

# The maximal chromium content in harzburgitic garnet: an experimental study at P-T conditions of the Earth's upper mantle

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## Abstract

A subcalcic Cr-rich pyrope is typical for inclusions in natural diamond and considered as the main indicator mineral in diamond exploration. The article presents the results of experiments in a model garnet-spinel-harzburgite with the aim to determine the maximal Cr content in the garnet. The study supplemented the CaO vs Cr<sub>2</sub>O<sub>3</sub> diagram with new data on Cr-rich garnets obtained experimentally. A high pressure apparatus (BARS) was used to conduct experiments at a pressure of 5.5 GPa and temperature 1300 °C, which correspond to the stability field of both garnet and diamond. The model harzburgite was obtained using natural Mg-serpentine, which decomposes at pressures and temperatures of experiment into olivine and orthopyroxene. Natural chromite and carbonatite were used as the sources of Cr and Ca, respectively. The obtained samples composed of forsterite, enstatite, Cr-pyrope and Cr-spinel. The maximal Cr<sub>2</sub>O<sub>3</sub> content, up to 16.23 wt.%, was detected in grains which grew in contact with chromite. The addition of 1-2 wt.% carbonatite has led to crystallisation of garnets with varying contents of Ca (2.83-7.49 wt.% CaO), but slightly influenced further increase of Cr in garnet. The experiments confirmed the boundary at 16 wt.% Cr<sub>2</sub>O<sub>3</sub> for subcalcic pyrope associating with diamond. It is concluded that the origin of natural



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samples of Ca-rich lherzolitic/wherlitic and Ca-poor harzburgitic garnets with more than 16 wt.% Cr<sub>2</sub>O<sub>3</sub> is attributed to the specific Ca/Cr/Al ratios of the medium.

## Introduction

The ratio of Cr<sub>2</sub>O<sub>3</sub> and CaO is very specific in pyrope from inclusions in natural diamond and has become a recognized instrument for paragenetic identification of mantle garnets from the cratonic lithosphere (Sobolev et al., 1973; Gurney, 1984). The garnets are classified as harzburgitic, lherzolitic and wherlitic according to their affinity with the hosted rocks (Sobolev, 1977; Dawson and Stephens, 1975; Gurney, 1984; Grütter et al., 2004; Griffin et al., 1999a, 2002; Schulze, 2003; Stachel and Harris, 2008). A unique subcalcic Cr-rich pyrope, termed in the international literature as G10 garnet (Grütter et al., 2004), is typical for inclusions in natural diamond and considered as the main indicator mineral in diamond exploration (Afanasiev and Pokhilenko, 2022). The garnet belongs to the harzburgitic suite and usually contains about 2-4 wt.% CaO and 6-12 wt.% Cr<sub>2</sub>O<sub>3</sub>. However, garnets with Cr<sub>2</sub>O<sub>3</sub> content exceeding 14 wt.% are rare. The “competition” for recording the maximal content of knorringite component (Mg<sub>3</sub>Cr<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>) in garnet started more than half a century ago. The recorded ratios of Cr<sub>2</sub>O<sub>3</sub> vs CaO (wt.%) include the following: 10.9 – 2.19 (Meyer, 1968); 12.6 – 1.74 (Meyer and Boyd, 1972); 13.7 – 3.38 (Sobolev et al., 1973); 17.7 – 0.93 (Meyer and Svisero, 1975); ≈15.5 – ≈1.5 (Gurney, 1984); 20.6 – 1.57 (Stachel and Harris, 1997b); 17.28 – 0.39 (Harris et al., 2004); ≈15 – ≈5 (Davis et al., 2004); 20.9 – 2.19 (Logvinova et al., 2005); ≈17.5 – ≈3 (Smith et al., 2009). Despite the few analyses, which show Cr<sub>2</sub>O<sub>3</sub> content in harzburgite garnet exceeding 20 wt.% (Stachel and Harris, 1997a,b; Logvinova et al., 2005), the vast majority (95%) of analysed samples worldwide contained less than 16 wt.% Cr<sub>2</sub>O<sub>3</sub> (Stachel and Harris, 2008; Turkin and Sobolev, 2009). It is pertinent to note that, on the one hand, the enrichment in Cr (over 20 wt.% Cr<sub>2</sub>O<sub>3</sub>) is not uncommon for a wherlitic garnet, however it is not the subcalcic variety as it is Ca-rich. On the other hand, natural samples usually demonstrate a negative correlation between Al<sub>2</sub>O<sub>3</sub> content of xenoliths and Cr<sub>2</sub>O<sub>3</sub> in their garnets (Griffin et al., 1999b). Therefore, the proportions of Cr, Al и Ca in rock can significantly affect the formation of specific varieties of garnets in peridotites.

The garnet formula is A<sub>3</sub>B<sub>2</sub>Si<sub>3</sub>O<sub>12</sub>, where A = Mg<sup>+2</sup>, Fe<sup>+2</sup>, Mn<sup>+2</sup>, Ca<sup>+2</sup>, Y<sup>+3</sup>, rarely Na<sup>+</sup> and B = Al<sup>+3</sup>, Fe<sup>+3</sup>, Cr<sup>+3</sup>, Mn<sup>+3</sup>, rarely V<sup>+3</sup>, Ti<sup>+4</sup>, Zr<sup>+4</sup>. As a result of experimental studies, it has become obvious that knorringite component – Mg<sub>3</sub>Cr<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> increases in garnet with increasing pressure (Malinovsky and Doroshev, 1977; Turkin et al., 1983; Irifune and Hariya, 1983; Nickel, 1986;

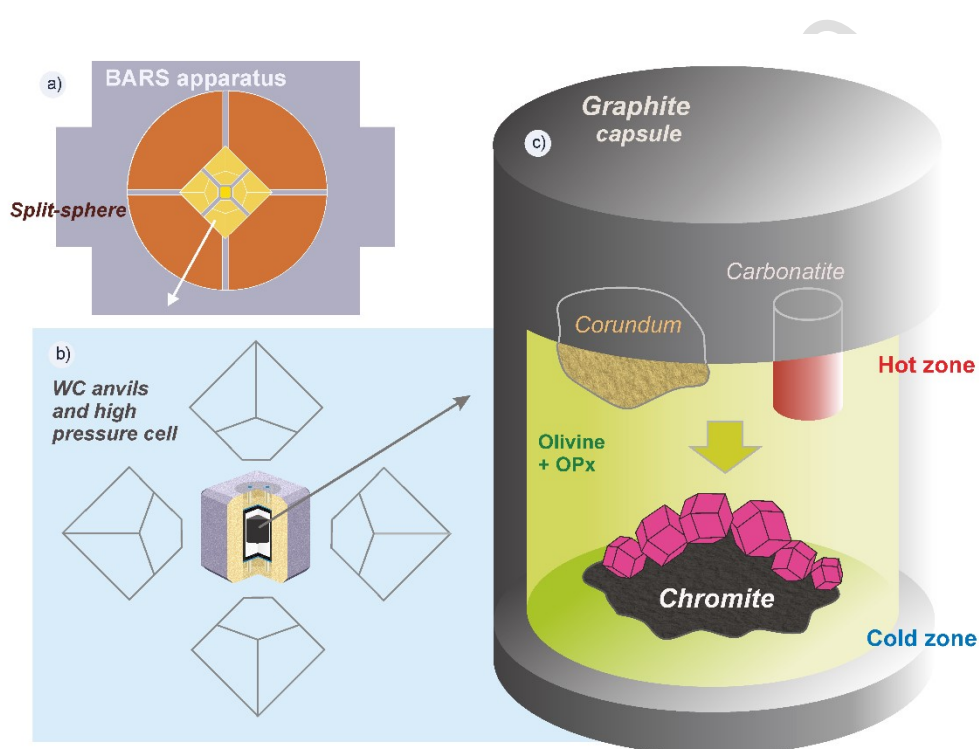
Doroshev et al., 1997) and thus Cr is higher in garnets formed at higher pressures (the basis of the Cr in garnet barometer, which assumes equilibrium with spinel). The increase of Cr in garnet can also be a result of the increase of uvarovite component ( $\text{Ca}_3\text{Cr}_2\text{Si}_3\text{O}_{12}$ ) in pyrope ( $\text{Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ ), which implies that such isomorphism is accompanied by a simultaneous increase of Ca, Cr and decrease of Mg, Al. The complexity of garnet compositions is due not only to the broad isovalent isomorphism between elements within A and B groups, but to more complex heterovalent substitutions as well (Godovikov, 1975). The possibility of excess silicon with coordination VI, which was reported for majoritic garnet in experiments above 9 GPa (Ringwood and Major, 1966; Ringwood, 1967) as well as the discovery of majorite in Coorara meteorite (Smith and Mason, 1970), has motivated the studies of garnet-pyroxene solid solutions at high pressures (Ringwood and Major, 1971; Akaogi and Akimoto, 1977; Jakubith and Hornemann, 1981; Jeanloz, 1981; Kato et al., 1987; Irifune, 1987; Herzberg and Gasparik, 1991; Hazen et al., 1994a,b; Ono and Yasuda, 1996; Nakatsuka et al., 1999; Gasparik, 2002; Sobolev et al., 2016; Thomson et al., 2021 and others). An isomorphic substitution of  $2\text{B}^{3+} = \text{A}^{2+} + \text{Si}^{4+}$  or  $\text{B}^{3+} + \text{A}^{2+} = \text{X}^{+} + \text{Si}^{4+}$  has been established for the classical garnet structure  $^{\text{VIII}}[\text{A}^{2+}]_3^{\text{VI}}[\text{B}^{3+}]_2^{\text{IV}}[\text{Si}^{4+}]_3\text{O}_{12}$  with increasing pressure. Here, Si displaces trivalent cations (including Cr) from the octahedral site. As a result,  $\text{Mg}_4\text{Si}_4\text{O}_{12}$  content can increase up to 4 mol.% in pyrope at a pressure of 5 GPa (Akaogi and Akimoto, 1977) and about 15 mol.% in knorringite at 8 GPa (Zou and Irifune, 2012). It should be noted that recalculation of chemical composition of harzburgitic knorringite-rich garnet (20.2 wt.%  $\text{Cr}_2\text{O}_3$  – Stachel and Harris, 1997b) demonstrated over 8 mol.% pyroxene component ( $\text{Mg}_{0.625}\text{Ca}_{0.385}\text{Si}_4\text{O}_{12}$ ).

