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Application of Fe K-edge XANES determinations of Fe3+/totalFe in garnet to peridotite xenoliths from the Udachnaya Kimberlite

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The garnet structure can accommodate both Fe2+ and Fe3+. Garnet Fe3+/$\sum$Fe in kimberlite-bourne garnet peridotite xenoliths can be used to determine the oxygen fugacity (fO_2) of the cratonic lithosphere. This is important as an indicator of diamond (versus carbonate) stability. In cratonic lithosphere the $f O_2$ of peridotite is expected to broadly decrease with increasing depth, and is consistent with graphite or diamond stability. However metasomatic events may locally perturb this trend, possibly leading to oxidation that could result in diamond breakdown or resorption. Such events will usually be recorded by the coexisting garnet.

Fe3+/$\sum$Fe of garnets has traditionally been determined by Mössbauer Spectroscopy of powdered samples. This lacks spatial resolution and the data for each measurement take several days to acquire. X-ray Absorption Near Edge Structure (XANES) spectroscopy is now commonly being used to determine Fe3+/$\sum$Fe in minerals, is capable of micron spatial resolution and spectra can be recorded in $\sim$15 minutes. We have recently reported a new method for quantifying Fe3+/$\sum$Fe from the XANES spectra of mantle garnets with an accuracy and precision comparable to Mössbauer Spectroscopy.

We applied the XANES technique to investigate the $f O_2$-depth variation in the Siberian Craton using a suite of fresh garnet lherzolites from the Udachnaya East kimberlite. Garnet Fe3+/$\sum$Fe was detemined using XANES spectroscopy on the X-ray Fluorescence Microscopy beamline of the Australian Synchrotron. XANES spectra were recorded in fluorescence mode from garnets prepared as either polished thin sections or electron probe mounts. A calibration curve relating the spectra to Fe3+/$\sum$Fe of mantle garnets previously analysed by Mössbauer spectroscopy allowed garnet unknowns to be quantified.

Thermobarometry established that the samples range in pressure from 3.9-7.1 GPa and lie along a typical cratonic geotherm. Several samples exhibit elevated abundances of Ti, Zr and Y in garnet and clinopyroxene, clear evidence for metasomatic enrichment consistent with an earlier study of another Udachnaya xenolith suite. Others are less or unaffected by metasomatism, with very low abundances of these elements.

Δlog10[$f O_2$]FMQ varies from -2.5 to -5.9 log units and broadly decreases with increasing pressure. The metasomatised samples all derive from $P > 5$ GPa and most exhibit a resolvable shift to $f O_2$ values $\approx$1.5-2.0 log units higher than the unmetasomatised ones, at given pressure. A possible mechanism for metasomatic enrichment relates to localized, low degree "redox melting", whereby upwardly percolating CH4$\pm H_2O$ fluids would encounter progressively more oxidizing peridotite wall-rock resulting in diamond crystallization and increased water activity in the fluid. This could lead to local partial melting and enriched melts could migrate into cooler parts of the lithosphere and crystallize, thus enriching parts of the lithosphere. Melts thus formed are expected to be relatively enriched in Fe3+ as it is moderately incompatible during partial melting. Lithospheric domains metasomatised by solidification of these melts would be relatively enriched in Fe3+ and garnets may therefore have higher Fe3+/$\sum$Fe values, thus recording relatively higher Δlog$f O_2$[FMQ] values.