

FIRST IN-SITU MEASUREMENTS OF $\text{Fe}^{3+}/\text{Fe}_{\text{TOT}}$ FOR OXIDES AND SILICATES INCLUDED IN NATURAL DIAMONDS WITH SYNCHROTRON MÖSSBAUER SOURCE

Milani S.*¹, Nestola F.¹, Cerantola V.², Anzolini C.¹, McCammon C.³,
Novella D.⁴, Kuppenko I.^{2,5}, Chumakov A.², Ruffer R.² & Harris J.W.⁶

¹ Dipartimento di Geoscienze, University of Padova, Italy

² European Synchrotron Radiation Facility, France

³ Bayerisches Geoinstitut, University of Bayreuth, Germany

⁴ Lawrence Livermore National Laboratory, United States of America

⁵ Institut für Mineralogie, University of Münster, Germany

⁶ School of Geographical and Earth Sciences, University of Glasgow, United Kingdom

P13, oral

synchrotron Mössbauer, diamond inclusions, ferric iron

Diamond is the paramount phase to understand the evolution and the physico-chemical condition of the deep portions of the Earth's mantle, mainly because: (i) it is the stable phase through which carbon is stored in the deep mantle for long geologic time; (ii) it does contain and preserve different types of inclusions (fluid, mineral, etc.); (iii) it is the only material sampling the mantle to depths of 800 km (e.g. Harte, 2010), although the majority of the mined diamonds worldwide derive from shallower depth (150 to 250 km). The study of mineral inclusions trapped in diamonds allows the retrieval of different pieces of information about the Earth's interior and its active geodynamics, providing important clues on the initiation of subduction processes (Shirey & Richardson, 2011; Smart et al., 2016), tracking the transfer of material through the mantle transition zone (Stachel et al., 2005; Walter et al., 2011), recording the timing of ingress of fluids to the continental lithosphere (e.g. Shirey et al., 2004), preserving carbonatitic fluid that trigger deep mantle melting (e.g. Schrauder & Navon, 1994; Kopylova et al., 2010), providing samples of primordial noble gases (e.g. Ozima & Igarashi, 2000), and capturing the redox state of the mantle (e.g. Rohrbach & Schmidt, 2011).

Unfortunately the majority of the techniques used so far to study the mineral inclusions are destructive. It is only in the last decade that the studies on inclusions in diamond have started to use non-destructive techniques, providing new information which would otherwise be lost using earlier destructive techniques. Such an example is the rim fluids around inclusions in diamonds. In this study we present details of the experimental setup on the determination of $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ ratios of mineral inclusions whilst still within the diamonds by a non-destructive approach using the Synchrotron Mössbauer Source (SMS; Potapkin et al., 2012) at the Nuclear Resonance beamline

ID18 (Rüffer & Chumakov, 1996), European Synchrotron Radiation Facility (ESRF), Grenoble. The extremely small X-ray spot size ($10 \times 15 \mu\text{m}^2$) is perfectly suited for our purposes as some inclusions are smaller than 30-50 μm and the $\text{Fe}^{3+}/\text{Fe}_{\text{tot}}$ variation over the same inclusion cannot be performed by using standard laboratory radioactive sources because of the larger beam size. The average collection time for thicker inclusions ($\sim 200 \mu\text{m}$) was 2 hours per spectrum, whilst the smallest inclusion ($\sim 30 \times 30 \times 30 \mu\text{m}^3$) required a collection time of approximately 10-12 hours in order to get a spectrum with nicely distinguishable features and a high signal-to-noise ratio. In general, application to a suite of silicate and oxide inclusions in diamonds produced comparable results with respect to those obtained using conventional Mössbauer sources (e.g. McCammon et al., 2004).

Harte, B. (2010): Diamond formation in the deep mantle; the record of mineral inclusions and their distribution in relation to mantle dehydration zones. *Mineral. Mag.*, **74**, 189-215.

Kopylova, M., Navon, O., Dubrovinsky, L. & Khachatryan, G. (2010): Carbonatitic mineralogy of natural diamond forming fluids. *Earth Planet. Sci. Lett.*, **291**, 126-137.

McCammon, C.A., Stachel, T. & Harris, J.W. (2004): Iron oxidation state in lower mantle mineral assemblages: II. Inclusions in diamonds from Kankan, Guinea. *Earth Planet. Sci. Lett.*, **222**, 423-434.

Ozima, M. & Igarashi, G. (2000): The primordial noble gases in the Earth; a key constraint on Earth evolution models. *Earth Planet. Sci. Lett.*, **176**, 219-232.

Potapkin, V., Chumakov, A.I., Smirnov, G.V., Celse, J.P., Rüffer, R., McCammon, C. & Dubrovinsky, L. (2012): The ^{57}Fe Synchrotron Mössbauer Source at the ESRF. *J. Synchrotron Radiat.*, **19**, 559-569.

Rohrbach, A. & Schmidt, M.W. (2011): Redox freezing and melting in the Earth's deep mantle resulting from carbon-iron redox coupling. *Nature*, **472**, 209-214.

Rüffer, R. & Chumakov, A.I. (1996): Nuclear-resonance beamline at ESRF. *Hyperfine Interact.*, **97**, 589-604.

Schrauder, M. & Navon, O. (1994): Hydrous and carbonatitic mantle fluids in fibrous diamonds from Jwaneng, Botswana. *Geochim. Cosmochim. Acta*, **58**, 761-771.

Shirey, S.B., Richardson, S.H. & Harris, J.W. (2004): Integrated models of diamond formation and craton evolution. *Lithos*, **77**, 923-944.

Shirey, S.B. & Richardson, S.H. (2011): Start of the Wilson cycle at 3 Ga shown by diamonds from subcontinental mantle. *Science*, **333**, 434-436.

Smart, K.A., Tappe, S., Stern, R.A., Webb, S. & Ashwal, L.D. (2016): Early Archaean tectonics and mantle redox recorded in Witwatersrand diamonds. *Nat. Geosci.*, **9**, 255-259.

Stachel, T., Brey, G.P. & Harris, J.W. (2005): Inclusions in sub-lithospheric diamonds: glimpses of deep earth. *Elements*, **1**, 73-87.

Walter, M.J., Kohn, S.C., Araujo, D., Bulanova, G.P., Smith, C.B., Gaillou, E., Wang, J., Steele, A., & Shirey, S.B. (2011): Deep mantle cycling of oceanic crust; evidence from diamonds and their mineral inclusions. *Science*, **334**, 54-57.