



	Experiment title: The redox state of marble-cake mantle: clues from deeply recycled C-bearing crustal materials	Experiment number: ES-958
Beamline: ID18	Date of experiment: Due to restrictions related to containing the COVID-19 pandemic, the experiment has taken place remotely from: 23/09/2020 at 8.00 a.m to: 29/09/2020 at 8 a.m.	Date of report: 05/03/2021
Shifts: 18	Local contact(s): Dr. Dimitrios Bessas	<i>Received at ESRF:</i>
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Report:

1. Introduction

The oxygen concentration in our atmosphere strongly depends on the long-term carbon cycle. One of the main carbon reservoirs is the Earth’s mantle, but we still poorly know the mechanism by which carbon moves from one portion to another of this deep repository. Also, the stability of graphite/diamond, relative to the more reactive CO₂ or carbonate is controlled by the oxidation state of the mineral assemblage.

2. Experiment details

We measured 5 samples of diamond- and graphite-bearing clinopyroxenites from Beni Bousera and Northern Apennines, which present native carbon (diamond/graphite) and sulphides showing decrepitation aloes of CH₄-bearing inclusions. The SMS measurements at the beamline ID18 was mandatory since pristine clinopyroxenes occur as micron-sized inclusions in garnets, and are not larger than 60 µm in diameter. We measured an average of 2 different points per garnet and 2 per clinopyroxene (5 samples) for a total of ~ 20 Mössbauer spectra on 150 µm thick double polished sections. We used the high-resolution cameras (aligned with the X-Rays) present at ID18 to perfectly locate the areas to analyse (garnet-clinopyroxene pairs and garnet measurements close and far from CH₄ inclusions). The experiments were carried out at ambient conditions with Be lenses and at velocities of ± 5 mm/s calibrated using 25 µm thick natural α-iron foil. The X-ray beam-size was 9 x 4 µm. The SMS linewidth was controlled before and after each sample measurement using K₂Mg₅₇Fe(CN)₆, whose Mössbauer spectrum consists of a single line. The data were then fitted with the software MossA with the full transmission integral and a Lorentzian-squared source line shape [1] in order to determine the hyperfine parameters for the analysed phases.

The experimental session was so successful that we had the possibility to extend further measurements on 4 garnet-clinopyroxene pairs (~ 10 Mössbauer spectra) in ultrahigh pressure carbonate-bearing garnet peridotites from Alpe Arami (Central Alps, Switzerland). Finally, a very challenging and successful experiment has been performed by measuring micron-sized magnetite inclusions in high pressure harzburgites from Almirez (Bètic Cordillera, Spain) thanks to the expertise and advice of the local contact Dr. Dimitrios Bessas.

3. Results

As demonstrated by [2], the redox state of high-pressure peridotites and pyroxenites is traditionally determined from the Fe³⁺ content of garnet in equilibrium with olivine and orthopyroxene. However, several phases besides garnet incorporate ferric iron, particularly clinopyroxene. Also, garnet and clinopyroxene present iron

distribution heterogeneities, i.e. zoning, in relation to its partitioning among mineral phases and/or to the occurrence of fluid fluxes at different redox conditions (e.g. CH₄ fluid inclusions).

We performed for the first time in-situ Fe³⁺ measurements of garnets and clinopyroxenes pairs in equilibrium with graphite/diamond and sulphides, in order to obtain high-resolution redox profiles in the zoned crystals. Results indicate that clinopyroxene preferentially partitions Fe³⁺ with respect to garnet and it has been possible to distinguish two different clinopyroxene generations with different oxidation state thanks to the high resolution SMS measurements (see Fig. 1).

Even more interesting results came out from Fe³⁺/Fe_{tot} measurements of clinopyroxene and garnet from Alpe Arami, where they unexpectedly show relatively oxidised conditions.

