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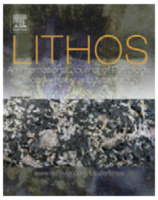

An oxygen fugacity profile through the Siberian Craton — Fe K-edge XANES determinations of $Fe^{3+}/\sum Fe$ in garnets in peridotite xenoliths from the Udachnaya East kimberlite

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ABSTRACT

The Udachnaya East kimberlite sampled garnet peridotite xenoliths from a pressure range of 1.2 to 7.1 GPa in the underlying Siberian cratonic lithosphere. Samples derived from <5.2 GPa lie close to a typical cratonic geotherm of 40 mW m^{-2}, whereas more deeply derived samples have temperatures ≥100 °C above this geotherm. Minor and trace element compositions of garnet and clinopyroxene indicate the presence of both depleted and metasomatically enriched material in the suite. Depleted material derives from the entire sampled depth interval, but enriched material is confined to pressures of 4.5 to 6.6 GPa. Thus, the Siberian cratonic lithosphere under the Undachnaya pipe consisted of a relatively cool and depleted upper layer about 150 km deep, underlain by a hotter layer which extended to at least 210 km depth and contained both depleted and enriched material. Fe K-edge XANES was applied to garnets from this suite to measure their $Fe^{3+}/\sum Fe$ values, enabling determination of a redox profile through the lithospheric section represented by the xenolith suite. $\Delta \log fO_2^{[FMQ]}$ varied from −2.5 to nearly −6.0 over the sampled pressure interval. An overall trend to lower $\Delta \log fO_2^{[FMQ]}$ values with increasing pressure was defined mostly by the depleted samples. A superimposed oxidation trend to $\Delta \log fO_2^{[FMQ]}$ values 1–2 units higher than the main trend mostly affected the deeper, enriched samples, indicating a clear link between metasomatism and oxidation. The amount of oxidation was insufficient to de-stabilize diamond in the deep lithosphere. A possible mechanism for metasomatic enrichment relates to localized, low degree "redox melting", whereby upwardly percolating $CH_4 \pm H_2O$ 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 Fe^{3+} as it is moderately incompatible during partial melting. Lithospheric domains metasomatised by solidification of these melts would be relatively enriched in Fe^{3+} and garnets may therefore have higher $Fe^{3+}/\sum Fe$ values, thus recording relatively higher $\Delta \log fO_2^{[FMQ]}$ values.

1. Introduction

The oxygen fugacity (fO_2) of the Earth's mantle is an important but often overlooked variable, which controls speciation of fluids in the CHOS system and therefore influences many processes such as partial melting, metasomatism and diamond stability (e.g. Taylor and Green, 1987, 1988). Oxygen fugacity of the deep cratonic mantle is recorded by garnet peridotite xenoliths, which have been accidentally entrained in, and rapidly transported by kimberlite magmas to the uppermost crust or surface, where they are quenched. Their mineral chemistry retains records of pressure (P), temperature (T) and fO_2 in the lithosphere from where they were sampled. fO_2 is recorded by the valence state of multivalent transition metals in the xenoliths' minerals. Fe is the most abundant transition metal in mantle assemblages, existing in both 2+ and 3+ oxidation states. Oxygen fugacity in peridotite is buffered by silicate–oxide exchange equilibria involving the phases in which Fe can exist in multiple oxidation states, spinel, garnet and pyroxenes. In the garnet peridotite facies, the most important reaction is

$$\underset{\text{skiagite}}{2Fe^{2+}{}_3Fe^{3+}{}_2Si_3O_{12}}[\text{garnet}] = \underset{\text{fayalite}}{4Fe_2SiO_4}[\text{olivine}] + \underset{\text{ferrosilite}}{2FeSiO_3}[\text{opx}] + O_2\,. \tag{1}$$

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Thus, garnet in peridotite acts as a redox sensor, recording mantle fO_2 from the garnet skiagite activity, or by the $Fe^{3+}/(Fe^{2+}+Fe^{3+})$ (or $Fe^{3+}/\sum Fe$) value of the garnet (Gudmundsson and Wood, 1995).

