

Ferric iron measurements of coexisting garnet and clinopyroxene in grosspydite xenoliths from Zagadochnaya kimberlite pipe (Yakutia, Siberian craton)

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Introduction

Mantle-derived eclogites allow to track the evolution of the ancient oceanic crust upon subduction in the lithospheric mantle in terms of chemistry, mineralogy, and redox conditions. Grosspydites represent a rare variety of eclogites composed of grossular–pyroxene–kyanite (disthene), often associated with coesite and sanidine and with no evidence for elemental carbon species. These unique samples have been collected in only a few localities like the Zagadochnaya kimberlite pipe (Yakutia, Siberia; Sobolev et al. 1968) and Roberts Victor kimberlite (South Africa; Smyth et al. 1977). However, these authors provided only general petrographic information. To date, in fact, no studies focused on the pressure, temperature and redox conditions (T-P- f_{O_2}) of formation of grosspydites, which could help to understand their origin in the mantle as well as the absence of graphite/diamond. In this study, we determined the chemical composition and $Fe^{3+}/\Sigma Fe$ of coexisting garnet and clinopyroxene fragments extracted from four diamond-free grosspydite xenoliths from the Zagadochnaya pipe, located 30 km away from the diamantiferous Udachnaya pipe (Siberia), to retrieve the f_{O_2} and model volatile speciation at depth.

Brief samples description

The investigated grosspydite xenoliths have a rounded and flattened-rounded shape with sizes from 0.5 to 15 cm (Fig. 1). The rock-forming minerals have diverse modal abundances like garnet from 20 to 50 vol.%, clinopyroxene from 10 to 30 vol.% and kyanite from 1 to 25 vol.%. Samples are granoblastic with coarse-grained massive texture. Fractured orange-brown garnet porphyroclasts have sizes from 0.5 to 1 mm, while light grey-green intensely fractured xenomorphic omphacite relicts have sizes from 100 μm to 2 mm. Additionally, light blue elongated prismatic kyanite crystals ranging in size from 0.3 to 0.8 mm were found within intergranular boundaries.

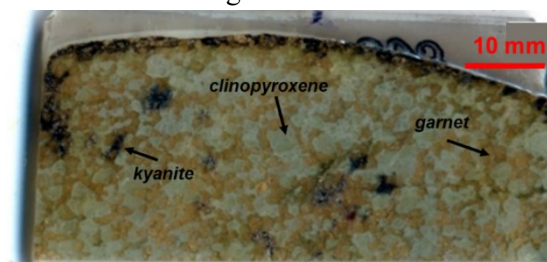


Figure 1: Zagadochnaya grosspydite xenolith with garnet (orange), clinopyroxene (green) and kyanite (blue).

Methods

The major element chemistry was measured by electron microprobe, while the $Fe^{3+}/\Sigma Fe$ ratio was determined by Mössbauer spectroscopy. $Fe^{3+}/\Sigma Fe$ ratios of four paired garnets and clinopyroxene fragments extracted from the same rock along with garnets from an additional sample were mounted as a mosaic (5 to 10 crystals) and measured by milliprobe Mössbauer spectroscopy at Bayerisches Geoinstitut (Germany). Additional garnets were powdered (20–30 mg each) and analyzed at Jožef Stefan Institute (Slovenia) using

a conventional source. Among the investigated garnets, three were measured by both conventional and milliprobe sources in order to test the $\text{Fe}^{3+}/\sum\text{Fe}$ ratios homogeneity of the samples. The Mössbauer spectra collected with the point source were fitted by a full transmission integral with a normalized pseudo-Voigt line shape, while those collected with the conventional one were fitted by a Lorentzian line shape. The fitting model consisted of one doublet for Fe^{3+} and one doublet for Fe^{2+} for garnet, and one doublet for Fe^{3+} and two doublets for Fe^{2+} for clinopyroxene. Hyperfine parameters used for the fitting are consistent with those previously reported for natural and experimental eclogitic garnets and clinopyroxenes (e.g., Stagno et al. 2015; Mikhailenko et al. 2020).

Composition and Fe^{3+} content of garnet and clinopyroxene

Garnets are solid solution of pyrope (12-43 %), almandine (14-40 %) and grossular (40-80 %), with two samples classified as B-type and five as C-type according to Coleman et al. (1965) ternary diagram. Clinopyroxenes have 5.1-10 wt% of MgO, 2-3.7 wt% of FeO and 5.5-7.7 wt% of Na_2O . $\text{Fe}^{3+}/\sum\text{Fe}$ ranges between 0.03 and 0.21 (± 0.01) for garnet and between 0.21 and 0.53 (± 0.02 -0.03) for clinopyroxene (Fig. 2). Interestingly, while the $\text{Fe}^{3+}/\sum\text{Fe}$ of garnet data of one sample shows same values within the error using the two sources (0.07 point and 0.06 conventional), two samples indicate a large shift in the $\text{Fe}^{3+}/\sum\text{Fe}$ contents from 0.04 with the conventional to 0.12 and 0.17 with the point (Fig. 2). This observation points out possible Fe^{3+} heterogeneities within the same grosspydite, which are not detected at the scale of bulk analysis on powdered samples, likely associated with the presence of secondary rims. Part of these $\text{Fe}^{3+}/\sum\text{Fe}$ data are higher than what was reported in the literature for diamantiferous Udachnaya eclogites (Mikhailenko et al. 2020; Aulbach et al. 2022) but agree with those measured in graphite/diamond-free eclogites from the V. Grib pipe (Arkhangelsk Diamond Province; Marras et al. under review; Fig. 2).