Cr-rich pyrope usually associates with silicate minerals, mainly with olivine and pyroxene, which are characterised by high Mg-numbers, typically of 92-94 in olivine. Additionally, the spinel, when present, is Cr-rich (Harris, 1968; Meyer and Boyd, 1972; Sobolev, 1977; Harris and Gurney, 1979; Grütter et al., 2006; Stachel and Harris, 2008; Lenaz et al., 2009). Taking into account this fact, the aim of present experiment was to examine the composition of garnet which crystallised in contact with chromite in model harzburgite under the P-T conditions of diamond stability field.

## Materials and methods

Six experiments (Table 1) were carried out using a multi-anvil split-sphere type high-pressure apparatus (BARS) developed according to the state assignment of IGM SB RAS (Fig. 1a, b). A high pressure cell was made of mixture based on  $\text{ZrO}_2$  oxide. The cell was a rectangular cuboid (20×20×23 mm) with truncated edges and vertices. A tubular heating element was made of

graphite. Pressure in the cell was calibrated at ambient temperature using reference substances Bi and PbSe (Turkin, 2003). Temperature was measured using a PtRh30-PtRh6 thermocouple without pressure correction. The temperature correction for pressure was determined by melting of metals Ag and Au (Tonkov and Ponyatovsky, 2004). Measurement errors were estimated as  $\pm 0.2$  GPa and  $\pm 25$  °C. The samples were heated by a gradual temperature increase and cooled by quenching. The P-T conditions for the experiments were 5.5 GPa and 1300 °C, which correspond to the garnet stability field (Turkin and Sobolev, 2009). In order to obtain relatively large grains of garnet, the experiments were run for 25 hours. Further details of the experimental procedure are described in our previous papers (Chepurov et al., 2016, 2018).



**Fig. 1.** Schematic drawing of high pressure apparatus BARS (a); WC anvils – internal block of anvils made of tungsten carbide and general view of high pressure cell (b); (c) demonstrates assembly of the sample: the sources of Al and Ca (corundum and carbonatite, respectively) were placed in the upper part which corresponds to higher temperature, while the garnet growth occurs on chromite at the bottom of the chamber. An arrow indicates direction of components flow.

The initial materials for the experiments were natural serpentine (antigorite), chromite and corundum. Chemical composition of serpentine collected from Eastern Sayan ophiolites (Russia): SiO<sub>2</sub> – 42.36; TiO<sub>2</sub> – 0.02; Al<sub>2</sub>O<sub>3</sub> – 0.93; Cr<sub>2</sub>O<sub>3</sub> – 0.74; FeO – 2.34; MnO – 0.07; MgO – 39.96; CaO – 0.34; NiO – 0.37; Na<sub>2</sub>O – 0.30; K<sub>2</sub>O – 0.02; SO<sub>3</sub> – 0.10; LOI – 12.42; total – 99.97. Serpentine was chosen as the starting component because at the P-T parameters of experiment it

decomposes into a mixture of olivine, orthopyroxene and an aqueous fluid (Ulmer and Trommsdorff, 1995). Hence, at initial stage of each experiment the sample represented a model peridotite with fluid of predominantly aqueous composition. Chromite grains 2-3 mm in size were hand-collected from xenoliths of peridotites from Udachnaya kimberlite pipe (Yakutia), and were used as a source of Cr. Chromite composition: TiO<sub>2</sub> – 0.67; Al<sub>2</sub>O<sub>3</sub> – 6.10; Cr<sub>2</sub>O<sub>3</sub> – 54.04; FeO – 26.97; MnO – 0.00; MgO – 11.51; total – 99.29. Corundum (Al<sub>2</sub>O<sub>3</sub>) grains of 0.1-0.2 mm in size were added to initial charge in order to increase the amount of Al, due to low Al<sub>2</sub>O<sub>3</sub> content in the initial chromite. Such methodology ensured the crystallisation of pyrope variety of garnet during the experiment. Natural carbonatite from Snap Lake dike (Canada) was added to the charge as a Ca source (Agashev et al., 2008). The carbonatite composition: SiO<sub>2</sub> – 3.74; TiO<sub>2</sub> – 0.12; Al<sub>2</sub>O<sub>3</sub> – 0.95; Fe<sub>2</sub>O<sub>3</sub> – 2.86; MnO – 0.19; MgO – 18.86; CaO – 31.88; Na<sub>2</sub>O – 0.00; K<sub>2</sub>O – 0.24; P<sub>2</sub>O<sub>5</sub> – 4.51; LOI – 36.82; total – 100.17.

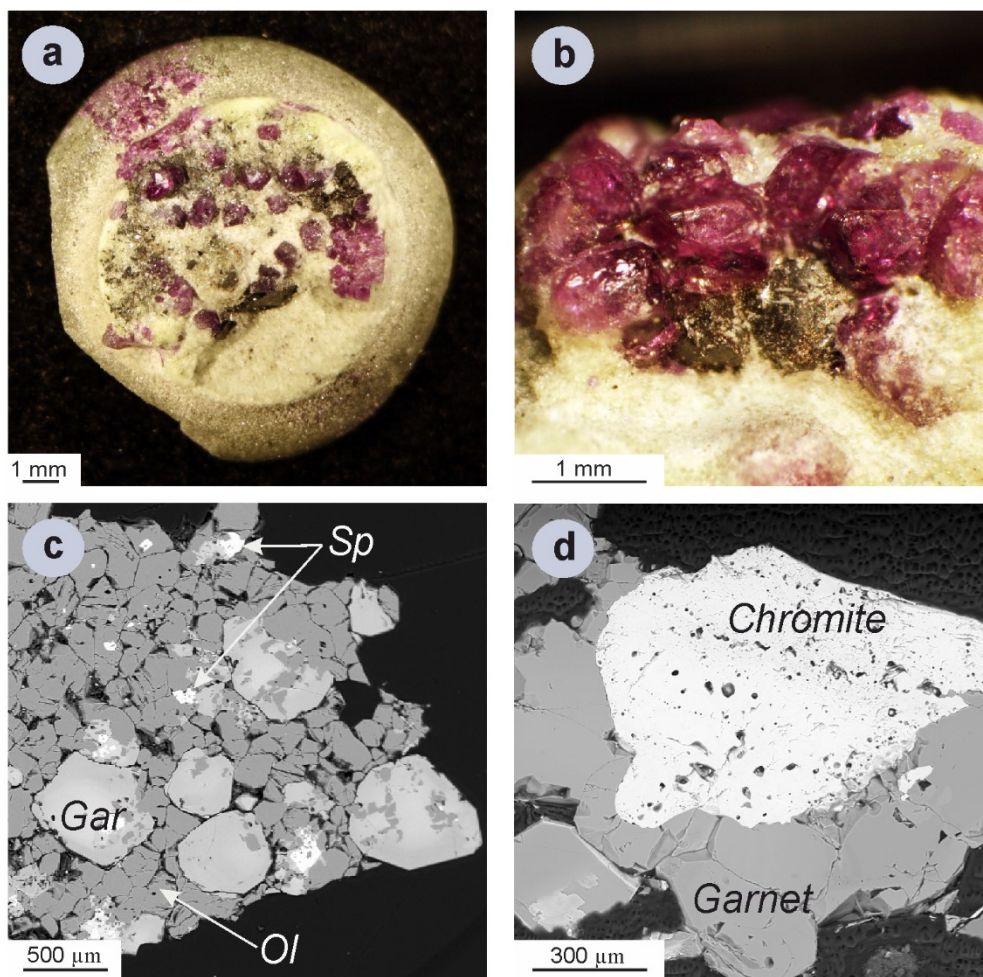
An assembly scheme of high pressure cell is shown in Fig. 1c. The sample was placed in a graphite capsule. The configuration without isolating Pt-capsule allowed the fluid to penetrate through the sample during experiment. Since no water-bearing phases were detected in the run products (Chepurov et al., 2012), the fluid participated in chemical reactions mainly as a transport of components. Temperature gradient, which exists in high-pressure cell induces the crystallisation of large grains of garnet in the colder zone (Fig. 1c). Thermocouple was placed next to the garnet crystallisation area (as in Fig. 1 of Sonin et al., 2019).