Experimental studies and thermodynamic modeling (e.g. Belonoshko and Saxena, 1992; Taylor and Green, 1987; Woodland and Koch, 2003) have shown that CHO-fluids under reduced fO_2 conditions exist predominantly as CH_4+H_2O, with the proportions of each molecular species dependent on fluid composition. According to thermodynamic calculations by Woodland and Koch (2003) a CHO-fluid at $\Delta\log fO_2^{[FMQ]}$ [fO_2 relative to the fayalite–magnetite–quartz redox buffer (Frost, 1991)] of about −5.5 may contain about 75% CH_4 and 25% H_2O at 6 GPa and 1400 °C. If such a reduced fluid encountered progressively more oxidized conditions, it could intersect the carbon-saturation surface (Taylor and Green, 1987) whereupon it would crystallize graphite or diamond (depending on the pressure and temperature conditions) leaving a H_2O-rich residual fluid. In the model of Woodland and Koch (2003) an increase in fO_2 by 3 orders of magnitude will result in oxidation of methane to diamond and almost all carbon will be removed from the fluid, leaving a H_2O-rich fluid. This increase in water activity in the fluid may flux melting of mantle peridotite leading to the process known as “redox melting” (Foley, 2011; Taylor and Green, 1987, 1988).

Mantle fO_2 is also an important variable controlling diamond/graphite stability. In peridotite assemblages, diamond/graphite versus carbonate stability is determined by buffering reactions such as EMOD/G:

$$\underset{\text{enstatite}}{MgSiO_3} + \underset{\text{magnesite}}{MgCO_3} = \underset{\text{olivine}}{Mg_2SiO_4} + C + O_2 \tag{2}$$

in harzburgitic assemblages or by EMFDD:

$$\underset{\text{enstatite}}{3MgSiO_3} + \underset{\text{calcite}}{CaCO_3} = \underset{\text{olivine}}{Mg_2SiO_4} + \underset{\text{diopside}}{CaMgSi_2O_6} + C + O_2 \tag{3}$$

in lherzolitic assemblages (Eggler and Baker, 1982; Luth, 1993). Therefore, direct measurement of the fO_2 recorded by mantle samples may allow constraints to be placed on processes such as diamond crystallization or resorption, partial melting and metasomatism. We report here the first redox measurements from a suite of garnet peridotite xenoliths from the Udachnaya East kimberlite. We have applied the newly developed Fe K-edge XANES technique (Berry et al., 2010) to measure $Fe^{3+}/\sum Fe$ in garnets from the suite. This technique has advantages over Mössbauer spectroscopy and the flank method, relating to superior spatial resolution and significantly shorter data acquisition times (Berry et al., 2008; Berry et al., 2010), but can determine garnet $Fe^{3+}/\sum Fe$ with similar precision (±0.01). In conjunction with conventional thermobarometry and trace element measurements in garnet and clinopyroxene using LA-ICPMS, we establish (1) a redox profile over a depth interval from ≈90 to ≈220 km in the Siberian Craton of decreasing $\Delta\log fO_2^{[FMQ]}$ with increasing depth, and (2) a superimposed oxidation clearly associated with metasomatism at depths greater than ≈130 km. We also show that all samples, including those oxidized by metasomatism, lie in the diamond/graphite stability field, at least 1.0–1.5 units below the EMOD/G buffering reaction in depth-fO_2 space.

2. Geological setting and nature of the samples

The Udachnaya kimberlite is one of >1100 kimberlite bodies in Yakutia in the Russian Federation (Ashchepkov et al., 2010). It was emplaced into the central Siberian Craton 367 Ma ago (Kinny et al., 1997). The kimberlite consists of two branches of a main pipe, the eastern (Vostok) and the western. The current samples were derived from depths of 400–480 m or more below the surface, in the eastern pipe, where recent mining operations have recovered very fresh peridotite xenoliths. Detailed petrographic, mineralogical and geochemical studies of other fresh garnet peridotite xenoliths from Udachnaya East kimberlite pipe were recently reported by Ionov et al. (2010) and Agashev et al. (2010).

