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:** Oxidation state of the deep mantle through inclusions in diamonds	**Experiment number**:
Beamline:	**Date of experiment**: from: 09.09.2020 to: 15.09.2020	**Date of report**:
Shifts:	**Local contact(s)**: Dimitrios Bessas	*Received at ESRF:*
Names and affiliations of applicants (* indicates experimentalists): Kiseeva Ekaterina (University of Oxford)		

Report:

This experiment took place remotedly during pandemics. During this tie beam scientists Dimitrios Bessas, Aleksandr Chumakov and Georgios Aprilis analysed a set of individual inclusions in ultra-deep diamonds. These were: majoritic garnets and ferropericlases. Overall, more than 10 inclusions were analysed.

As a result, the PI has written a paper that was submitted to Nature Communications. It was reviewed and received critical, but positive reviews. The second round of reviews is still in process (as per 11.09.2022). All beam scientists are within co-authors of this article and the PI is in touch with all updates.

Scientic report:

The lower mantle comprises > 50% of Earth's volume, and compositionally is considered largely homogeneous and primitive or pyrolitic (McDonough, 2016). It has been acknowledged, however, that modern-day subducted slabs can penetrate deep into the lower mantle, causing heterogeneities and locally oxidised regions (van Keken et al., 2014). The mineralogy of the upper part of the lower mantle is relatively simple: in a pyrolitic system it should consist of approximately 70 vol% bridgmanite ($(Mg, Fe)SiO_3$), less than 20 vol% ferropericlase $(Mg,Fe)O$ and less than 10 vol% Ca-Si-perovskite ($CaSiO_3$)(Ringwood, 1991). Diamonds and their inclusions are the only available natural samples from Earth's lower mantle. Of more than 300 inclusions reported to date to have derived from the lower mantle, ferropericlase is the most common (Kaminsky, 2012). Figure 1 shows the distribution of Mg# in magnesiowüstite (Mg# < 50) and ferropericlase (Mg# > 50) inclusions in lower mantle diamonds reported in the literature.

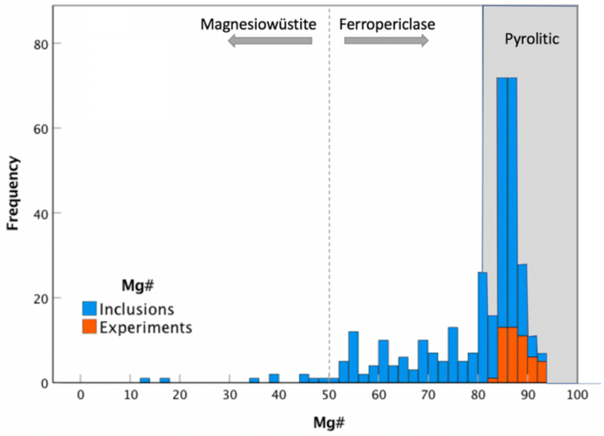

Figure 1. Mg# of (Fe,Mg)O inclusions in diamonds from localities worldwide and selected experimental studies in pyrolite and fertile lherzolite KLB-1 compositions.

The wide range of compositions displayed in Figure 1 and the extreme Fe-enrichment (up to 93 wt% FeO) is unlikely to have resulted from a single mechanism. As a consequence, only a fraction of the reported inclusions could be in equilibrium with bridgmanite in pyrolitic lower mantle or with garnet and ringwoodite at the mantle transition zone, suggesting that the sublithospheric mantle is likely to contain highly heterogeneous regions with non-pyrolitic compositions. These regions may contain transported sediments and oceanic crust from the surface of subducting slabs, which are also likely to be more oxidised than the ambient sublithospheric mantle (Kiseeva et al., 2018).

The purpose of this study is to measure the oxidation state of iron in ferropericlase and magnesiowüstite inclusions in diamond displaying a range of Mg# and to explore the link between their compositions and iron oxidation state. This has particular importance for the storage of oxidised material in the deep mantle, as well as for the speciation of deep mantle fluids, diamond formation, rheological and melting properties at the depths inaccessible for direct sampling.

Methods and results

Five diamonds, 4–5 mm in size, recovered from alluvial deposits in Sao Luiz, Juina, Brazil were selected for this study. The diamonds were polished flat on both sides so that the inclusions were exposed to the surface prior to analysis. Their size ranged between 20 and 80 μm. Three inclusions (SL14, SL14_2 and SL24) are ferropericlase with Mg# = 79–85, and two inclusions (SL82 and SL5_2) are magnesiowüstite with Mg# = 16 and 40, respectively.

