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Thermal state, oxygen fugacity and C–O–H fluid speciation in cratonic lithospheric mantle: New data on peridotite xenoliths from the Udachnaya kimberlite, Siberia

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ABSTRACT

Oxygen fugacity (fO_2) and temperature variations in a complete lithospheric mantle section (70–220 km) of the central Siberian craton are estimated based on 42 peridotite xenoliths in the Udachnaya kimberlite. Pressure and temperature (*P–T*) estimates for the 70–140 km depth range closely follow the 40 mW/m^2 model conductive geotherm but show a bimodal distribution at greater depths. A subset of coarse garnet peridotites at 145–180 km plots near the "cold" 35 mW/m^2 geotherm whereas the majority of coarse and sheared rocks at $\geq$145 km scatter between the 40 and 45 mW/m^2 geotherms. This *P–T* profile may reflect a perturbation of an initially "cold" lithospheric mantle through a combination of (1) magmatic under-plating close to the crust–mantle boundary and (2) intrusion of melts/fluids in the lower lithosphere accompanied by shearing. fO_2 values estimated from $Fe^{3+}/\sum Fe$ in spinel and/or garnet obtained by Mössbauer spectroscopy decrease from +1 to −4 Δlog fO_2 (FMQ) from the top to the bottom of the lithospheric mantle ($\sim$0.25 log units per 10 km) due to pressure effects on Fe^{2+}–Fe^{3+} equilibria in garnet. Garnet peridotites from Udachnaya appear to be more oxidized than those from the Kaapvaal craton but show fO_2 distribution with depth similar to those in the Slave craton. Published fO_2 estimates for Udachnaya xenoliths based on C–O–H fluid speciation in inclusions in minerals from gas chromatography are similar to our results at $\leq$120 km, but are 1–2 orders of magnitude higher for the deeper mantle, possibly due to uncertainties of fO_2 estimates based on experimental calibrations at $\leq$3.5 GPa. Sheared peridotites containing garnets with u-shaped, sinusoidal and humped REE patterns are usually more oxidized than Yb, Lu-rich, melt-equilibrated garnets, which show a continuous decrease from heavy to light REE. This further indicates that mantle redox state may be related to sources and modes of metasomatism.

1. Introduction

Mantle xenoliths brought up by kimberlitic magmas are the main source of data on the composition of cratonic mantle and its physical conditions at the time of eruption: pressure (*P*), temperature (*T*) and oxygen fugacity (fO_2). Thermal profiles with depth (geotherms) establish vertical distribution of rock types in the lithospheric mantle and identify thermal perturbations related to geological events, like intrusion of melts and fluids. Oxygen fugacity is a key factor in the stability of carbon-rich phases (diamond, graphite, carbonates) and the speciation of C–O–H-bearing fluids, which in turn affect melting, metasomatism and mineral–melt element partitioning (e.g., Frost and McCammon, 2008; Wood et al., 1990).

Oxygen fugacity (i.e. chemical activity of oxygen) in mantle peridotites is estimated from the compositions of coexisting spinel (spl), garnet (gar), olivine (ol) and orthopyroxene (opx) in two exchange reactions:

$$\underset{\text{olivine}}{6Fe_2SiO_4} + O_2 = \underset{\text{opx}}{3Fe_2Si_2O_6} + \underset{\text{spinel}}{2Fe_3O_4} \quad (1)$$

$$\underset{\text{garnet}}{2Fe_3Fe_2Si_3O_{12}} = \underset{\text{opx}}{Fe_2Si_2O_6} + \underset{\text{olivine}}{4Fe_2SiO_4} + O_2 \quad (2)$$

It can be calculated from activities of Fe-rich end-members of minerals in reactions (1) and (2) (Frost and McCammon, 2008 and references therein). The key parameter in such calculations is the ratio of ferric to ferrous iron (or ferric iron to total iron, $Fe^{3+}/\sum Fe$) in garnet and spinel. While these can be estimated

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from microprobe analyses, the most reliable data are obtained by Mössbauer spectroscopy (e.g., Wood and Virgo, 1989). The fO_2 estimates are strongly affected by P and T, hence require good knowledge of thermal lithospheric profiles.