After the experiments samples were sawed along vertical axis and studied under optical microscopes MC2-Zoom, Olympus BX35 equipped with UC50 camera. Backscattered electron images (BSE) were obtained using MIRA 3 LMU scanning electron microscope equipped with X-ray microanalysis system INCA Energy 450 Xmax-80 energy dispersive spectrometer in the Analytical Center for multi-element and isotope research SB RAS (Novosibirsk, Russia). Mineral compositions were determined by electron probe microanalysis (EMPA) using JEOL JXA-8100 microanalyzer.

## Results

The experimental samples composed of newly formed olivine, orthopyroxene, garnet and spinel (Table 1). According to the planning of the experiment, garnet crystallised in the bottom part of the sample where chromite grains were initially placed (Fig. 1c). The garnet has typical shape with well-developed {110} faces and purple-rich colour (Fig. 2a,b). Representative chemical analyses of garnet with the highest contents of Cr were obtained by studying the grains in contact with initial chromite (Fig. 2d). The maximal Cr content was 16.25 wt.% Cr<sub>2</sub>O<sub>3</sub>. Calcium in these garnets is as low as 2-4 wt.% CaO, however, individual grains showed 6-7 wt.% CaO. Titanium is very

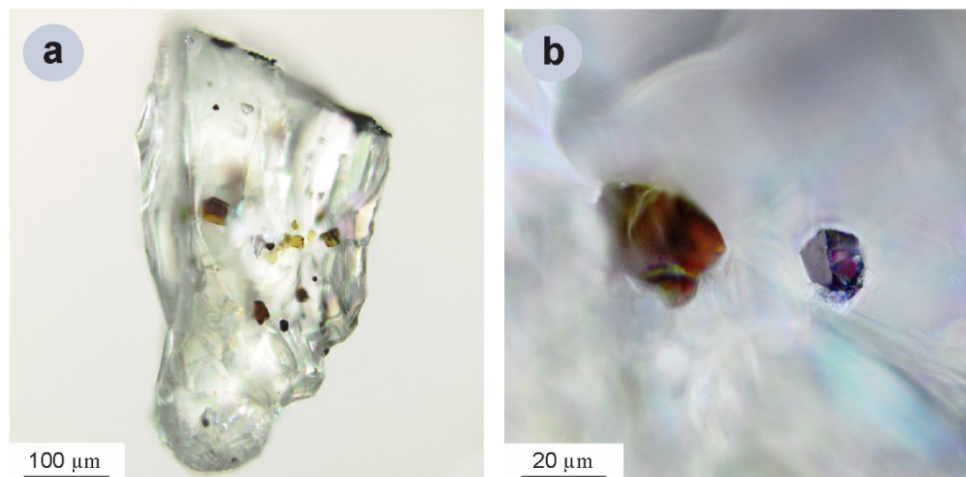
low and does not exceed 0.06 wt.% TiO<sub>2</sub>. Manganese ranged from 0.17 to 0.38 wt.% MnO. The values of Fe# and Cr# ranged within 7.48 - 9.45 and 46.12 - 50.43, respectively. We also noted a slightly increased silicon content, Si (f.u.) = 3.057 - 3.084 (Table 2).



**Fig. 2.** Representative microphotographs of samples after the experiments: (a) general view of the sample which consists mainly of olivine + orthopyroxene (white groundmass) and garnet (purple grains); (b) detailed view of Cr-pyrope crystals which grew on chromite (black grain exposed partially in the center); note an intensive color of garnet. BSE images of experimental products: (c) garnet (Gar) and spinel (Sp) grains in the groundmass which consists of olivine (Ol); (d) initial chromite which is overgrown by garnet.

Olivine is represented by a fine-grained aggregate as well as elongated grains reaching 1 mm in size (Fig. 3a). Olivine is highly magnesian (Mg# 97) and contains only 2.63 - 3.11 wt.% FeO. Microprobe analysis revealed an admixture of Cr up to 0.27 wt.% Cr<sub>2</sub>O<sub>3</sub> (Table 3). Orthopyroxene is characterised by low Fe content (2.5 - 2.8 wt.% FeO) (Table 4). No clinopyroxene was found in the run products. Newly formed Cr-spinel in the form of small grains, evenly distributed over the whole sample, was observed (Fig. 2c). The spinel and garnet were found together as inclusions in

the large transparent olivine grains (Fig. 3b). The composition of spinel varied within Cr# 84.64-86.59 and Fe# 19.44-36.06 (Table 5).



**Fig. 3.** Colorless transparent crystal of olivine with numerous inclusions of other minerals (a); enlarged view of Cr-garnet (right) and Cr-spinel (left) in olivine (b).

## Discussion

The experiments have demonstrated the growth of Cr-rich garnet both in groundmass and on initial chromite. The largest grains of garnet were synthesised in the bottom zone of reaction chamber in contact with the chromite (Fig. 1c). These garnets are characterised by deep purple colour in comparison with garnets of the groundmass (Fig. 2). The mechanism of crystallisation was described in detail in the previous publication (Chepurov et al., 2019). Here, it should be emphasised that garnet and other phases grew under subsolidus conditions in the presence of a fluid. As shown in the Methods section, at the beginning of each experiment the fluid has a predominantly aqueous composition (Ulmer and Trommsdorff, 1995; Chepurov et al., 2012), but during the run water reaction with carbon of the graphite capsule (which surrounded the sample) resulted in formation of oxygen-containing hydrocarbons (Sonin et al., 2023). Thus, the fluid becomes a C-O-H system. The similar effect is expected with the addition of carbonate: decomposition of carbonate at high temperatures and thus the appearance of CO<sub>2</sub>, which reacts with carbon of the graphite capsule and water, also may lead to formation of fluid rich in oxygen-containing hydrocarbons. Such system corresponds to the conditions of C-CO buffer which is close to buffer fayalite-magnetite-quartz (FMQ) at pressure of 5.5 GPa and temperature of 1300°C. Such oxidized environment well corresponds to the realistic geological scenarios at mantle depths less than 250 km. Here, such fluid composition is a good candidate to model a natural metasomatic agent of the lithospheric mantle: investigations of fluid inclusions in natural diamonds confirms

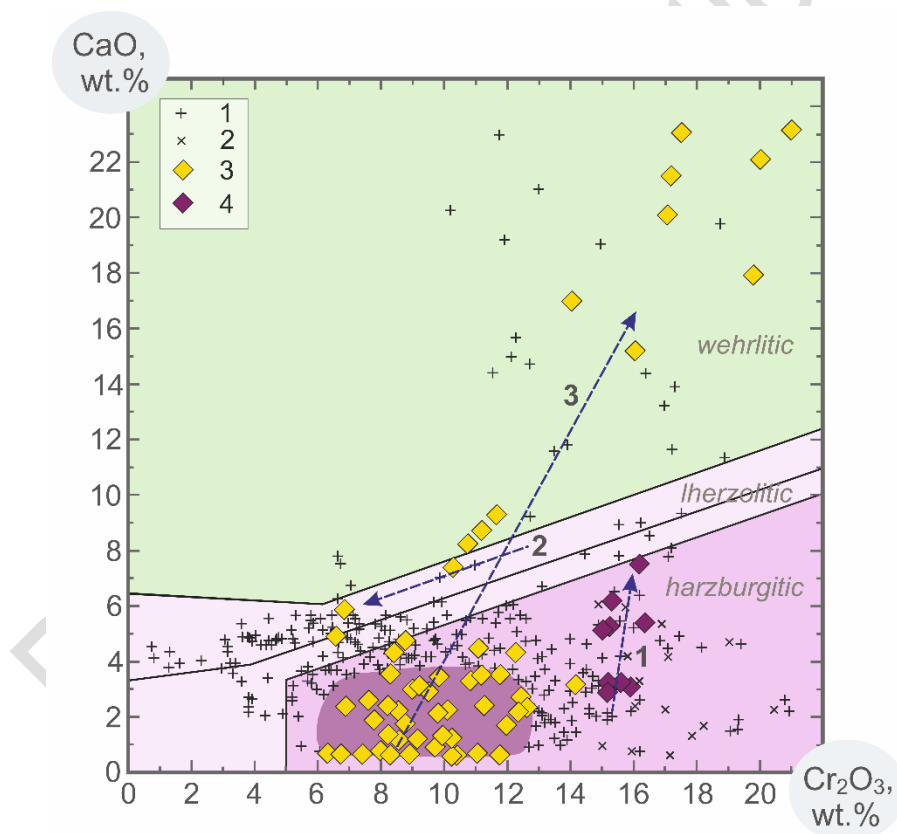
the presence of a mixture, which is characterised by wide variations of H<sub>2</sub>O, CO<sub>2</sub> and hydrocarbons; Si, Al, K, Ca and Cl as well as LILE (large ion lithophile elements), HFSE (high field strength elements) and REE (rare earth elements) may also present in different proportions. These so-called “Highly Density Fluids” (HDFs) are proposed as a diamond forming medium (Tomlinson et al., 2006; Klein-BenDavid et al., 2009; Zedgenizov et al., 2009; Shirey et al., 2013; Weiss et al., 2014; Klein-BenDavid et al., 2014; Sobolev et al., 2019). In the present experiment the fluid was a transporter of main petrological components through interstices between mineral grains, because their sources (corundum and carbonatite, respectively) were placed apart from the garnet crystallization zone (Fig. 1c). Therefore, the growth of garnet in the presence of fluid of complex composition has demonstrated metasomatic formation of Cr-rich pyrope in natural peridotite, although more magnesian (because of the choice of starting serpentine), at P-T parameters of the Earth’s upper mantle.

