases in crystalline lower mantle phases at high *P/T* conditions is therefore a key parameter necessary to evaluate the noble gas storage capacity of the Earth's mantle. We have recently performed an *in-situ* XAS experiment on the solubility of Kr into iron-alloys and its partitioning between metallic iron and (Mg1-x,Fex)O to simulate the earliest conditions of Earth's core formation (**ES-435**). **The results of this previous experiment and part of the present ones have been published [3,4].** In this work(s), we could show based on analysis of the quenched samples (elemental concentrations and Kr-K edge XAS data) and thermodynamic modelling that (Mg1-x,Fex)O, the second most abundant phase of the Earth's lower mantle, exhibits a high storage capacity for noble gases and might thus be a likely host at depth.

ID24 run:

We have conducted additional *in-situ* high *P/T* experiments on the energy dispersive EXAFS beamline ID24 of the ESRF in order to complement this previous results and to investigate the noble gas incorporation mechanism in-situ at high *P/T*. The uptake of the noble gases Ne, Ar and Kr in Fe, FeO and $(Mg_{1-x},Fe_x)O$ were investigated between 35 and 85 GPa and temperatures up to 2500 K using the laser-heated diamond anvil cell and the set-up installed at ID24 [**5**]. The energy of the beamline was tuned to the iron absorption edge (7.112 keV). The incorporation of noble gases was deduced from the edge position change that is directly related to the inter-atomic distance. Our previous results [**3**] revealed that noble gases should be incorporate in oxygen vacancies of (Mg1-x,Fex)O. This mechanism would directly affect the local atomic environment of the next-nearest neighbour iron atom and therefore should be detectable at this edge. In order to monitor these subtitle changes in the absorption edge-position we used a Si(311) polychromator crystals that provides the highest energy resolution. In this optical configuration ID24 offers a highly focused beam (7x5 μm^2) at the Fe K-edge compatible with stable and uniform laser heating. The reduction in flux required the use of samples with a higher iron content than previously foreseen (pure FeO and Fe).

Prior to the heating runs, we acquired a set of high-quality high pressure data on FeO contained in neon up to 40 GPa (**Figure 1**). This data set serves as a reverence to interpret the high *P/T* data. We have successfully performed 18 heating runs in a pressure and temperature range of 30-85 GPa and 1500-2500 K. Heating durations ranged between 15 and 30 minutes to ensure equilibrium reactions. During heating XAS data were acquired every minute, with an acquisition time of 10 ms per spectrum and a number of 20 spectra that were accumulated in order to improve the data quality. In **Figure 2** an example of a set of in-situ Fe K-edge spectra acquired during laser-heating is shown for krypton incorporation into a compressed pellet of FeO that has been placed on a KCl disked. In the first 6 minutes of the heating run at 2000 K and 35 GPa the spectra show no changes (blue and red spectra). Upon further heating important changes in the pre-edge and edge region are observed that include a change of the pre-edge region (7115 eV) possibly indicating an oxidation of Fe^{2+} to more Fe^{3+} in FeO, which could be related to the formation of neutral oxygen vacancies as Schottky defects and the incorporation of Kr. Moreover, the shape of the white line changes: It develops a more pronounced shoulder at 7125 eV and the second XANES peak vanishes (green spectrum compared to the red or blue). These changes are also manifested in the spectrum acquired after T quenched (violet spectrum). This suggest a non-reversible change of the local environment of iron during the heating run and possibly linked to the incorporation of krypton.

