



	<b>Experiment title:</b> Determination of the redox states of mantle rocks using synchrotron Moessbauer spectroscopy	<b>Experiment number:</b> ES-566
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<b>Shifts:</b> 18	<b>Local contact(s):</b> Valerio Cerantola	<i>Received at ESRF:</i>
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### Report:

While H<sub>2</sub>O and CO<sub>2</sub> dominate the planetary surface in many aspects, including its habitability, the largest reservoir for both compounds is Earth's deep mantle<sup>1-3</sup>.

Quantification of the magmatic fluxes of volatiles such as C and H<sub>2</sub>O between the mantle and the Earth's outer envelopes remains however highly controversial, owing in part to challenges in accurately determining volatile concentrations and redox conditions of recycled oceanic crust (i.e. eclogites) as well as those in the source regions of mantle-derived melts<sup>1-9</sup>. Numerous mantle source regions may have experienced interactions between melts of recycled eclogite and ambient peridotitic mantle<sup>10,11</sup>.

The aim of this study is to refine the redox state of mantle sources regions and associated melts from determination of Fe<sup>3+</sup>/ΣFe ratios in garnet crystals of peridotite and eclogite, using the state-of-the-art synchrotron Moessbauer spectroscopy at ID18.

The application of the synchrotron Moessbauer spectroscopy to *synthetic high pressure experimental samples* will allow the determination of the redox state of peridotite and eclogite in equilibrium with the full mantle rock assemblages under controlled pressure, temperature and *f*O<sub>2</sub> conditions in which the relative stabilities of solid C (diamond or graphite), carbonate and partial melting are also monitored.

In addition, we have assembled *a suite of natural, compositionally homogenous standard peridotitic and eclogitic garnets*, covering the natural and experimental compositional range, for which we have determined Fe<sup>3+</sup>/ΣFe by conventional Mössbauer spectroscopy and partly also by Fe K-edge X-ray absorption near-edge structure (XANES) and electron microprobe Flank method<sup>12-16</sup>. The application of the synchrotron Moessbauer spectroscopy to natural standard peridotitic and eclogitic garnets allows to test the reliability, accuracy and precision of determined Fe<sup>3+</sup>/ΣFe in the garnets by conventional Moessbauer spectroscopy, XANES and Flank method.

Synchrotron Moessbauer spectroscopy now allows analyses of  $\text{Fe}^{3+}$  in garnets with a spatial resolution of  $\sim 10 \mu\text{m}$ , reveal  $\text{Fe}^{3+}/\Sigma\text{Fe}$  heterogeneities in mantle rocks at the micro-scale<sup>17,18</sup>. Instead, conventional Moessbauer spectroscopy analyses require grain sizes of  $\gg 40 \mu\text{m}$  (or milliprobes of  $\sim 50 \mu\text{m}$ ), which may incorporate  $\text{Fe}^{3+}/\Sigma\text{Fe}$  heterogeneities present in the garnets in the acquired data. In addition, grain sizes of  $\gg 40 \mu\text{m}$  are usually not achievable in small high pressure experimental run products<sup>17</sup>.

**Experimental technique(s), set-up(s), measurement strategy, sample details:**

**Samples:** *Natural garnet standards* are presented as garnet crystals separated from crushed whole rock and mounted and polished in round, 1" diameter epoxy buttons (Fig. 1). Some free-standing natural eclogitic garnets were loaded in diamond-anvil cells for analysis (Fig. 2).

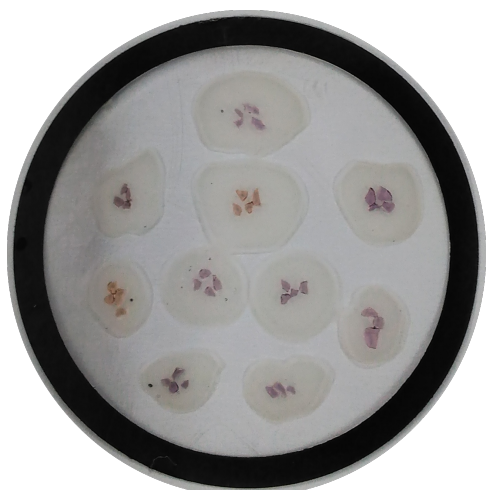


Fig. 1. Typical 1" diameter epoxy buttons, containing double-polished free-standing natural garnets from different localities.