Discussing the obtained experimental results, it is important to take into account the association of minerals usually accompanying Cr-rich garnet in mantle xenoliths or within diamond: olivine, orthopyroxene and spinel. Natural chromite, as an important mineral of the harzburgite-dunite paragenesis, usually contains more than 62 wt.% Cr<sub>2</sub>O<sub>3</sub> along with low TiO<sub>2</sub>. Findings of such chrome spinel together with Cr-rich pyropes serve as a reliable criterion for the diamond potential of kimberlites (Sobolev, 1971). The synthesised spinel has very high Cr content, up to 70 wt.% Cr<sub>2</sub>O<sub>3</sub> (Table 5). On the one hand, such value is noticeably higher than that of the initial spinel before experiment, presumably because the Al is preferentially incorporated into the garnet. On the other hand, such composition is in agreement with the data on natural spinel inclusions in diamonds of peridotitic suite (Sobolev and Logvinova, 2005; Lenaz et al., 2009). Orthopyroxene from inclusions in natural diamond is most often represented by Mg-rich enstatite characterised by small admixture of Al (less than 1 wt.% Al<sub>2</sub>O<sub>3</sub>). The Cr-number (Cr/Cr+Al) of natural enstatite usually demonstrate a positive correlation with that of the associating pyrope. The values of up to 0.5 wt.% Cr<sub>2</sub>O<sub>3</sub> are typical for enstatites from inclusions in diamonds of South Africa and Yakutia (Sobolev, 1977). The results of our experiments demonstrated the synthesis of pyroxene of similar composition, which correlates with high Cr content of the synthesised garnet (Table 4). Olivine in the samples well reproduces the diversity of xenolithic olivines from kimberlites in terms of their high Mg/(Mg+Fe) ratio (Tychkov et al., 2020). Additionally, synthetic olivines contained an admixture of Cr (Table 2). The elevated Cr<sub>2</sub>O<sub>3</sub> concentrations in pyroxene and olivine from diamond-bearing assemblages have long been a topic for discussion (Meyer and Boyd, 1972). The present experiment confirmed that olivine, which crystallises together with Cr-pyrope at 5.5 GPa in the presence of C-O-H fluid, which corresponds to C-CO or fayalite-magnetite-quartz (FMQ) buffers, can contain an admixture of 0.27 wt.% Cr<sub>2</sub>O<sub>3</sub> typically observed in olivines from diamond



inclusions worldwide (Stachel and Harris, 1997a). Although higher values of Cr<sub>2</sub>O<sub>3</sub> are known, such as olivine inclusion in Luobusa mantle chromitite, which contains up to 1.49 wt.% Cr<sub>2</sub>O<sub>3</sub> (FengHua et al., 2014) or olivine in chromite from De Beers Pool Kimberlites (Phillips et al., 2004) of 1.10 wt.% Cr<sub>2</sub>O<sub>3</sub>, the detection of high Cr<sub>2</sub>O<sub>3</sub> values in olivine should always be considered with caution due to the possible presence of Cr-spinel either in the form of numerous chromite intergrowths (Dobrzhinetskaya et al., 1996) or microinclusions, such as observed in synthetic olivines (Fig. 3).

Regarding the target composition of garnet, it was not intended to add much Ca into the experiment. The choice of such system made it possible to synthesise Cr-rich pyrope in which CaO content was less than 3 wt.% in case of 1 wt.% carbonatite in the initial charge. Such garnet compositions are very interesting, because they are similar to the typical Ca-poor garnet inclusions in diamonds (Fig. 4).



**Fig. 4.** CaO-Cr<sub>2</sub>O<sub>3</sub> plot for Cr-rich garnet in natural diamond combined with the experimental data: 1 – natural garnets from the localities worldwide, data source: Sobolev, 1977; Kovalsky et al., 1979; Griffin et al., 1993; Sobolev et al., 1973, 1997, 2004; Zedgenizov et al., 1998; Harris et al., 2004; Meyer and Svisero, 1975; Stachel et al., 2000, 2004a,b; Logvinova et al., 2005; 2 – Representative harzburgitic garnets with Cr<sub>2</sub>O<sub>3</sub> content higher than 14 wt.% (Stachel and Harris, 2008); Oval field represents 95% of all garnets analysed, data reproduced from Turkin and Sobolev, 2009; 3 – Summarized data on garnets synthesised in previous experiments – data taken from Chepurov et al., 2018, 2019; Turkin et al., 2021; 4 – Cr-rich garnets from the present experiments. The arrows: 1 – low-carbonatite trend of the present experiment; 2 – silicate metasomatism trend after Pokhilenko et al. (2015); 3 – high-Ca high-Cr trend after the previous

experiments by Chepurov et al. (2018, 2019) and Turkin et al. (2021); for further explanation the reader is referred to the main text.

The use of carbonatite is interesting, because it is considered as one of the main metasomatic agents in the Earth's mantle (Shu and Brey, 2015). It should be noted that the experimental samples modelled a natural harzburgite with a relatively low percentage of garnet in the bulk. Such rock is considered to have experienced only a slight degree of mantle metasomatism (Doucet et al., 2012; Ilyina et al., 2022). Further small addition of Ca into the medium (2 wt.% carbonatite) has led to the crystallisation of pyrope with up to 16 wt.% Cr<sub>2</sub>O<sub>3</sub> and 7.5 wt.% CaO (Fig. 4, Table 2) in the absence of clinopyroxene.

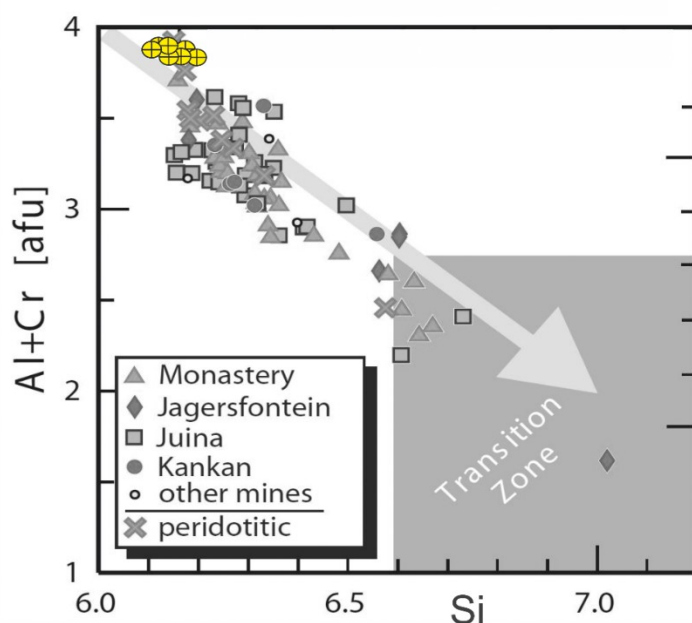
On the CaO vs Cr<sub>2</sub>O<sub>3</sub> diagram the natural garnets, which contain high Cr<sub>2</sub>O<sub>3</sub>, show variable amounts of CaO (Fig. 4). The garnet compositions in the experiment demonstrated an increase of CaO and only a slight increase of Cr<sub>2</sub>O<sub>3</sub> (Fig. 4, trend line 1). This suggests that small amount of carbonatite in the medium (1-2 wt.%) slightly influenced further increase of Cr in garnet. Among natural garnets the samples U-4-76 (Howarth et al., 2014) and U-105-89 (Pokhilenko et al., 1999) are representative cases: they show vivid Ca-zoning and, at the same time, stable Cr<sub>2</sub>O<sub>3</sub> content. This is explained by the effect of carbonatite metasomatism (Pokhilenko et al., 2015), when percolating fluids introduce mainly Ca. Here, the role of CaO/Al<sub>2</sub>O<sub>3</sub> ratio of the growth medium should also be taken into account, because natural peridotites demonstrate a positive correlation between CaO and Al<sub>2</sub>O<sub>3</sub> (Pearson, Wittig, 2008). The introduction of both CaO and Al<sub>2</sub>O<sub>3</sub> through metasomatic process may induce the formation of more garnet in the system, but in such case the new garnet will not be of Ca-poor varieties. Additionally, a negative correlation between Al<sub>2</sub>O<sub>3</sub> content of xenoliths and Cr<sub>2</sub>O<sub>3</sub> in their garnets (Griffin et al., 1999b) suggests that Cr-rich and Ca-poor garnet can grow in peridotite only at early stages of mantle metasomatism. Additionally, Al<sub>2</sub>O<sub>3</sub> deficiency in such ultra-depleted rock may even grind to a halt the growth of pyrope, as was already shown experimentally (Chepurov et al., 2016). Another trend, which should be mentioned, is the effect of so-called silicate metasomatism (Pokhilenko et al., 2015), which implies significant mineralogical and geochemical changes in the mantle rocks. In the present study it was out of focus, since the process tends to form Cr-poor garnet compositions (Fig. 4, trend line 2).