All inclusions were initially studied by X-ray diffraction. Mg-rich inclusions SL14, SL14_2 and SL24 contained monophase ferropericlase single crystals. The ferric iron content of these inclusions, analysed by Mössbauer spectroscopy, was below the detection limit of ~0.03 Fe^{3+}/Fe_{tot}.

Single crystal X-Ray diffraction at the P02.2 beamline, DESY, identified single crystal inclusions with the sizes larger that 2–5 μm based on X-ray absorption on inclusions exposed at the diamond surface and inside the diamond. X-ray diffraction of SL82 and SL5_2 confirmed the presence of two coexisting monocrystalline phases, magnesiowüstite and magnesioferrite. X-ray absorption was used in order to locate and centre on X-ray beam inclusions and the sizes were determined from absorption scans. These scans show different phases spatially separated (i.e. that is not intergrowth) but crystallographically orientated ([111] direction of spinel-structured phase parallel to the [100] direction of the cubic phase). This relationship indicates that they magnesiowüstite and magnesioferrite are cogenetic. Based on XRD and SMS data, magnesioferrite has a magnetite structure or inverse spinel, with some divalent iron substituted by magnesium. Indirect estimates from the integrated peak areas of Mössbauer spectra for SL82 sample (Figure 2A) are in a good agreement with X-ray diffraction data, identifying two phases containing iron. The signal for SL5_2, however, is too low to resolve for the ferric iron doublet and the fit of SL 5_2 shows only magnesiowüstite (Figure 2B). Relative areas in the Mössbauer spectrum (Figure 2A) combined with chemical compositions allow us to estimate the proportion of magnesiowüstite in the SL82 inclusion as 42% (considering only the molar ratio of iron-bearing phases, which are magnesiowüstite and magnesioferrite 42% and 58%, respectively). Nevertheless, scanning electron microscopy showed no exsolution phases on the surface of inclusion SL82 (Supplementary figure 4). Thus, we interpret SL82 and SL5_2 inclusions as intergrowths of magnesiowüstite with magnesioferrite.

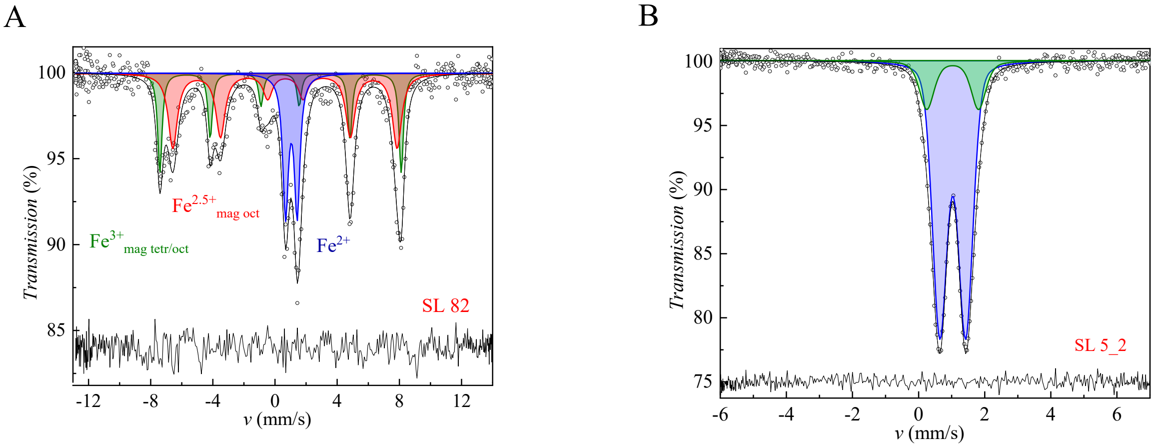

Figure 2. Mössbauer spectra of inclusions SL 82(A) and SL5_2 (B). (A) Blue doublet corresponds to Fe^{2+} in the octahedral site of magnesiowüstite. Green magnetic sextet corresponds to Fe^{3+} in octahedral and tetrahedral sites of magnesioferrite, red sextet corresponds to $Fe^{2.5+}$; i.e., $Fe^{3+}\leftrightarrow Fe^{2+}$ rapid electron hopping between octahedral sites of magnesioferrite. (B) Green and blue doublets correspond to Fe^{2+} in the octahedral site of magnesiowüstite.

Conclusions

We argue that the wide range of Fe concentrations observed in (Mg,Fe)O inclusions in diamonds and the appearance of magnesioferrite in Fe-rich inclusions result from oxidation of ferropericlase triggered by the introduction of subducted material into sublithospheric mantle.