



## APPLICATION OF Fe K-EDGE XANES DETERMINATIONS OF Fe<sup>3+</sup>/ΣFe IN GARNET TO PERIDOTITE XENOLITHS FROM THE UDACHNAYA KIMBERLITE

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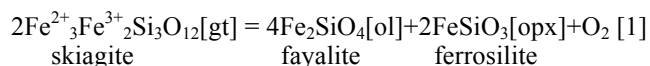
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### INTRODUCTION

The oxygen fugacity ( $fO_2$ ) of the Earth's mantle is an important variable which can control fluid speciation in the CHOS-system, melting phase relations and diamond versus carbonate stability in both peridotite and eclogite. Garnet peridotite xenoliths transported to the surface in kimberlites and related volcanics preserve  $fO_2$  information, which, when combined with estimates of their pressures (P) and temperatures of origin (T) based on conventional thermobarometric calculations, can be used to determine the variation of  $fO_2$  with the depth in cratonic lithosphere, i.e. the redox profile. Mineral trace and minor element compositions can also potentially relate this variation to metasomatic and other processes that may have operated in the deep cratonic lithosphere.

The upper mantle phases spinel, garnet and pyroxenes can accommodate both Fe<sup>2+</sup> and Fe<sup>3+</sup>. Oxygen fugacity is controlled by silicate-oxide exchange reactions between Fe-bearing components in these phases. In the garnet peridotite facies, the reaction



has been calibrated as a function of  $fO_2$ , P, T and mineral component activities (Gudmundsson and Wood, 1995). Thus, if garnet Fe<sup>3+</sup>/ΣFe in kimberlite-borne garnet peridotite xenoliths can be precisely measured, the oxygen fugacity ( $fO_2$ ) of the sample can be calculated. In cratonic lithosphere the  $fO_2$  of peridotite is expected to broadly decrease with increasing depth, and is generally 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.

Fe<sup>3+</sup>/ΣFe 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 or weeks to acquire. Fe K-edge X-ray Absorption Near Edge Structure (XANES) spectroscopy is now commonly being used to determine Fe<sup>3+</sup>/ΣFe in minerals, is capable of micron spatial resolution and spectra can be recorded in ~15 minutes. We have recently reported a new method for quantifying Fe<sup>3+</sup>/ΣFe from the XANES spectra of mantle garnets with an accuracy and precision comparable to Mössbauer spectroscopy (Berry et al., 2010). In the current investigation, we have applied the XANES technique to a suite of fresh garnet lherzolite xenoliths from the Udachnaya East kimberlite and determined the first  $fO_2$ -depth profile in the Siberian Craton.

### SAMPLES AND GEOLOGICAL SETTING

We examined 21 fragments (typically a few cm across) of larger, fresh garnet peridotite xenoliths extracted from depths of about 400-480 m below the surface in the eastern branch of the 367 Ma old (Kinny et al., 1997) Udachnaya kimberlite, in Yakutia in the central Siberian Craton. Texturally the samples vary from coarse granular to porphyroclastic to sheared types and are very similar in this respect to other Udachnaya garnet peridotite samples described recently by Agashev et al. (2010) and Ionov et al. (2010).

### ANALYTICAL METHODS

Samples were mounted in 1 inch diameter round epoxy buttons and polished using diamond paste.



The major and minor element compositions of constituent mineral phases in the samples were determined by WDS electronprobe microanalysis (EPMA) using an Cameca SX-100 at the University of Tasmania. An accelerating voltage of 15 kV and beam current of 20 nA were used. Calibration was performed using series of natural mineral standards. Trace element compositions of garnet and clinopyroxene were determined with LA-ICPMS using an Agilent 7500 instrument and an Excimer UV laser (193nm) at the Australian National University. Analytical and data reduction protocols followed those reported by Eggins et al. (1998).

Garnet  $\text{Fe}^{3+}/\Sigma\text{Fe}$  was determined using XANES spectroscopy on the X-ray Fluorescence Microscopy beamline of the Australian Synchrotron using the method recently established by Berry et al. (2010). XANES spectra were recorded in fluorescence mode from garnets prepared as either polished thin sections or electron probe mounts (Figure 1).

