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:** Revealing crystal structure of novel high-pressure tungsten borides	**Experiment number**: **HC-5074**
Beamline: ID11, ID18	**Date of experiment**: from: 27 June 2023 to: 03 July 2023	**Date of report**: 10.09.2023
Shifts: 12/15	**Local contact(s)**: Pierre-Olivier Autran / Ilya Kupenko, Georgios Aprilis	*Received at ESRF:*

Names and affiliations of applicants (* indicates experimentalists):

Dr. Elena Bykova*

Mineralogie/Kristallographie, FB 11, Goethe-Universität Frankfurt

Report:

The aim of the proposed combined experiment at ID11 and ID18, was to apply methods of single-crystal X-ray diffraction (XRD) and Moessbauer spectroscopy in laser-heated diamond anvil cells (DACs) in order to reveal a role of iron oxides as structural prototypes for high-pressure silicates. A growing body of evidence suggests that a majority of lower mantle and some of transition zone minerals have structural analogs among iron oxides which form at much milder conditions. On the other hand, the amount of recently discovered iron oxides outnumbers their silicate counterparts. Therefore the objective of the current experiment was to synthesize novel iron silicates isostructural to novel iron oxides, and to characterize their crystal structure and compressional behavior.

We have investigated the reactivity between iron oxides (Fe_3O_4, Fe_2O_3) with quartz (SiO_2) at pressures ranging from 20 to 150 GPa and temperatures up to 3000 K. Where it was possible we refined Fe,Si-atomic occupancies and determined approximate Fe/Si ratios in the structures. Our preliminary findings suggest that between 30 and 150 GPa no iron silicates can be synthesized by the reaction between simple oxides. Above 50 GPa, we detected only minor incorporation of Si into the crystal structure of the high-pressure polymorph of Fe_3O_4 (sp. gr. *Bbmm*). Structural refinement, based on single-crystal XRD data, indicates that silicon fills the octahedral position with an occupancy of 5-10%, which approaches the detection limit for XRD methods.

On the other hand, we have detected a reaction between Fe_2O_3 and SiO_2 at 20 GPa, resulting in the formation of a novel phase with the composition $Fe_{1.5}Si_2O_6$ that adopts a structural type of clinoenstatite. The structure, as shown in Fig. 1 (left), is similar to $Fe_2Si_2O_6$ (Fig. 1, right), which was previously described by Pakhomova *et al.* (*Am. Miner.*, **102**, 666, 2017). The crystal structure of $Fe_2Si_2O_6$ features two octahedral sites, each occupied by Fe^{2+} cations. In contrast, $Fe_{1.5}Si_2O_6$ has one octahedral site occupied by Fe^{3+} and one 8-fold coordinated site that is filled by only half of Fe^{2+} cation. Compared to $Fe_2Si_2O_6$, $Fe_{1.5}Si_2O_6$ has a 2.6% larger unit cell volume.

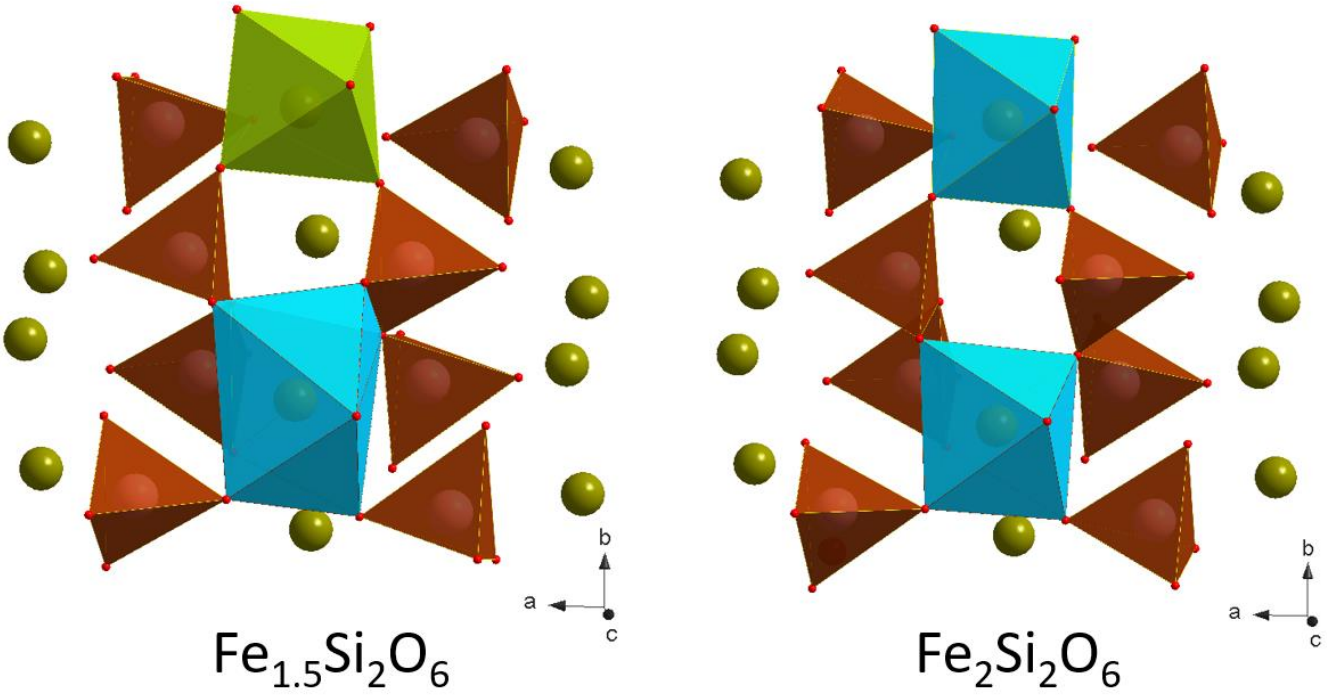

Figure 1. Fragments of crystal structures of $Fe_{1.5}Si_2O_6$ (current work) and $Fe_2Si_2O_6$ (Pakhomova *et al. Am. Miner.*, **102**, 666, 2017). The crystal structures consist of corner-sharing SiO4-tetrahedral (brown) chains. In $Fe_2Si_2O_6$, there are two distinct octahedral sites occupied by Fe^{2+} cations (blue octahedra). However, in $Fe_{1.5}Si_2O_6$ one octahedral site is occupied by Fe^{3+} (green); Fe^{2+} has an 8-fold coordination and occupies the position by only ½.

Our preliminary results indicate that reactions between pure iron oxides and silica are hindered above 30 GPa. However, studies on shock-induced minerals suggest that the formation of iron silicates with structures of complex iron oxides is plausible at extreme conditions. The mineral silicate elgoresite, $(Mg,Fe)_5Si_2O_9$, found in the Suizhou L6 chondrite, contains Si in presence of Mg. Therefore, in our next experiments, we aim to investigate the influence of Mg on the solubility of Si in iron oxides.