Further discussion of Ca/Cr/Al ratio of the medium should also involve the garnet compositions of more than 16 wt.% Cr<sub>2</sub>O<sub>3</sub>. The present experiment was not aimed to further enrich the charge with Ca and demonstrate an intensive carbonatite effect, which is accompanied by the appearance of clinopyroxene and crystallisation of Ca-rich garnet. In such case, the introduction of much Ca into Cr-rich system may cause the crystallisation of garnet which contains both very high Cr and Ca. An interesting example is the garnet found in Kao kimberlite pipe which was called knorringite (Nixon and Hornung, 1968). The referenced sample is very Cr-rich (17.4 wt.% Cr<sub>2</sub>O<sub>3</sub>), but Ca

content is high (8.14 wt.% CaO) as well. Additionally, this garnet has a green hue. Such green coloured Cr-rich garnets have been already synthesised in association with olivine, orthopyroxene and clinopyroxene: Cr content can be extremely high (up to 21.62 wt.% Cr<sub>2</sub>O<sub>3</sub>) as well as Ca content (13-24 wt.% CaO) (Chepurov et al., 2018). This was explained by the deficiency of Al in Cr-rich medium and thus the introduction of Ca leads to substitution of (Mg+Al) pair by (Ca+Cr) and thus increasing the uvarovite component in pyrope (Fig. 4, tend 3). Therefore, crystallisation of garnet with Cr<sub>2</sub>O<sub>3</sub> content higher than 16 wt.% can be well explained, although high content of CaO as well as greenish colour set them apart from harzburgitic varieties, which typically contain less Ca (1-4 wt.% CaO) (Fig. 4) and are of purple colour. Oversaturation of the crystallisation medium with Cr<sub>2</sub>O<sub>3</sub> is a possibility to produce very Cr-rich garnet as well. The present experiment has demonstrated that Cr in synthetic garnet varied upon the distance from the source (initial chromite). As a result, garnets with the maximal Cr<sub>2</sub>O<sub>3</sub> content of 16.23 wt.% were formed in contact with the initial chromite. Such conditions can be considered as a Cr-saturated medium. The chemical composition of the present samples is close to natural harzburgite, which usually has Cr-numbers of less than 0.3. The increase of Cr/Cr+Al of the medium may produce garnets with Cr<sub>2</sub>O<sub>3</sub> higher than 16 wt.%, as was shown by Canil and Wei (1992), although the medium in their experiment has Cr-number of 0.84. Natural rocks of such composition are very rare, here the reference example may be harzburgites from ophiolites in the Papuan Ultramafic Belt, which have Cr/Cr + Al of up to 0.8 (Jaques and Chappell, 1980). It can be concluded that Ca-rich wherlitic garnets (Cr<sub>2</sub>O<sub>3</sub> >16 wt.%) or garnets probably originated from extremely Cr-saturated Ca-poor media (Cr/Cr+Al of 0.8) are very rare in nature and thus the conditions which lead to their formation rarely existed in the Earth's mantle. The decades of collecting the analytical data on chemical composition of garnets of the ultramafic paragenesis in diamonds indicated a maximum content of the knorringite component in natural garnets, not exceeding 60 mol.% (Sobolev et al., 2004; Stachel, Harris, 2008). Therefore, the present experiment justified the boundary at 16 wt.% Cr<sub>2</sub>O<sub>3</sub> proposed by N.V. Sobolev based on the analysis of more than 1500 natural Cr-garnets from Yakutia (Fig. 4). Such knorringite-rich garnets demonstrate a significant predominance in concentrates of the heavy fraction of all diamondiferous kimberlite deposits worldwide (Sobolev et al., 1973; Gurney and Switzer, 1973; Gurney, 1984; Sobolev, 1984; Pokhilenko et al., 2004).

The performed experiments have elucidated some important aspects of mechanism, which may lead to crystallisation of garnet with high knorringite component in nature. The possibility to grow Cr-rich garnet through a metasomatic process, at pressures and temperatures corresponding to the conditions of formation of lithospheric diamonds, well agrees with the experimental results obtained earlier by Canil and Wei (1992). The authors have demonstrated that the residues of one stage melting of typical peridotites at high pressures (> 3 GPa) produce garnets with less than 3-

4 wt.% Cr<sub>2</sub>O<sub>3</sub>. It was suggested that more Cr-rich population of low Ca garnets requires a multiple melt extraction: on the one hand, whether such conditions can be widespread in the Earth's history remains unclear; on the other hand, the formation of such residues can be well explained by melting in the stability region of spinel, e.i. by low pressure melting that leaved a residue with high Cr/Al ratios (Ringwood, 1977). According to the idea of this study, growth of garnet occurred in subsolidus conditions at 5.5 GPa and 1300 °C in Cr-rich starting compositions. The mechanism of growth of garnet crystals in the experiment represents the formation of so-called “metacrystals” which grew metasomatically in a solid medium due to thin capillary films of feeding solution surrounding them, replacing the surrounding minerals (Grigoriev and Zhabin, 1975). During the experiments, fluid of C-O-H composition located in the interstices between mineral grains and transported the petrological components. Such interstices between minerals are clearly seen in the microphotographs and SEM images (Fig. 2). In the present experiment temperature was not changed. As was shown by Brey et al. (1990) in experiments with natural lherzolitic compositions, Cr in garnet does not change with increasing temperature in the range of 900-1300 °C. Further increase of temperature in our system leads to the appearance of melt, which most probably will decrease the role of fluid phase due to its dissolution in the melt. The pressure in experiments was not changed as well. The experiments performed by Canil and Wei (1992) with spinel-harzburgite, when the authors obtained garnets with very high Cr<sub>2</sub>O<sub>3</sub> contents, were conducted at higher pressure (8 GPa). Here, it should be taken into account that at such pressures an excess of SiO<sub>2</sub> in garnet becomes noticeable (majoritic component). As noted above, the synthesised Cr-rich garnets were obtained at 5.5 GPa, however, they contained a minor Si excess. The obtained fact does not allow to discuss the presence of majorite in experiment as such, although the following considerations should be taken into account: Akaogi and Akimoto (1977) studied pyroxene-garnet solid-solutions in the system Mg<sub>4</sub>Si<sub>4</sub>O<sub>12</sub>-Mg<sub>3</sub>Al<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> in the pressure range of 4-20 GPa and showed that the solubility of pyroxene component in garnet increases gradually with increasing depth. They suggested that pyroxenes begin to react with the already present pyrope-rich garnet at depths around 150 km, which corresponds to the pressures close to that of the present experiment. Most probably, the minor excess of Si in obtained garnets is characteristic of a blurred transition between the normal and majorite-containing garnet. It should also be taken into account that “Majoritic knorringite becomes more Cr-deficient with increasing pressure, which is similar to the Al-deficient nature of majoritic garnet in the MgSiO<sub>3</sub> – Al<sub>2</sub>O<sub>3</sub> system” (Zou and Irifune, 2012). In other words, further increase of pressure would mostly increase Si content, but not Cr in garnet. Additionally, plotted on Si vs (Al+Cr) diagram (Fig. 5) the synthesised garnets matches the trend proposed by Stachel et al. (2005) for majoritic garnets from diamond inclusions.



**Fig. 5.** Si vs Al+Cr for garnet inclusions in natural diamonds worldwide, reproduced after Stachel et al., 2005. Yellow circles with crosses – experimental data of the present study.

In this context, diamond crystal with inclusions of both majoritic and “normal” garnet is worth noting (Sobolev et al., 2004) – the genesis of this diamond is explained by growth under the decrease of pressure. This suggests that the limit of 16 wt.% Cr<sub>2</sub>O<sub>3</sub>, which characterises 95% of natural peridotitic garnets, corresponds to the pressures at which the displacement of Cr (Al) by majoritic component is not noticeable.

## Conclusions

The article presents the results of experiments on crystallisation of a subcalcic pyrope with the aim to determine the maximal Cr content in the garnet. The system chemistry coincides with that of natural spinel-harzburgite characterised by typical Cr/Cr+Al and the mineral association in experimental products consisted of Mg-olivine, orthopyroxene, Cr-spinel and Cr-garnet. The garnet synthesis occurred in subsolidus conditions in the presence of C-O-H fluid, which demonstrated a possible scenario of metasomatic formation of Cr-rich pyrope at P-T parameters of the formation of typical lithospheric diamonds. The use of natural carbonatite as a source of Ca showed the crystallisation of garnet with varying contents of Ca and almost the same Cr, which is in agreement with the existing trend for carbonatite metasomatism – introduction of small amount of Ca-carbonatite into depleted harzburgite (approximately 2 wt.%) shifts the garnet compositions to more Ca-rich, but did not lead to further increase of Cr. The experiments confirmed the boundary at 16 wt.% Cr<sub>2</sub>O<sub>3</sub> for subcalcic Cr-rich pyrope associating with diamond as was proposed earlier by N.V. Sobolev. It is concluded that garnets with higher Cr cannot form due to the change

of pressure or temperature. The origin of natural samples of Ca-rich Iherzolitic/wherlitic and Ca-poor harzburgitic garnets with more than 16 wt.% Cr<sub>2</sub>O<sub>3</sub> is attributed to the specific Ca/Cr/Al ratios of the medium, although the rarity of such garnets indicates that such conditions rarely occurred in the Earth's history.