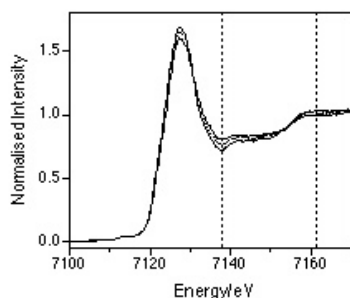


Figure 1: Representative Fe K-edge XANES spectra of two Udachnaya garnet unknowns (solid lines) and one Diavik garnet standard (dotted line). The vertical dashed lines are post-edge energies of 7138.4 and 7161.7 eV.

This technique requires establishment of a calibration curve relating the normalised ratio of the intensity of post-edge features at 7138.4 eV and 7161.7 eV to the  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of mantle garnet standards, previously analysed by Mössbauer spectroscopy (Figure 2). The standard garnets were from garnet peridotite xenoliths from the Diavik kimberlite in the Slave Craton in northern Canada (Yaxley, unpublished data) and from a variety of locations in the Kaapvaal Craton (South Africa and Lesotho) (Woodland and Koch, 2003). These garnets have  $\text{Fe}^{3+}/\Sigma\text{Fe}$  ranging from 0.034 to 0.134.

## RESULTS

Olivine grains from the Udachnaya samples have  $\text{Mg\#}$  [ $100 \times \text{Mg}/(\text{Mg} + \text{Fe}^{2+})$ ] which vary from 89.6 to 92.3. In general, samples exhibiting sheared textures tend to have  $\text{Mg\#}$ s at the lower end of the range. Orthopyroxene grains contain 0.35 to 0.90 wt%  $\text{Al}_2\text{O}_3$  and 0.27 to 1.22 wt% CaO.

Garnet  $\text{Fe}^{3+}/\Sigma\text{Fe}$  as determined by XANES varies from 0.026 to 0.14. The uncertainty is estimated as  $\pm 0.01$ .  $\text{Mg\#}$

varies from 80.4 to 84.8, CaO from 4.34 to 6.89 wt% and  $\text{Cr}_2\text{O}_3$  from 2.81 to 9.21 wt%. All garnets classify as G9 (lherzolitic) using the classification scheme of Grütter et al. (2004). Systematics in Ti-Y-Zr contents of mantle garnets have been used by Griffin and Ryan (1995) as an indicator of whether or not samples are depleted (Ti < 1000 ppm, Zr < 20 ppm, Y < 5 ppm) or enriched by metasomatism. Garnets from 16 samples were measured for trace elements by LA-ICPMS. Six of them contained < 350 ppm Ti and the rest contained from 900 to 8550 ppm Ti. Ti content correlates positively with garnet Y and Zr contents (Figure 3). Thus, the current suite contains both depleted and metasomatically enriched samples. This distinction is evident in garnet REE chemistry as well. Depleted garnets (based on Ti, Zr and Y contents) have strongly sinusoidal normalised REE patterns, whereas enriched garnets have weakly sinusoidal to normal normalised REE patterns (Figure 4).

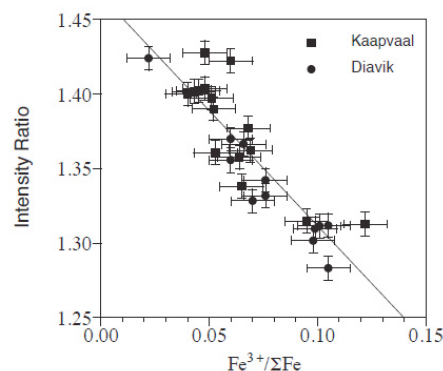


Figure 2: Calibration curve (including line of best fit) relating the intensity ratio of post-edge features at 7138.4 and 7161.7 eV to  $\text{Fe}^{3+}/\Sigma\text{Fe}$  of standard garnet from Kaapvaal (Woodland and Koch, 2003) and Diavik (Yaxley, unpublished data), as determined by Mössbauer spectroscopy.

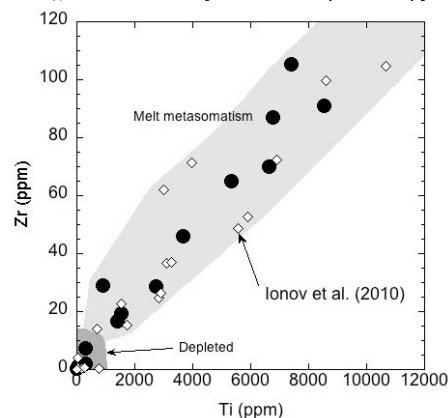


Figure 3: Garnet Ti vs. Zr contents in Udachnaya garnets. Black dots are from current suite. White diamonds are from the study of Ionov (2010). "Depleted" and "melt metasomatism" fields are from Griffin and Ryan (1995).