Oxygen fugacity in cratonic mantle has so far been explored using data on xenoliths from the Slave craton in North America (Creighton et al., 2010; McCammon and Kopylova, 2004) and the Kaapvaal craton in South Africa (Lazarov et al., 2009; Woodland and Koch, 2003). These data show that fO_2 generally decreases by several orders of magnitude with depth due to the effect of pressure on Fe^{2+}–Fe^{3+} equilibria involving garnet (Wood et al., 1990), but also demonstrated important lateral fO_2 variations. The latter are commonly attributed to melt extraction or ingress of fluids or melts, but precise effects of mantle processes on fO_2 remain to be constrained and require data on well-studied xenoliths from other cratons. Here, we report Mössbauer $Fe^{3+}/\sum Fe$ analyses of spinel and garnet from 36 peridotite xenoliths from the Udachnaya kimberlite in the central Siberian craton.

2. Geological context and samples

The 360 Ma Udachnaya-East pipe (66°26 N; 112°19 E) (KML map) is mined for diamonds and hosts abundant mantle xenoliths (Pokhilenko et al., 1999; Sobolev, 1977). Deformed garnet peridotites are most common, followed by granular garnet peridotites, spinel harzburgites, eclogites and pyroxenites (see Ionov et al. (2010) for references). The 42 xenoliths in this study come from deep levels of the mine and are less altered than those reported earlier (Boyd et al., 1997). They are modally homogeneous spinel and garnet (both coarse and sheared) peridotites selected to represent main rock types and a broad depth range. Table 1 gives essential petrologic information on the samples and results of this study. 23 xenoliths are from the suite reported by Ionov et al. (2010), 9 samples were previously investigated by Glebovitsky et al. (2007) and 10 samples were kindly provided by N.V. Vladykin. P–T–fO_2 values were calculated using mineral compositions reported by Ionov et al. (2010) for their suite and our new data for other samples.

Pure garnet and spinel grains were handpicked under microscope from 0.5 to 2.0 mm size fractions of crushed and sieved rock material. The minerals were crushed in an agate capsule filled with acetone to avoid iron oxidation in contact with air, mixed with polyethylene and pressed into cone-shaped pellets. The density of the natural iron absorber was 5 mg/cm^3.

3. Analytical methods

Major element analyses of minerals were done on a scanning electron microscope (SEM) JEOL JSM-6510LA with JED-2200 detector at the Institute of Precambrian Geology and Geochronology (IPGG), Saint-Petersburg, Russia, using an acceleration potential of 20 kV, a beam current of 5 nA and a spot size of 3 μm. Standards were natural minerals and pure oxides and metals. The ZAF algorithm was used for matrix correction.

The $Fe^{3+}/\sum Fe$ values of garnet and spinel were determined using an SM-1201 Mössbauer spectrometer at the IPGG at room temperature in a constant acceleration mode with a nominal 50 mCi ^{57}Co source in a Cr matrix. The spectra were collected over a velocity range of about ± 7 mm/s with a multi-channel analyzer. The velocity was calibrated relative to metal iron at room temperature. The spectra were approximated by the sum of Lorentz form lines using the MOSSFIT© software. The relative amounts of Fe^{2+} and Fe^{3+} and their site positions in crystal lattice were determined using integral doublet intensities assuming equal Mössbauer effect probabilities for Fe^{2+} and Fe^{3+} and at different sites. Spectral model for the garnet included a single doublet for Fe^{2+} and Fe^{3+}. The relative peak widths and areas of the Fe^{2+} doublet were left unconstrained to account for spectra asymmetry (Amthauer et al., 1976). The doublet attributable to octahedrally coordinated Fe^{3+} was constrained to have peaks with equal widths. For garnets low in Fe^{3+}, the peak width was fixed at a maximum of 0.4 mm/s to obtain a physically meaningful fit. For spinel, a model with two Fe^{2+} and one Fe^{3+} doublets was employed with equal relative peak widths and areas of each doublet (e.g., Li et al., 2002). Detection limits are ± 0.01 mm/s for velocity parameters of the spectra and ± 1.5–3% for the proportions of Fe^{2+} and Fe^{3+} at different sites.