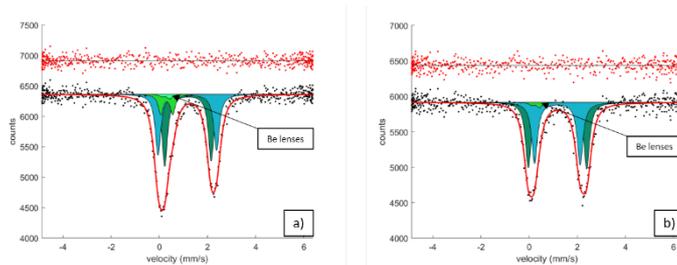


Fig. 1 Mössbauer spectra of two clinopyroxene generations revealed from different Fe oxidation states: Fe³⁺ (a) and Fe²⁺ (b).

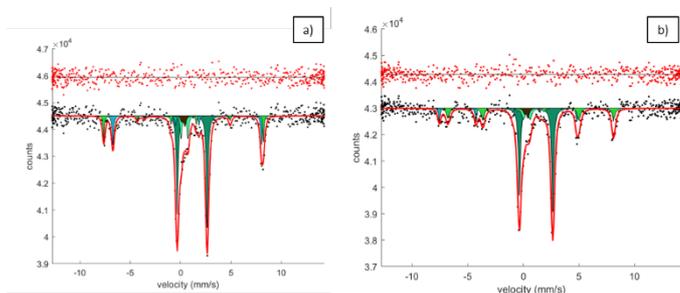


Fig. 2 Mössbauer spectra of a magnetite inclusion from Almirez in two different orientations upon a rotation of 90°.

Moreover, we were also able to conduct a “pilot experiment” on a few magnetic inclusions in the harzburgites from Almirez in order to explore the possibility to extract the hyperfine magnetic field strength and direction. The procedure was absolutely successful and allowed us to explore also the possibility to perform measurements on the same magnetite inclusion in two different orientations upon a rotation of 90° (see Fig. 2)

4. Conclusions and future work

This was one of the best synchrotron session ever (compared to other lines in ESRF and Diamond Light Source). The results will enable us to model the composition of garnet pyroxenites, interpreted as remnants of an ancient recycled crust, in terms of redox budget and to investigate the role of C and S in the melting of their protolith. The carbon transfer from one mantle reservoir to the other is still a matter of debate, particularly in the mantle far from subduction zones, containing gem diamonds. As pointed out by Luth^[3], C-bearing peridotites would undergo decarbonation reaction during their upwelling, liberating CO₂. In contrast, C-bearing eclogitic rocks would contain diamond/graphite rather than carbonate and therefore would not experience decarbonation. This implies that carbon can be transported from the deepest to the shallow portions of the mantle during the recycling of ancient slabs, appearing the best candidates able to survive the trip to the surface [3]. In this scenario the determination of the oxidation state of the mineral assemblage of both subduction peridotites (Almirez and Alpe Arami) and lithospheric mantle garnet pyroxenites (Beni Bousera and Ligurides) and the role of sulfur will enable us to unravel the role of graphite/diamond stability, relative to the more reactive CO₂ or carbonate.

Moreover, a potential follow up study on oriented magnetite inclusions in olivine hosted in harzburgites from the Almirez Complex (Bètic Cordillera, Spain), using the polarized x-ray beam of the synchrotron Mössbauer source (SMS), will allow us to correlate the magnetic information deduced by these measurements with existing crystallographic data (e.g., reciprocal orientation between the host and the inclusion, see [4]) with the aim to constrain the magnetic and growth history of the whole system. Unfortunately, due to difficulties caused by the covid pandemic we did not published the results yet. However, we aim to publish two papers on high quality peer review journals and present these results in the next international conferences (e.g. EGU, AGU, Goldshmidt).

5. References

- [1] Prescher et al. 2012 : Journal of Applied Crystallography, 45(2), 329-331. [2] Malaspina et al. 2012: Lithos 146–147, 11–17. [3] Luth 1993: Science 261, 66-68 [4] Campione et al. 2020: ACS Earth and Space Chemistry, 4(6), 825-830.