Clinopyroxene grains contain from 16.60 to 23.75 wt% CaO, 0.05 to 1.89 wt% Na<sub>2</sub>O and 0.21 to 2.01 wt% Cr<sub>2</sub>O<sub>3</sub>. Again Ti abundances are bimodal, with 6 samples having <0.05 wt% TiO<sub>2</sub> and the remainder having >0.15 wt% TiO<sub>2</sub>. Clinopyroxenes with low Ti have sinusoidal REE patterns whereas those with high Ti have normal REE patterns (Figure 5).

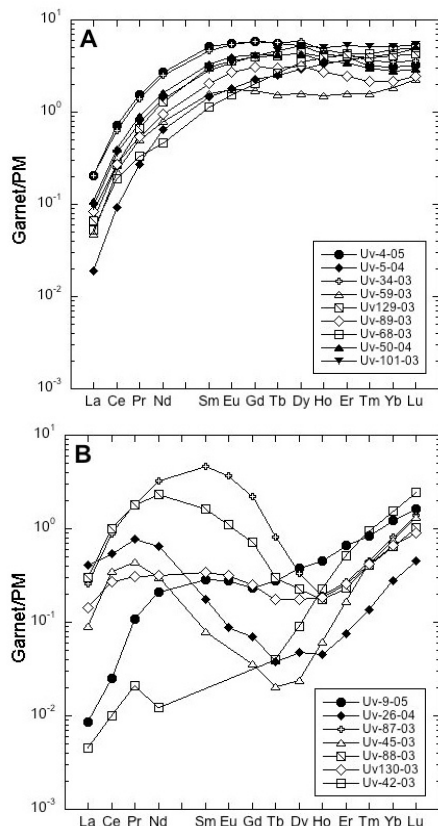


Figure 4: REE patterns for Udachnaya garnets with (A) normal to weakly sinusoidal patterns and (B) strongly sinusoidal patterns.

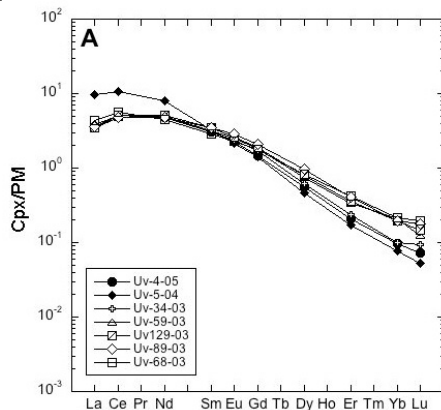


Figure 5A: REE patterns for Udachnaya clinopyroxenes with "normal" patterns.

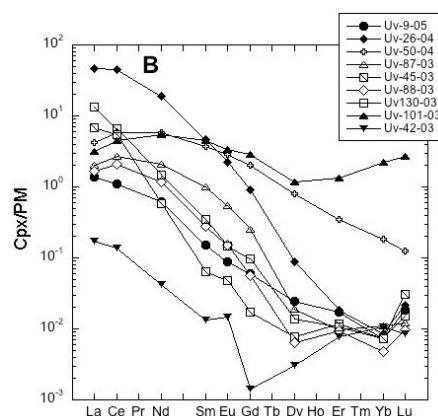


Figure 5B: REE patterns for Udachnaya clinopyroxenes with "sinusoidal" patterns.

## DISCUSSION

### Thermobarometry and oxygen fugacity calculations

The EPMA data were used to establish the P and T conditions experienced by the xenoliths before entrainment in the host kimberlite using the thermobarometric approach recommended by Nimis and Grütter (2010). The samples range in pressure from 3.9 to 7.1 GPa and in temperature from 723 to 1364°C, but fall into two groups. A low T, low P group (T<1000°C, P<5.2 GPa) defines an approximate 40 mWm<sup>-2</sup> geotherm, and a high T, high P group (T>1150°C, P>5.2 GPa) clusters at temperatures ≥100°C above this geotherm. As with many other cratonic garnet peridotite suites, most of the high temperature samples exhibit sheared textures.