4. Petrography and major element composition

Spinel peridotites in this study are medium- to coarse-grained with protogranular to mosaic equigranular microstructures; eight are harzburgites with 1–4% clinopyroxene (cpx), one is a low-cpx (6%) lherzolite and two are dunites. Spinel (0.2–2%) forms irregular grains of different sizes, thin interstitial segregations or is intergrown with opx (Fig. 1a).

Granular garnet peridotites have microstructures (Fig. 1b) similar to those in the spinel peridotites; they range from harzburgites (0–4.5% cpx) to low-cpx (6–7%) lherzolites, some contain spinel. Garnet (1–8%) mainly forms irregular aggregates and may contain inclusions of olivine and opx. Deformed garnet peridotites (Fig. 1d) are porphyroclastic to fluidal mosaic; they are mainly lherzolites, with subordinate harzburgites and wehrlites. Garnets are typically round or ellipsoidal and usually have thick kelyphite rims and opx and olivine inclusions (Fig. 1c). The variation ranges of modal cpx (0–21%) and garnet (1–17%) are much broader than for the granular rocks.

Major oxide compositions and LOI data are given in Table 1 of Electronic Supplement. Coarse peridotites are low in CaO (0.3–1.6 wt%) and Al_2O_3 (0.1–1.8 wt%) and have high MgO ($\geq$44% wt%) and Mg# [$Mg/(Mg+Fe)_{at}$] (0.91–0.93). Deformed peridotites show much broader compositional ranges: 0.4–4.4 wt% CaO, 0.3–4 wt% Al_2O_3, 0.04–0.28 wt% TiO_2, 37–47 wt% MgO and generally lower Mg# (0.87–0.915). The compositions of the coarse peridotites are consistent with an origin as residues of high-degree melt extraction (Fig. 2), but the wehrlites and sheared peridotites are enriched in garnet and/or cpx, Fe and light and medium rare earth elements (LREE–MREE), i.e. show modal and cryptic metasomatism (Ionov et al., 2010).

The minerals usually show no significant major element core-rim zoning. Average $Cr\#_{Sp}$ [$Cr/(Cr+Al)_{at}$ in spinel], Cr_2O_3 in garnet and $Mg\#_{Ol}$ are listed in Table 1. $Mg\#_{ol}$ in spinel peridotites (0.92–0.93) is higher than in coarse (0.87–0.925) and sheared (0.87–0.92) garner peridotites. The garnets contain 6.7–9.8 wt% $\sum$FeO, 4.1–7.1 wt% CaO and 1.8–12.3 wt% Cr_2O_3 (ES Table 1). The Ca and Cr contents are positively correlated (Fig. 3a), as is common for cratonic garnets (Grütter et al., 2004; Ionov et al., 2010; Pearson et al., 2003). $Cr\#_{Sp}$ ranges broadly (0.26–0.84) but is generally higher in dunites and gar-bearing peridotites (0.72–0.84; Fig. 3b). $\sum$FeO in spinel (11–22 wt%) is generally higher in Cr-rich spinel (Fig. 3b).

5. *P–T* estimates and thermal state of the mantle

5.1. Methodology and results

Equilibration pressures and temperatures (Table 1) were estimated from average core compositions of minerals using a combination of the opx–gar barometer of Nickel and Green (1985)