



	Experiment title: Investigation of iron oxidation state in Mg-chromite inclusions in lithospheric P-type diamonds: implications for diamond formation and the redox state of the upper mantle	Experiment number: ES-1333
Beamline: ID18	Date of experiment: from: 24/01/2023 to: 30/01/2023	Date of report: 07/09/2023
Shifts: 18	Local contact(s): Ilya Kupenko	<i>Received at ESRF:</i>
Names and affiliations of applicants (* indicates experimentalists): Giulia Marras, Department of Earth Sciences, Sapienza University of Rome Vincenzo Stagno, Department of Earth Sciences, Sapienza University of Rome Antonio Angellotti, Department of Earth Sciences, Sapienza University of Rome Federica Benedetti, Department of Earth Sciences, Sapienza University of Rome		

Report:

The focus of the experiment *ES-1333* performed at ID18 was the determination of the iron oxidation state of Mg-chromite inclusions in natural lithospheric diamonds to develop a model of diamond formation and carbon freezing through redox processes involving spinel minerals. Nine diamonds from the Udachnaya kimberlitic pipe (Siberian craton) were selected based on the occurrence of multiple dark inclusions (Fig. 1) and their size varying from 50 to 200 microns. Diamonds with some exposed inclusions after polishing were also preferred for which the chemical composition could be directly analyzed by electron microprobe. Few tiny almost transparent inclusions were also observed under the microscope but not analysed. The proposed measurements were successfully conducted with a $6 \times 15 \mu\text{m}^2$ focused beam aligned with the camera with a total of 18 collected Mössbauer spectra. In detail, we measured 1) multiple Mg-chromite inclusions (both exposed on the polished surface and entrapped) in the same diamonds and 2) performed rim-to-core analyses on two large inclusions. Spectra were collected in about 3 hours and were fitted following literature models, including two doublets for Fe^{2+} and one doublet for Fe^{3+} (Fig. 1). The contribution from Fe impurities in the Be-lenses was well constrained by fitting an extra singlet using previous background measurements, as we also discussed in a manuscript recently published on *Lithos*, including data from ID18 (<https://doi.org/10.1016/j.lithos.2023.107337>). These measurements were, then, integrated with chemical analyses on the exposed inclusions.

Our results can be summarized as follows,

- The $\text{Fe}^{3+}/\sum\text{Fe}$ ratio of Mg-chromite inclusions ranges from 0.07 to 0.22 ($\pm 0.02-0.03$);
- One spectrum shows the contribution of olivine, for which a more accurate investigation is needed;
- Different inclusions trapped within the same host diamond show variable $\text{Fe}^{3+}/\sum\text{Fe}$ ratios with the largest difference being 0.12;
- We were able to determine a 0.03 difference in $\text{Fe}^{3+}/\sum\text{Fe}$ between rim and core.

This last observation is worthy of further investigation as rim-to-core variations might reflect changes in the redox conditions during diamond growth.

Our calculations of the local oxygen fugacity are made possible thanks to the collected data and resulted in $\log f_{O_2}$ lower (about -2 log units FMQ) than the Udachnaya spl-peridotite xenoliths from which these diamonds were extracted, implying that these inclusions are likely to be protogenetic. On the other hand, a stronger application of current oxythermobarometry would require the determination of $Fe^{3+}/\Sigma Fe$ also in olivine, orthopyroxene and clinopyroxene also entrapped in the same diamonds.

Finally, the collected data will be integrated with already available synchrotron X-ray tomography and diffraction analysis aimed to elastic barometry applications for accurate P-T estimates.

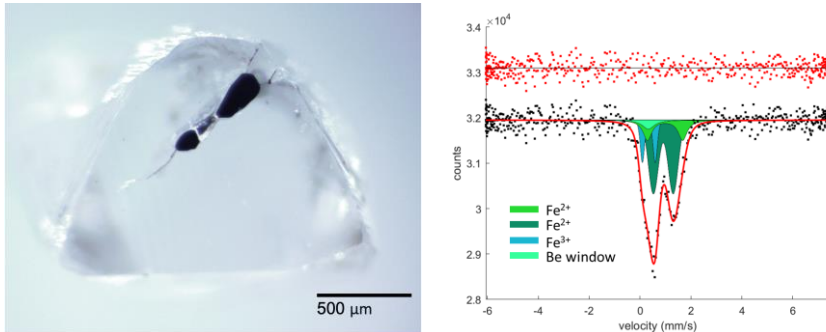


Figure 1 P-type diamond with inclusions analyzed at ID18 (left) and example of Mössbauer spectrum acquired on a Mg-chromite during experiment ES-1333 (right).

The feasibility of the proposed research certainly relies on the beamline set-up, in particular on the possibility of easily centering the selected inclusions using the camera aligned with the X-ray. For this reason, the beamtime session was efficient and allowed measuring the $Fe^{3+}/\Sigma Fe$ of all the selected Mg-chromite inclusions achieving the beamtime goal. The presence of additional minerals was noted while loading the sample holders thanks to the high zoom of the provided microscope sited in the preparation lab. To date, the $Fe^{3+}/\Sigma Fe$ of mineral inclusions in P-type diamonds like olivine, orthopyroxene and clinopyroxene remains poorly investigated and we anticipate this being the target of a next beamtime request. Further investigations of these mineral inclusions could help to constrain not only the P - T - f_{O_2} conditions for diamond formation but also the partitioning behavior of Fe^{3+} among minerals in diamonds.

Some preliminary analyses on different samples were also performed that allowed to end on-going projects. Among these, three analyses were conducted on mineral inclusions in a lithospheric diamond from Brazil, for which in situ synchrotron single crystal X-ray diffraction assisted by tomography, micro-FTIR and Raman, electron microprobe and laser ablation data were already available. A manuscript is going to be submitted. Two $Fe^{3+}/\Sigma Fe$ measurements of spinel inclusions in olivine crystals were performed with the aim to retrieve the redox conditions of a wehrlitic sample from Mt. Vulture. These analyses are included in a paper recently published in the European Journal of Mineralogy (<https://doi.org/10.5194/ejm-35-665-2023>). One measurement was conducted on a carbonate-silicate glass for which the atomic structure, Raman and FTIR data were already available. The result was included in a manuscript submitted to Geochimica et Cosmochimica Acta (Stopponi and coauthors, under review). Finally, preliminary analyses were performed on synthetic charges polished on both sides to expose coexisting glass (with basalt composition) and minerals. These test analyses allow the Fe^{3+} partitioning ($D_{Fe^{3+}}$) between glass and mineral to be determined by Mössbauer measurements. The successfully acquired spectra on the synthetic glasses and the coexisting pyroxenes will be used to support the next beamtime application, but they will be also presented in the frame of the AGU fall meeting (2023).