Oxygen fugacity was determined using the XANES garnet Fe<sup>3+</sup>/ΣFe data, the thermobarometric results described above and an experimental calibration of the *f*O<sub>2</sub> buffering reaction [1] (Gudmundsson and Wood, 1995). Δlog*f*O<sub>2</sub><sup>[FMQ]</sup> (i.e. *f*O<sub>2</sub> reported relative to the FMQ buffer at the P-T conditions of each sample) varies from -2.5 to -5.9. The uncertainty is estimated to be ±0.6 log units.

### Metasomatism and redox conditions

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 (Ionov et al., 2010). Others are less or unaffected by metasomatism, with very low abundances of these elements reflecting their more depleted character. When these mineralogical indicators of metasomatism are plotted against the xenoliths' calculated pressures, it is clear that (1) depleted material existed throughout the entire sample depth range, and (2) enriched



samples are restricted to the pressure interval of 4.5 to 6.6 GPa.

When the samples'  $\Delta\log fO_2^{[FMQ]}$  values are plotted against pressure, the redox distribution through much of the thickness of the lithosphere under Udachnaya 367 Ma ago is profiled. An overall trend to lower  $\Delta\log fO_2^{[FMQ]}$  values with increasing pressure is exhibited by 5 of the samples and of these 4 are depleted in garnet and clinopyroxene chemistry (Figure 6). This trend most likely relates mainly to the molar volume change of reaction [1] which requires that increased pressure will result in decreased  $fO_2$  (Frost and McCammon, 2008). Superimposed on this trend, is an oxidation trend to  $\Delta\log fO_2^{[FMQ]}$  values 1-2 log units greater than the main molar volume-related trend. Most of these more oxidised samples are metasomatically enriched; the oxidised samples are almost exclusively from pressures corresponding to the enriched zone between 4.5 and 6.6 GPa.

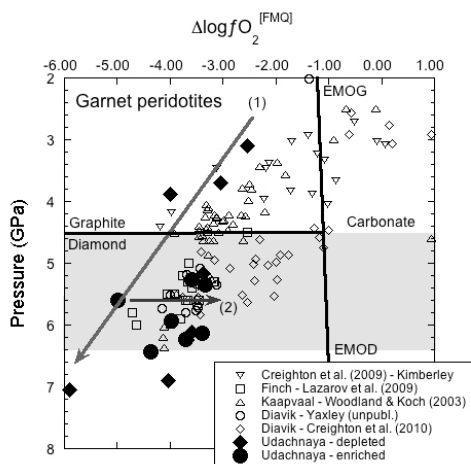


Figure 6: Plot of  $\Delta\log fO_2^{[FMQ]}$  versus equilibration pressure for the current depleted (black diamonds) and enriched samples (black circles), and other samples from various locations in the Kaapvaal Craton and the Diavik Diamond Mine. The grey arrow labeled (1) is interpreted as the main trend of decreasing oxygen fugacity with increasing pressure (depth) in the Siberian Craton and is mainly exhibited by depleted samples. The grey arrow labeled (2) represents an oxidation trend associated with metasomatic enrichment. The grey shaded field represents the depth interval in which most Udachnaya samples were enriched. The pressure of the graphite/diamond transition is based on a 40 mWm<sup>-2</sup> geotherm. EMOG and EMOD refer to the diamond limiting reaction enstatite + magnesite = olivine + C + O<sub>2</sub> (Woodland and Koch 2003) in the graphite and diamond stability fields respectively.

It is unlikely that metasomatic agents responsible for the enrichment were carbonatitic. CHO-fluids present in the very deepest parts of the lithosphere would have been CH<sub>4</sub>-rich at the  $fO_2$  values indicated by the deepest, depleted and most reduced xenoliths ( $\Delta\log fO_2^{[FMQ]} \approx -6$ ). A feasible mechanism for the metasomatism may involve localized, low degree “redox melting” as upwardly migrating CH<sub>4</sub>+H<sub>2</sub>O fluids encounter progressively more oxidizing peridotite wall-rock, eventually becoming oxidized, leading to diamond crystallization and increased in water activity in the residual fluid. This could lead to local partial melting and enriched melts could migrate into cooler parts of the lithosphere and crystallize, thus metasomatically enriching parts of the lithosphere. Melts thus formed are expected to be relatively enriched in Fe<sup>3+</sup> as it is moderately incompatible during partial melting. Therefore, lithospheric domains metasomatised by solidification of these melts would be relatively enriched in Fe<sup>3+</sup> and garnets may therefore have higher Fe<sup>3+</sup>/ΣFe values, thus recording relatively higher  $\Delta\log fO_2^{[FMQ]}$  values.

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