The current 21 samples are small fragments of larger xenoliths. Our samples are typically a few centimeters across. They are generally very fresh with only minor or no visible serpentinization of olivines and minor development of kelyphitic breakdown rims on garnets. All samples are garnet peridotites and clinopyroxene was observed in 18 of them. The small size of most samples in this study makes it difficult to estimate reliable phase proportions. Texturally, the samples vary from coarse granular textures (e.g. Uv28/05, Uv129/03, Uv101/03) to porphyroclastic (which exhibit minor recrystallisation of olivine to fine-grained neoblasts along porphyroblastic olivine margins — e.g. Uv67/03, Uv101/03) to sheared samples in which coarse euhedral garnets and coarse pyroxenes are set in very fine-grained, sheared matrix of olivine crystals (e.g. Uv68/03).

3. Analytical methods

Major and minor element compositions of constituent phases in the xenoliths were determined by WDS electronprobe microanalysis using the Cameca SX-100 in the Central Science Laboratory, University of Tasmania. The accelerating voltage was 15 kV and the beam current was 20 nA. The beam diameter was focused to 1 μm. Elemental calibration was performed on a range of well-characterized natural mineral standards.

Trace element compositions of garnet and clinopyroxene from 16 of the 21 samples were determined by LA-ICPMS using the Agilent 7500 instrument at The Australian National University. Analytical protocols were similar to those reported in Eggins et al. (1998).

The Fe^{3+} content of garnet was determined for 14 of the 21 samples using the Fe K-edge XANES technique recently described by Berry et al. (2010). This technique depends on the establishment of an empirical calibration curve, which relates the ratio of the intensity of post-edge features at 7138.4 and 7161.7 eV in the Fe K-edge XANES spectra of a series of standard garnets to their $Fe^{3+}/\sum Fe$ value previously determined by Mössbauer spectroscopy. Berry et al. (2010) noted that the normalized intensity ratio of these features correlated with $Fe^{3+}/\sum Fe$ for a suite of standard garnets which cover most of the compositional range exhibited by garnets from garnet peridotite xenoliths hosted by kimberlites.

The standard garnets were from garnet peridotite xenoliths from Diavik kimberlite (Slave Craton, Canada) (Yaxley, *unpublished data*) and from the several kimberlite localities in the Kaapvaal Craton (Kimberley, Jagersfontein, Frank Smith Mine and Monastery in South Africa and Letseng-la-Terae, Liqhobong and Matsoku in Lesotho) (Woodland and Koch, 2003). These samples have $Fe^{3+}/\sum Fe$ ranging from 0.034 to 0.134 as established by Mössbauer spectroscopy. A correction for recoil-free fractions in the Mössbauer spectra was made following the derivation of Woodland and Ross (1994). Woodland et al. (2009) demonstrated that this correction is also valid for Cr-bearing garnets such as the standard garnets used here.

The Fe K-edge XANES spectra were recorded at the X-ray Fluorescence Microscopy (XFM) beamline (Paterson et al., 2011) of the Australian Synchrotron. The excitation energy was selected using a Si(111) double crystal monochromator. The energy was calibrated for each sample by simultaneously recording an Fe foil spectrum using light scattered by a sheet of plastic (2 mm thick) inserted in the beam path (upstream of the normalization ion chamber used for the microprobe) and a foil mounted in front of a photodiode (e.g. Cross and Frenkel, 1999). The first derivative of this Fe spectrum was defined to be 7112.0 eV. The beamline spectral resolution was 1.9 eV. The spatial resolution was defined by KB mirrors, which produced an analysis spot of ~3×3 μm for this study. Samples were mounted at 45° to both the incident beam and a single element silicon drift energy dispersive detector (Vortex EM, SII Nanotechnology, Northridge, CA) with digital signal processing (DXP Saturn, XIA LLC,