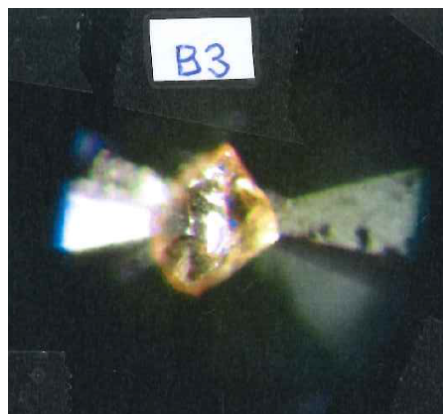


Fig. 2. A natural garnet ( $\sim 50 \mu\text{m}$  in diameter) loaded in a diamond-anvil cell for synchrotron Moessbauer analyses.

Eclogitic garnets are compositionally distinct from peridotitic garnets, in having little or no  $\text{Cr}_2\text{O}_3$  (cf  $\leq 15$  wt%  $\text{Cr}_2\text{O}_3$  in peridotitic garnets), higher CaO and FeO (typically from 10-25 wt%  $\text{FeO}+\text{Fe}_2\text{O}_3$ ), but lower MgO contents<sup>3-5,7-9,16,18,19</sup>.

We also *synthesized* a first sub-set of *garnets* of eclogitic<sup>19</sup>+ $\text{CO}_2$ + $\text{H}_2\text{O}$  and peridotitic<sup>4,5</sup> compositions at 4, 6, 8 and 10 GPa at a range of temperatures from subsolidus to those where a large degree of partial melt form. Glassy sintered oxide powders for eclogitic and peridotitic starting bulk compositions were prepared using established procedures<sup>4,5,19</sup>, and doped with Ir powder as a redox sensor<sup>7-9</sup>, as well as  $^{57}\text{Fe}$  for Moessbauer analysis of  $\text{Fe}^{3+}$  [ref. 17].

Run products contained well-equilibrated eclogitic phase assemblages, including varying proportions and compositions of garnet and clinopyroxene, and subordinate carbon (diamond or graphite), carbonate, IrFe-alloys,  $\pm$  coesite/stishovite and  $\pm$  quenched melt/fluids (glasses). Samples that contain sufficiently large mineral phases ( $>20 \mu\text{m}$ ) for analysis by synchrotron Moessbauer<sup>5</sup> were prepared as doubly polished free-standing thin sections, in which the crystals are exposed on the top and bottom surfaces, ensuring a beam path through only the mineral of interest; essential for  $\text{Fe}^{3+}$  analyses using synchrotron Moessbauer<sup>8,9</sup> (Fig. 3).

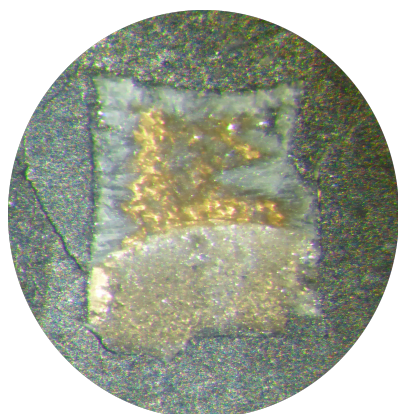


Fig. 3. Doubly polished free-standing thin section of representative eclogitic run products of eclogite +  $\text{CO}_2$  +  $\text{H}_2\text{O}$  at 6 GPa, containing garnet, clinopyroxene and quenched glass. The experiment is  $\sim 0.8 \text{ mm}$  wide,  $\sim 1 \text{ mm}$  long and  $\sim 100 \mu\text{m}$  thick.

## Analysis of the valence state of iron in natural and synthetic garnets using synchrotron Moessbauer spectroscopy:

We employed synchrotron Moessbauer spectroscopy at the nuclear resonance beamline ID18 at ESRF<sup>20</sup>. The focus of the beam of  $\gamma$ -radiation emitted by the SMS was 10-15 mm in spot size.

The garnets contain around 6-20 wt% FeO. We estimated that for a natural garnet, an ideal synchrotron Moessbauer spectrum should be recorded in approx. 3 hours, while an experimental synthetic <sup>57</sup>Fe-enriched garnets would require approx. 30 mins to an hour only.

However, an ideal synchrotron Moessbauer spectrum at ID18 could be already recorded in average of 60 mins, some even within 10-20 mins. Exceptionally, counting times were extended to over two hours. Sufficiently good analyses of the valence state of iron using synchrotron Moessbauer spectroscopy for the much more minute experimentally derived and 100% <sup>57</sup>Fe-enriched garnets could be already achieved within approx. 5 mins only.