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## References

- Agashev A.M., Pokhilenko N.P., Takazawa E., McDonald J.A., Vavilov M.A., Watanabe T. and Sobolev N.V. (2008) Primary melting sequence of a deep (>250 km) lithospheric mantle as recorded in the geochemistry of kimberlite–carbonatite assemblages, Snap Lake dyke system, Canada. *Chemical Geology*, **255**, 317–328.
- Afanasiev V.P. and Pokhilenko N.P. (2022) Approaches to the diamond potential of the Siberian craton: A new paradigm. *Ore Geology Reviews*, **147**, 104980. <https://doi.org/10.1016/j.oregeorev.2022.104980>
- Akaogi M. and Akimoto S. (1977) Pyroxene-garnet solid-solution equilibria in the systems  $Mg_4Si_4O_{12}$ - $Mg_3Al_2Si_3O_{12}$  and  $Fe_4Si_4O_{12}$ - $Fe_3Al_2Si_3O_{12}$  at high pressures and temperatures. *Physics of the Earth and Planetary Interiors*, **15**, 90–106.
- Brey G.P., Kohler T. and Nickel K.G. (1990) Geothermobarometry in Four-phase Lherzolites I. Experimental Results from 10 to 60 kb. *Journal of Petrology*, **31**(6), 1313–1352.
- Canil D. and Wei K. (1992) Constrains on the origin of mantle-derived low Ca garnets. *Contributions to Mineralogy and Petrology*, **109**, 421–430.
- Chepurov A.A., Faryad S.W., Agashev A.M., Strnad L., Jedlicka R., Turkin A.I., Mihaljevic M. and Lin V.V. (2019) Experimental crystallization of a subcalcic Cr-rich pyrope in the presence of REE-bearing carbonatite. *Chemical Geology*, **509**, 103–114. <https://doi.org/10.1016/j.chemgeo.2019.01.011>
- Chepurov A.A., Dereppe J.M., Turkin A.I. and Lin V.V. (2018) From subcalcic pyropes to uvarovites: experimental crystallization of Cr-rich garnets in ultramafic systems with presence of Ca-bearing hydrous fluid. *Neues Jahrbuch für Mineralogie Abhandlungen*, **195**(1), 65–78.
- Chepurov A.A., Turkin A.I. and Dereppe J.M. (2016) Interaction of serpentine and chromite as a possible formation mechanism of subcalcic chromium garnet in the upper mantle: an experimental study. *European Journal of Mineralogy*, **28**(2), 329–336.
- Chepurov A.I., Tomilenko A.A., Zhimulev E.I., Sonin V.M., Chepurov A.A., Kovyazin S.V., Timina T.Yu. and Surkov N.V. (2012) The conservation of an aqueous fluid in inclusions in minerals and their interstices at high pressures and temperatures during the decomposition of antigorite. *Russian Geology and Geophysics*, **53**(3), 234–246.
- Davies R.M., Griffin W.L., O'Reilly S.Y. and Doyle B.J. (2004) Mineral inclusions and geochemical characteristics of microdiamonds from the DO27, A154, A21, A418, DO18, DD17 and Ranch Lake kimberlites at Lac de Gras, Slave Craton, Canada. *Lithos*, **77**(1–4), 39–55.
- Dawson J.B. and Stephens W.E. (1975) Statistical classification of garnets from kimberlite and associated xenoliths. *Journal of Geology*, **83**(5), 589–607.

- Dobrzhinetskaya L., Green H.W. and Wang, S. (1996) Alpe Arami: A peridotite massif from depths of more than 300 kilometers. *Science*, **271**, 1841–1845.
- Doroshev A.M., Brey G.P., Girmis A.V., Turkin A.I. and Kogarko N. (1997) Pyrope-knorringite garnets in the Earth's Mantle: experiments in the MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–Cr<sub>2</sub>O<sub>3</sub> system. *Russian Geology and Geophysics*, **38**, 559–586.
- Doucet L.S., Ionov D.A., Golovin A.V. and Pokhilenko N.P. (2012) Depth, degrees and tectonic settings of mantle melting during craton formation: inferences from major and trace element compositions of spinel harzburgite xenoliths from the Udachnaya kimberlite, central Siberia. *Earth and Planetary Science Letters*, **359**, 206–218. <https://doi.org/10.1016/j.epsl.2012.10.001>
- FengHua L., Jingsui Y., ZhiQin X. and JiaNan Z. (2014) Chromium in the olivine lattice: Chromium-rich olivines and their implication of deep mantle origin in the Luobusa mantle peridotite and chromitite, Tibet. *Acta Petrologica Sinica*, **8**, 2125–2136.
- Gasparik T. (2002) Experimental investigation of the origin of majoritic garnet inclusions in diamonds. *Physics and Chemistry of Minerals*, **29**(3), 170–180.
- Godovikov A.A. (1975) Mineralogy. Nedra, Moscow, USSR (In Russian).
- Griffin W.L., Fisher N.I., Friedman J.H., O'Reilly S.Y. and Ryan C.G. (2002) Cr-pyrope garnets in the lithospheric mantle 2. Compositional populations and their distribution in time and space. *Geochemistry Geophysics Geosystems*, **3**(12), 1073. <https://doi.org/10.1029/2002GC000298>
- Griffin W.L., Fisher N.I., Friedman J., Ryan C.G. and O'Reilly S.Y. (1999a) Cr-pyrope garnets in the lithospheric mantle. 1. Compositional systematics and relations to tectonic setting. *Journal of Petrology*, **40**(5), 679–704.
- Griffin W.L., O'Reilly S.Y. and Ryan C.G. (1999b) The composition and origin of subcontinental lithospheric mantle. In: Fei Y., Bertka C.M., Mysen B.O. (eds) *Mantle Petrology: Field Observations and High Pressure Experimentation: a Tribute to Francis R. (Joe) Boyd*. Geochemical Society, Special Publications. **6**, 13–45.
- Griffin W.L., Sobolev N.V., Ryan C.G., Pokhilenko N.P., Win T.T. and Yefimova E.S. (1993) Trace elements in garnets and chromites: diamond formation in the Siberian lithosphere. *Lithos*, **29**, 235–256.
- Grigoriev D.P. and Zhabin A.G. (1975) Onotogenesis of minerals. Nauka, Moscow, USSR (in Russian).
- Grütter H., Latti D. and Menzies A. (2006) Cr-Saturation Arrays in Concentrate Garnet Compositions from Kimberlite and their Use in Mantle Barometry. *Journal of Petrology*, **47**(4), 801–820.



- Grütter H.S., Gurney J.J., Menzies A.H. and Winter F. (2004) An updated classification scheme for mantle-derived garnet for use by diamond explorers. *Lithos*, **77**(1–4), 841–857. <https://doi.org/10.1016/j.lithos.2004.04.012>
- Gurney J.J. (1984) A correlation between garnets and diamonds in kimberlites. In: *Kimberlite occurrence and origin: a basis for conceptual models in exploration* (J.E. Glover and P.G. Harris, editors). Geology Department and University Extension, University of Western Australia.
- Gurney J.J. and Switzer G. (1973) The discovery of garnets closely related to diamonds in the Finch Pipe, South Africa. *Contributions to Mineralogy and Petrology*, **39**, 103–116.
- Harris J.W. (1968) The recognition of diamond inclusions. Part 1: syngenetic mineral inclusions. *Industrial Diamond Review*, **28**, 402–410.
- Harris J.W., Stachel T., Leost I. and Brey G.P. (2004) Peridotitic diamonds from Namibia: Constraints on the composition and evolution on their mantle source. *Lithos*, **77**, 209–223.
- Harris J.W. and Gurney J.J. (1979) Inclusions in diamond. Pp. 555–591 in: *The properties of diamond* (J.E. Field, editor). Academic press, London.
- Hazen R.M., Dawns R.T., Conrad O.G., Finger L.W. and Gasparik T. (1994a) Comparative compressibilities of majorite-type garnets. *Physics and Chemistry of Minerals*, **21**, 344–39.
- Hazen R.M., Downs R.T., Finger L.W., Conrad P.G. and Gasparik T. (1994b) Crystal chemistry of Ca-bearing majorite. *American Mineralogist*, **79**, 581–584.
- Herzberg C. and Gasparik T. (1991) Garnet and pyroxenes in the mantle: A test of the majorite fractionation hypothesis. *Journal of Geophysical Research*, **96**(B10), 16263–16247. <https://doi.org/10.1029/91JB01481>
- Howarth G.H., Barry P.H., Pernet-Fisher J.F., Baziotis I.P., Pokhilenko N.P., Pokhilenko L.N., Bodnar R.J., Taylor L.A. and Agashev A.M. (2014) Superplume metasomatism: Evidence from Siberian mantle xenoliths. *Lithos*, **184–185**, 209–224.
- Ilyina O.V., Agashev A.M., Pokhilenko L.N., Kozhemyakina E.A. and Pokhilenko N.P. (2022) Sheared and Granular Peridotites from the Udachnaya-East Kimberlite (Yakutia): Mineralogy, Chemistry, and PGE Patterns. *Russian Geology and Geophysics*, **63**(9), 1001–1019. <https://doi.org/10.2113/RGG20204320>
- Irifune T. and Hariya Yu. (1983) Phase relationships in the system  $Mg_3Al_2Si_3O_{12}$ - $Mg_3Cr_2Si_3O_{12}$  at high pressure and some mineralogical properties of synthetic garnet solid solutions. *Mineralogical Journal*, **11**(6), 269–281. <https://doi.org/10.2465/minerj.11.269>