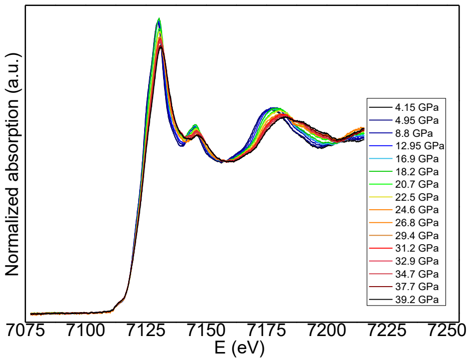

Figure 1. *Fe-Kedge XANES data acquired on FeO contained in neon up to 40 GPa.*

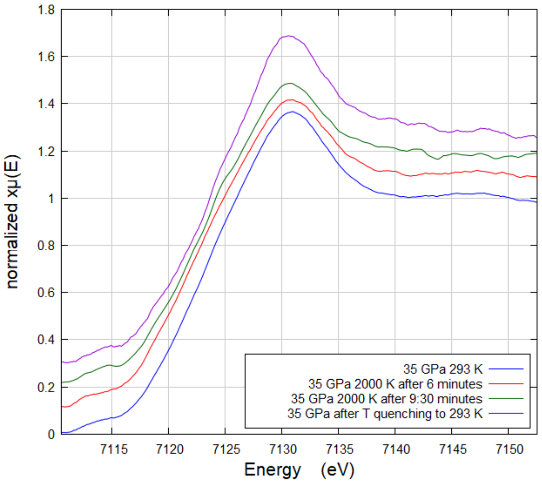

Figure 2. *Fe-kedge data on FeO during laser-heating in contact with krypton at 40 GPa. Note the change of pre-edge features and edge features upon heating that indicate most likely the incorporation of krypton as observed previously on quenched samples [**3**].*

The analysis of the XANES data is currently ongoing and the experimental data will be complemented with full multiple scattering calculations as well as concentration measurements of noble gases retained in the quenched samples. The results will provide the first *in-situ* observations on the incorporation of noble gases in oxide phases at lower mantle conditions and a validation of the proposed mechanism in our previous work [**3**]. Moreover, the data will allow to derive information on the diffusion of noble gases at lower mantle conditions which remain presently completely unconstrained.

BM23 run

Originally we planned to investigate the incorporation mechanism of krypton and xenon in the laser-heated samples maintained at high pressure using EXAFS at BM23. The time-span between the two beamtimes (November-February) was however too long to reserve the cells for the measurements. Therefore we have used the beamtime at BM23 to investigated the compression behaviour of xenon up to 150 GPa from EXAFS and XRD, which is similarly important to deduce their incorporation mechanism in lower Earth's mantle phases. For the experiments, the X-ray beam was tuned to the energy of the Xe K-edge (34.5 keV) using a double-crystal fixed exit monochromator equipped with two Si(311) crystals. Beam focusing to 6×6 μm^2 and harmonic rejection was achieved through a Kirkpatrick Baez mirror system with Pt coating inclined to 2 mrad. EXAFS data up to a k-range of 16 $Å^{-1}$ were acquired in transmission mode using ionchambers filled with a gas mixture of krypton and nitrogen in appropriate proportions (Figure 3). XRD data were acquired in the sample and on the Re gasket for pressure calibration at 34 keV using a MARCCD detector.