We collected Moessbauer spectra for approx. 100 samples (Fig. 4). The fast collection of Moessbauer spectra was ensured by the high intensity and small size of the beam<sup>17</sup>.

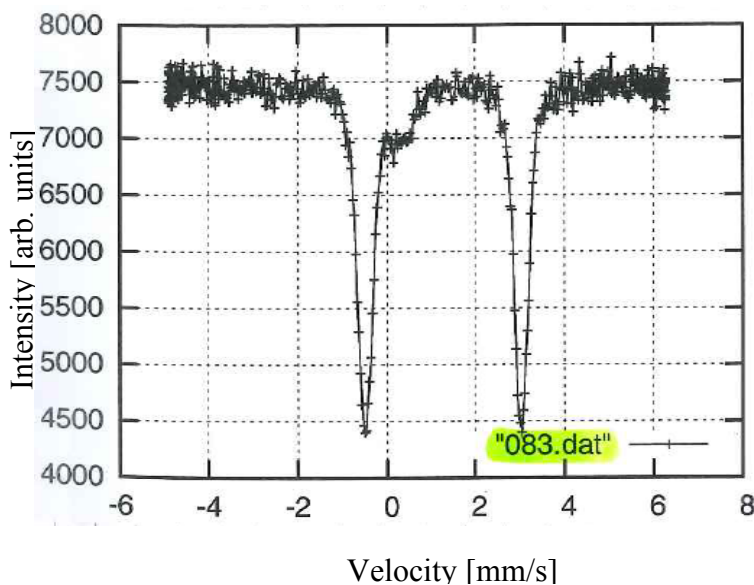


Fig. 4. *Folded synchrotron Moessbauer spectrum of a representative natural eclogitic garnet, collected in 1600 seconds.*

The velocity scale were calibrated relative to a 25 mm-thick  $\alpha$ -Fe foil. Moessbauer spectra will be fitted using the software package MossA<sup>21</sup>.

The primary outcome will be to provide a well-studied suite of peridotitic and eclogitic garnets as calibration standards for continued study by us and others; the addition of synchrotron Moessbauer data on these samples complements the conventional Moessbauer, XANES and Flank methods already applied to the same samples, sourced from world-wide localities and contributed by numerous groups. This provides then the largest database of cross-calibrated garnet samples.

The second outcome will be to analyse those eclogitic samples produced under relevant mantle conditions in order to provide the determination of the redox state of mantle rocks. This research will provide urgently needed insights on how subduction and recycling of volatile-bearing oceanic crustal materials leads to diverse changes in the redox states of the deep Earth's mantle, and associated mantle-derived magmatism and volcanic degassing.

The data obtained during this ESRF-session (ES-566) will be written up as a manuscript for publications.

**References:** 1. Dasgupta & Hirschmann (2010) *Earth Planet Sci Lett* 298, 1-13. / 2. Hirschmann & Dasgupta (2009) *Chem Geol* 262, 4-16. / 3. Rosenthal et al. (2015) *Earth Planet Sci Lett* 412, 77-87. / 4. Green et al. (2010) *Nature* 467, 448-451. / 5. Green et al. (2014) *J Petrol* 55, 2067-2096. / 6. Kovacs et al. (2012) *J Petrol* 53, 10, 2067-2093. / 7. Stagno & Frost (2010) *Earth Planet Sci Lett* 300, 72-84. / 8. Stagno et al. (2013) *Nature* 493, 84-88. / 9. Stagno et al. (2015) *Contrib Mineral Petrol* 151, 169:16. / 10. Hofmann

(2003) *Treatise Geochem* 2, 2.03, 61-101. / **11.** Sobolev et al. (2007) *Science* 316, 412-417. / **12.** Berry et al. (2010) *Chem Geol* 278, 31-37. / **13.** Pinter et al. (2015) *AGU Fall Meeting Abstr* V33C 3113. / **14.** Rosenthal et al. (2014) *AGU Fall Meeting Abstr* 1, 4744. / **15.** Vasilyev et al. (2015) *Goldschmidt Abstr* 2015 3248. / **16.** Yaxley et al. (2012). *Lithos* 140-141, 142-151. / **17.** Potapkin et al. (2012). *J Synchrotron Radiation* 19, 559-569. / **18.** Woodland & Koch (2003) *Earth Planet Sci Lett* 214, 295-310. / **19.** Yaxley & Green (1994) *Earth Planet Sci Lett* 128, 313-325. / **20.** Rueffer & Chumakov (1996) *Hyperfine Interact* 97, 589-604. / **21.** Prescher et al. (2012) *J Appl Crystallogr* 45, 329-331.