- Irifune T. (1987) An experimental investigation of the pyroxene-garnet transformation in a pyrolite composition and its bearing on the constitution of the mantle. *Physics of the Earth and Planetary Interiors*, **45**(4), 324–336. [https://doi.org/10.1016/0031-9201\(87\)90040-9](https://doi.org/10.1016/0031-9201(87)90040-9)
- Jakubith M. and Hornemann U. (1981) Majorite formation from enstatite by experimental shock-loading. *Physics of the Earth and Planetary Interiors*, **27**(1), 95–99.
- Jaques A. and Chappell B.H. (1980) Petrology and trace element geochemistry of the Papuan Ultramafic Belt. *Contributions to Mineralogy and Petrology*, **75**, 55–70.
- Jeanloz R. (1981) Majorite: Vibrational and compressional properties of a high-pressure phase. *Journal of Geophysical Research*, **86**(B7), 6171–6179.
- Kato T., Irifune T. and Ringwood A.E. (1987) Majorite partition behavior and petrogenesis of the earth's upper mantle. *Geophysical Research Letters*, **14**(5), 546–549.
- Klein-BenDavid O., Pearson D.G., Nowell G.M., Ottley C., McNeill J.C.R., Logvinova A. and Sobolev N.V. (2014) The sources and time-integrated evolution of diamond-forming fluids – Trace elements and isotopic evidence. *Geochimica et Cosmochimica Acta*, **125**, 146–169.
- Klein-BenDavid O., Weiss Y., Navon O., Logvinova A.M., Sobolev N.V., Schrauder M., Spetius Z.V., Hauri E.H. and Kaminsky F.V. (2009) High-Mg carbonatitic microinclusions in some Yakutian diamonds – a new type of diamond-forming fluid. *Lithos*, **112**, 648–659.
- Kovalsky V.V., Bulanova G.P., Nikishov K.N., Botkunov A.I., Makhotko V.F., Shestakova O.E. and Gotovtsev V.V. (1979) Composition of garnets, chromites and rutiles associated with diamonds from Yakutian kimberlite pipes. *Doklady Akademii Nauk SSSR*, **247**, 946–951.
- Lenaz D., Princivalle F., Logvinova A.M. and Sobolev N.V. (2009) Structural parameters of chromite included in diamond and kimberlites from Siberia: a new tool for discriminating ultramafic source. *American Mineralogist*, **94**, 1067–1070.
- Logvinova A.M., Taylor L.A., Floss C. and Sobolev N.V. (2005) Geochemistry of Multiple Diamond Inclusions of Harzburgitic Garnets as Examined In Situ. *International Geology Review*, **47**, 1223–1233. <https://doi.org/10.2747/0020-6814.47.12.1223>
- Malinovsky I.Yu. and Doroshev A.M. (1977) Evaluation of P-T conditions of diamond formation with reference to chrome-bearing garnet stability Extended Abstracts, 2nd International Kimberlite Conference, Santa Fe, unpaginated.
- Meyer H.O.A. and Boyd F.R. (1972) Compositions and origin of crystalline inclusions in natural diamond. *Geochimica et Cosmochimica Acta*, **36**, 1255–1273.
- Meyer H.O.A. (1968) Chrome pyrope: An inclusion in natural diamond. *Science*, **160**, 1446–1447.
- Meyer H.O.A. and Svisero D.P. (1975) Mineral inclusions in Brazilian diamonds. *Physics and Chemistry of the Earth*, **9**, 785–795.

- Nakatsuka A., Yoshiasa A., Yamanaka T. and Ito E. (1999) Structure refinement of a birefringent Cr-bearing majorite  $\text{Mg}_3(\text{Mg}_{0.34}\text{Si}_{0.34}\text{Al}_{0.18}\text{Cr}_{0.14})_2\text{Si}_3\text{O}_{12}$ . *American Mineralogist*, **84**(1–2), 199–202.
- Nickel K.G. (1986) Phase equilibria in the system  $\text{SiO}_2\text{-MgO-Al}_2\text{O}_3\text{-CaO-Cr}_2\text{O}_3$  (SMACCR) and their bearing on spinel/garnet lherzolite relationships. *Neues Jahrbuch Fur Mineralogie Abhandlungen*, **155**(3), 259–287.
- Nixon P.H. and Hornung G. (1968) A new chromium garnet end member, knorringite, from Kimberlite. *American Mineralogist*, **53**(11-12), 1833–1840.
- Ono S. and Yasuda A. (1996) Compositional change of majoritic garnet in a MORB composition from 7 to 17 GPa and 1400 to 1600°C. *Physics of the Earth and Planetary Interiors*, **96**(2–3), 171–179. [https://doi.org/10.1016/0031-9201\(96\)03149-4](https://doi.org/10.1016/0031-9201(96)03149-4)
- Pearson D.G. and Wittig N. (2008) Formation of Archaean continental lithosphere and its diamonds: the root of the problem. *Journal of the Geological Society*, **165**(5), 895–914.
- Phillips D., Harris J.W. and Viljoen K.S. (2004) Mineral chemistry and thermobarometry of inclusions from De Beers Pool diamonds, Kimberley, South Africa. *Lithos*, **77**, 155–179. <http://doi.org/10.1016/j.lithos.2004.04.005>
- Pokhilenko N.P., Agashev A.M., Litasov K.D. and Pokhilenko L.N. (2015) Carbonatite metasomatism of peridotite lithospheric mantle: implications for diamond formation and carbonatite-kimberlite magmatism. *Russian Geology and Geophysics*, **56**, 280–295. <http://doi.org/10.1016/j.rgg.2015.01.020>
- Pokhilenko N., Sobolev N., Kuligin S. and Shimizu N. (1999) Peculiarities of distribution of pyroxenite paragenesis garnets in Yakutian kimberlites and some aspects of the evolution of the Siberian craton lithospheric mantle. In: *Proceedings of the 7th International Kimberlite Conference*. Red Roof Design, Cape Town, 689–698.
- Pokhilenko N.P., Sobolev N.V., Reutsky V.N., Hall A.E. and Taylor L.A. (2004) Crystalline inclusions and C isotope ratios in diamonds from the Snap Lake/King Lake kimberlite dyke system: evidence of ultradeep and enriched lithospheric mantle. *Lithos*, **77**, 57–67.
- Ringwood A.E. (1967) The pyroxene-garnet transformation in the earth's mantle. *Earth and Planetary Science Letters*, **2**(3), 255–263.
- Ringwood A.E. (1977) Synthesis of pyrope-knorringite solid solution series. *Earth and Planetary Science Letters*, **36**(3), 443–448.
- Ringwood A.E. and Major A. (1966) High-pressure transformations in pyroxenes. *Earth and Planetary Science Letters*, **1**, 351–357.
- Ringwood A.E. and Major A. (1971) Synthesis of majorite and other high pressure garnets and perovskites. *Earth and Planetary Science Letters*, **12**(4), 411–418.