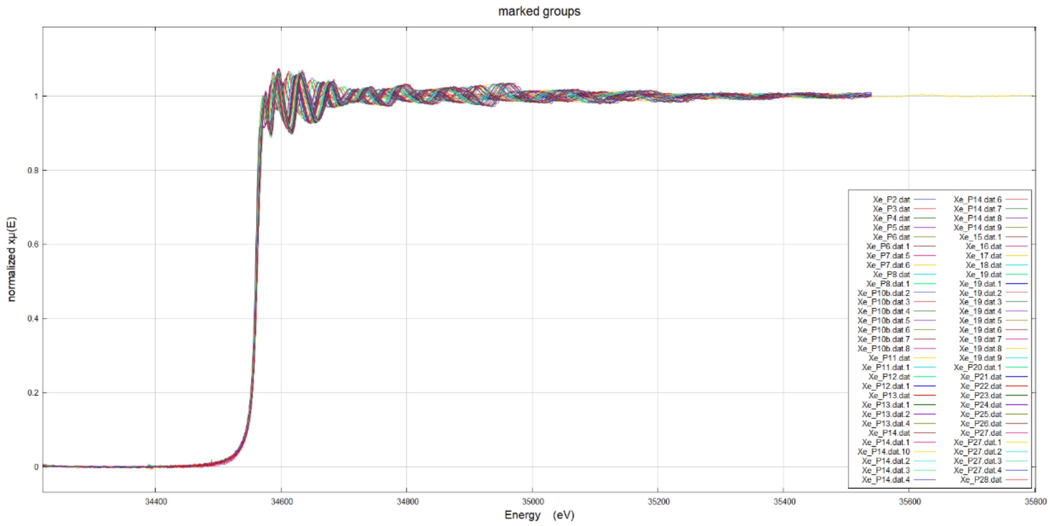

Figure 3. *Xe K-edge data acquired from 3 to 150 GPa in ~5 GPa steps.*

The EXAFS data analysis has now been finalized and revealed important changes of the compression mechanism in xenon as previously observed for krypton from XRD and XANES [**4**]. We have also analysed krypton EXAFS data acquired at ID24 (**ES-435**) and compared the results to those obtained on xenon. For both phases we observed compression anomalies with increasing volume fraction of the hcp phase. These anomalies are more pronounced at a local scale (seen by XAS) as those observed in the bulk lattice from XRD data. **The results are currently compiled and close to submission to the journal Physical Review B.**

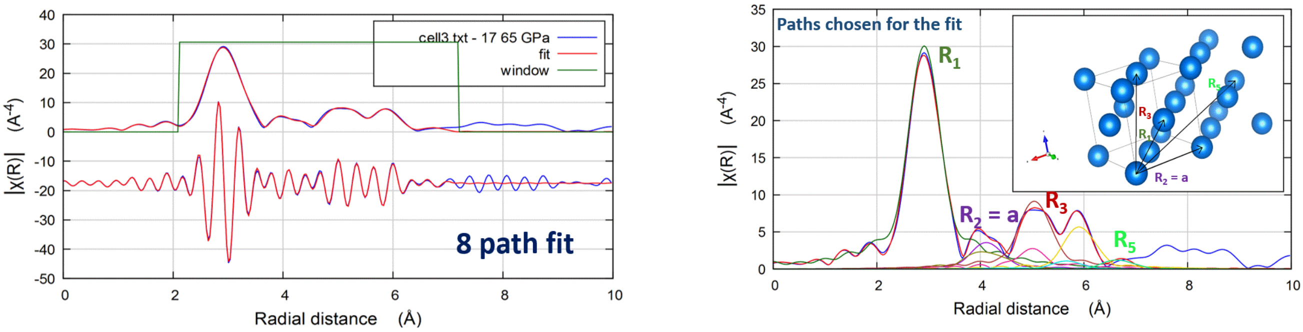

Figure 4. ***Left:*** *Fourier transform (FT), back Fourier transformed phase and fit of the krypton K-edge spectrum EXAFS spectrum taken at 65 GPa (blue and red lines).* ***Right****: Fourier transform phase of the EXAFS spectrum as above (blue line) together with the Fourier transform of the eight individual paths used in the EXAFS fit. For clarity, an inlet with the location of these paths in the FCC unit cell is shown.*

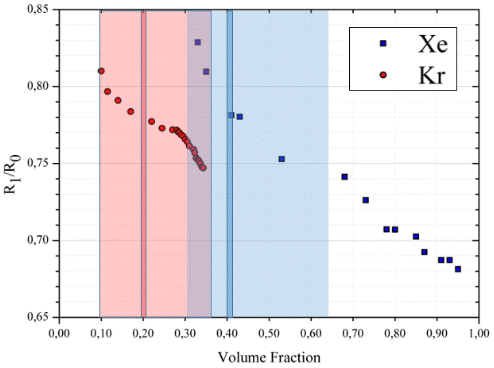

Figure 5. *Evolution of* R_1/R_0 *for fcc krypton and xenon extracted from EXAFS analysis as a function of the volume fraction of the hcp phase. The latter has been extracted from XRD data. Kr data have been translated by 0.26 along y for better comparison to Xenon data. Note, the similarities in trends for Kr and Xe. The red and blue shaded area and line delineate the regions and points in which an anomalous compression behaviour has been observed in the XRD data [i.e.,* ***4*** *for Kr].*

Acknowledgements

We want to thanks the ESRF for allocating beamtime to this experiment and especially the staff of the beamline ID24 and BM23, and J. Jacobs for their assistance.

References:

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