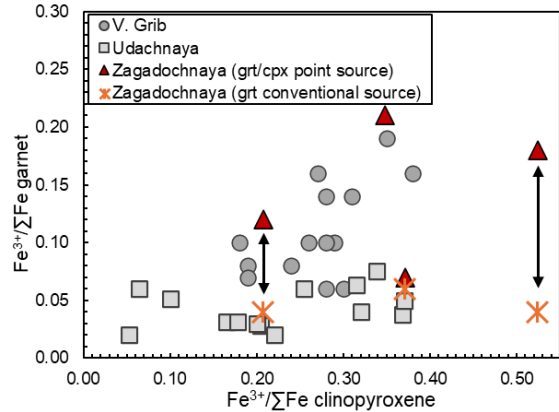


Figure 2: $\text{Fe}^{3+}/\sum\text{Fe}$ of paired garnet and clinopyroxene for Zagadochnaya grosspydites and literature eclogites (see the text). Double arrows indicate same samples for which garnet was measured by both point and conventional source, recording Fe^{3+} heterogeneities.

Preliminary P-T- f_{O_2} estimates

We estimated P-T- f_{O_2} employing the available literature models to constrain the equilibrium conditions of grosspydites eclogites. P-T were calculated using two different approaches, i) a combination of Nakamura (2009) thermometer and Beyer et al. (2015) barometer; ii) Krogh (1988) thermometer projecting the obtained T onto regional geothermal gradients. The first approach was applied only on samples having Si clinopyroxene (apfu) < 1.985 as required by Beyer et al. (2015). The retrieved P-T are 3.3-7.7 GPa and 915-1400 °C, respectively (Fig. 3a). The sample recording the highest P-T conditions (7.7 GPa and 1400 °C), has garnet with grossular content of 80 %. Interestingly, plotting the obtained data along with typical cratonic geotherms, Zagadochnaya grosspydites seem to have (re)equilibrated under different thermal regimes (Fig. 3a). As proposed by Aulbach et al. (2022), we exploited this evidence to solve T by Krogh (1988) iteratively with the appropriate geotherms (36 mW/m² and 40 mW/m²; Hasterok & Chapman 2011), based on Figure 3a observations. The resulting P-T are 3.2-5.2 GPa and 830-1001 °C, respectively (Fig. 3b). Regardless the used method, three samples fall in the graphite stability field. The use of Krogh (1988) model combined with the geotherm allows a direct comparison with literature data for Udachnaya (Aulbach et al. 2022) and V. Grib (Marras et al. under review; Fig. 3b).

The calculated f_{O_2} using the Stagno et al. (2015) oxy-thermobarometer, ranges from -2.3 to 1.5 log units (FMQ). In the case of the two samples where heterogeneities were observed in terms of Fe^{3+} in garnets, the f_{O_2} varies up to +2 log units. According to these preliminary results, Zagadochnaya grosspydites are among

the most oxidized eclogitic samples studied to date, potentially explaining the absence of elemental carbon (either graphite or diamond) within the rock matrix.

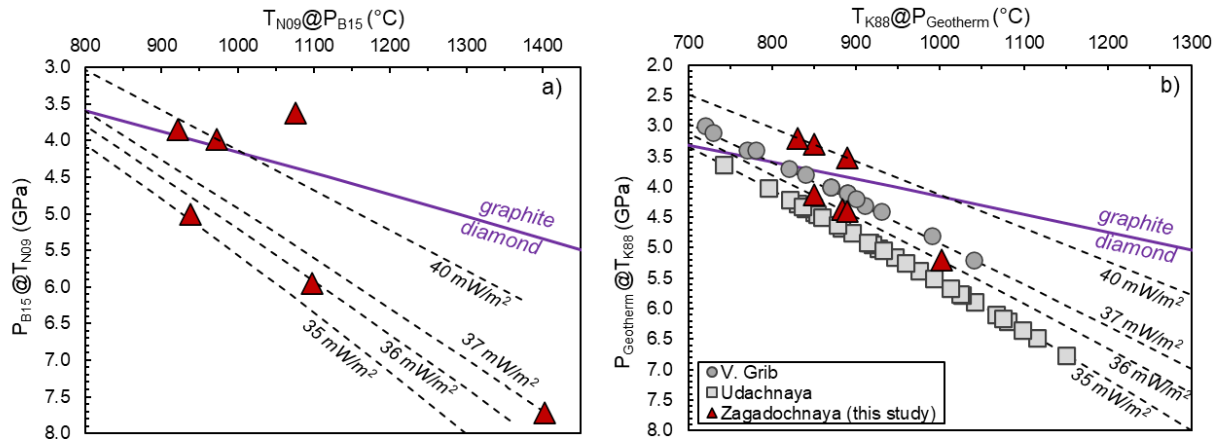


Figure 3: P-T estimates for Zagadochnaya grosphydites according to a) Nakamura (2009) thermometer against Beyer et al. (2015) barometer and b) Krogh (1988) thermometer projected onto 36 and 40 mW/m² geotherms (Hasterok & Chapman 2011). The graphite-diamond boundary (Day 2012) is also shown. Data for V. Grib and Udachnaya eclogites are reported (see the text for references).

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