- Schulze D.J. (2003) A classification scheme for mantle-derived garnets in kimberlite: a tool for investigating the mantle and exploring for diamonds. *Lithos*, **71**(2–4), 195–213.
- Shirey S.B., Cartigny P., Frost D.J., Keshav S., Nestola F., Nimis P., Pearson D.G., Sobolev N.V. and Walter M.J. (2013) Diamonds and the geology of mantle carbon. *Reviews in Mineralogy and Geochemistry*, **75**, 355–421.
- Shu Q. and Brey G.P. (2015) Ancient mantle metasomatism recorded in subcalcic garnet xenocrysts: Temporal links between mantle metasomatism, diamond growth and crustal tectonomagmatism. *Earth and Planetary Science Letters*, **418**, 27–39.
- Smith C.B., Pearson D.G., Bulanova G.P., Beard A.D., Carlson R.W., Wittig N., Sims K., Chimuka L. and Muchemwa E. (2009) Extremely depleted lithospheric mantle and diamonds beneath the southern Zimbabwe Craton. *Lithos*, **112S**, 1120–1132.
- Smith J.V. and Mason B. (1970) Pyroxene-garnet transformation in Coorara meteorite. *Science*, **168**(3933), 832–833. <https://doi.org/10.1126/science.168.3933.832>
- Sobolev N.V. (1971) On mineralogical criteria of a diamond potential of kimberlites. *Geologia i Geofizika*, **3**, 70–79.
- Sobolev N.V. (1977) Deep-seated Inclusions in Kimberlites and the Problems of the Composition of the Upper Mantle, (F.R. Boyd, editor), American Geophysical Union, Washington.
- Sobolev N.V. (1984) Kimberlites of the Siberian Platform: their geological and mineralogical features. Pp. 275–287 in: *Kimberlite occurrence and origin: a basis for conceptual models in exploration*, Vol. 8 (J.E. Glover, P.G. Harris, editors). University of Western Australia Publications.
- Sobolev N.V., Lavrent'ev Yu.G., Pokhilenko N.P. and Usova L.V. (1973) Chrome-rich garnets of Yakutia and their parageneses. *Contributions to Mineralogy and Petrology*, **40**(1), 39–52.
- Sobolev N.V. and Logvinova A.M. (2005) Significance of accessory chrome spinel in identifying serpentinite paragenesis. *International Geology Review*, **47**(1), 58–64.
- Sobolev N.V., Logvinova A.M., Tomilenko A.A., Wirth R., Bul'bak T.A., Luk'yanova L.I., Fedorova E.N., Reutsky V.N. and Efimova E.S. (2019) Mineral and fluid inclusions in diamonds from the Urals placers, Russia: Evidence for solid molecular N<sub>2</sub> and hydrocarbons in fluid inclusions. *Geochimica et Cosmochimica Acta*, **266**, 197–219.
- Sobolev N.V., Logvinova A.M., Zedgenizov D.A., Seryotkin Y.V., Yefimova E.S., Floss C. and Taylor L.A. (2004) Mineral inclusions in microdiamonds and macrodiamonds from kimberlites of Yakutia: a comparative study. *Lithos*, **77**, 225–242.
- Sobolev N.V., Kaminsky F.V., Griffin W.L., Yefimova E.S., Win T.T., Ryan C.G. and Botkunov A.I. (1997) Mineral inclusions in diamonds from the Sputnik kimberlite pipe Yakutia. *Lithos*, **39**, 135–157.

- Sobolev N.V., Wirth R., Logvinova A.M., Yelissejev A.P. and Kuzmin D.V. (2016) Retrograde isochemical phase transformations of majoritic garnets included in diamonds: A case study of subcalcic Cr-rich majoritic pyrope from a Snap Lake diamond, Canada. *Lithos*, **265**, 267–277.
- Sonin V.M., Leech M., Chepurov A.A., Zhimulev E.I. and Chepurov A.I. (2019) Why are diamonds preserved in UHP metamorphic complexes? Experimental evidence for the effect of pressure on diamond graphitization. *International Geology Review*, **61**(4), 504–519.
- Sonin V.M., Tomilenko A.A., Zhimulev E.I., Bul'bak T.A., Chepurov A.A., Timina T.Yu., Chepurov A.I. and Pokhilenko N.P. (2023) Crystallization of diamonds and phase composition of the FeNi–Graphite–CaCO<sub>3</sub> system at 5.5 GPa: the role of subduction in their formation. *Geology of Ore Deposits*, **65**(3), 255–270.
- Stachel T., Aulbach S., Brey G.P., Harris J.W., Leost I., Tappert R. and Viljoen K.S. (2004a) The trace element composition of silicate inclusions in diamonds: a review. *Lithos*, **77**(1–4), 1–19.
- Stachel T., Brey G.P. and Harris J.W. (2000) Kankan diamonds (Guinea) I: from lithosphere down to the transition zone *Contributions to Mineralogy and Petrology*, **140**, 1–15.
- Stachel T., Brey G.P. and Harris J.W. (2005) Inclusions in Sublithospheric Diamonds: Glimpses of Deep Earth. *Elements*, **1**(2), 73–78.
- Stachel T. and Harris J.W. (1997a) Syngenetic inclusions in diamond from the Birim field (Ghana) - a deep peridotitic profile with a history of depletion and re-enrichment. *Contributions to Mineralogy and Petrology*, **127**, 336–352.
- Stachel T. and Harris J.W. (1997b) Diamond precipitation and mantle metasomatism - evidence from the trace element chemistry of silicate inclusions in diamonds from Akwatia, Ghana. *Contributions to Mineralogy and Petrology*, **129**(2–3), 143–154.
- Stachel T. and Harris J.W. (2008) The origin of cratonic diamonds – Constraints from mineral inclusions. *Ore Geology Reviews*, **34**(1–2), 5–32.
- Stachel T., Viljoen K.S., McDade P. and Harris J.W. (2004b) Diamondiferous lithospheric roots along the western margin of the Kalahari Craton — the peridotitic inclusion suite in diamonds from Orapa and Jwaneng. *Contributions to Mineralogy and Petrology*, **147**, 32–47.
- Thomson A.R., Kohn S.C., Prabhu A. and Walter M. J. (2021) Evaluating the Formation Pressure of Diamond-Hosted Majoritic Garnets: A Machine Learning Majorite Barometer. *Journal of Geophysical Research: Solid Earth*, **126**, e2020JB020604.
- Tomlinson E.L., Jones A.P. and Harris J.W. (2006) Co-existing fluid and silicate inclusions in mantle diamond. *Earth and Planetary Science Letters*, **250**, 581–595.
- Tonkov E.Yu. and Ponyatovsky E.G. (2004) *Phase transformations of elements under high pressure* (J.N. Fridlyander, D.G. Eskin, editors). CRC Press, pp. 392.

- Turkin A.I. and Sobolev N.V. (2009) Pyrope–knorringite garnets: overview of experimental data and natural parageneses. *Russian Geology and Geophysics*, **50**, 1169–1182.
- Turkin A.I. (2003) Lead selenide as a continuous internal indicator of pressure in solid-media cells of high-pressure apparatus in the range of 4 - 6.8 GPa. *High Temperatures - High Pressures*, **35/36**, 371–376.
- Turkin A.I., Chepurov A.A., Zhimulev E.I., Lin V.V. and Sobolev N.V. (2021) Experimental modeling of the formation of zoned magnesian garnet at various starting Ca, Al, and Cr concentrations controlled by H<sub>2</sub>O-rich fluid. *Geochemistry International*, **59**, 778–790.
- Turkin A.I., Doroshev A.M. and Malinovsky Yu.I. (1983) Study of the phase composition of garnet-bearing associations of the system MgO–Al<sub>2</sub>O<sub>3</sub>–SiO<sub>2</sub>–Cr<sub>2</sub>O<sub>3</sub> system at high temperatures and pressures. P. 5 in: *Silicate Systems Under High Pressure*. Novosibirsk (in Russian).
- Tychkov N.S., Agashev A.M., Pokhilenko N.P., Tsykh V.A. and Sobolev N.V. (2020) Types of Xenogenic Olivine from Siberian Kimberlites. *Minerals*, **10**(4), 302.
- Ulmer P. and Trommsdorff V. (1995) Serpentine stability to mantle depths and subduction-related magmatism. *Science*, **268**(5212), 858–861.
- Weiss Y., Kiflawi I., Davis N. and Navon O. (2014) High-density fluids and growth of monocrystalline diamonds. *Geochimica et Cosmochimica Acta*, **141**, 145–159.
- Zedgenizov D.A., Logvinova A.M., Shatskii V.S. and Sobolev N.V. (1998) Inclusions in microdiamonds from some kimberlite diatremes of Yakutia. *Doklady Earth Sciences*, **359**, 204–208.
- Zedgenizov D.A., Ragozin A.L., Shatsky V.S., Araujo D., Griffin W.L. and Kagi H. (2009) Mg and Fe-rich carbonate–silicate high-density fluids in cuboid diamonds from the Internationalnaya kimberlite pipe (Yakutia). *Lithos*, **112**, 638–647.
- Zou Y. and Irifune T. (2012) Phase relations in Mg<sub>3</sub>Cr<sub>2</sub>Si<sub>3</sub>O<sub>12</sub> and formation of majoritic knorringite garnet at high pressure and high temperature. *Journal of Mineralogical and Petrological Sciences*, **107**(5), 197–205. <https://doi.org/10.2465/jmps.120318>

**Table 1.** Products after the experiments at 5.5 GPa and 1300 °C.

Run No.	Starting charge: Serp+Chr+Cor, wt.%	Carbonatite in starting charge, wt.%	Run products	Growth of garnet on chromite
1	94-3-3	-	Ol, Opx, Gar, Sp, Chr, Cor	+
2	94-3-3	-	Ol, Opx, Gar, Sp, Chr, Cor	+
3	93-3-3	1	Ol, Opx, Gar, Sp, Chr, Cor	+
4	93-3-3	1	Ol, Opx, Gar, Sp, Chr, Cor	+
5	92-3-3	2	Ol, Opx, Gar, Sp, Chr, Cor	+
6	92-3-3	2	Ol, Opx, Gar, Sp, Chr, Cor	+

Notes: Serp – serpentine, Ol – olivine, Opx – orthopyroxene, Gar – garnet, Sp – spinel, Chr – chromite, Cor – corundum.

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**Table 2.** Representative chemical composition of garnet synthesised in contact with chromite (wt.%).

sample	1	2	3	4	5	6	7	8	9
SiO <sub>2</sub>	42.05	41.93	42.03	42.31	42.07	42.05	41.96	41.87	41.63
TiO <sub>2</sub>	0.09	0.10	0.10	0.08	0.09	0.11	0.12	0.12	0.17
Al <sub>2</sub> O <sub>3</sub>	11.58	11.88	12.02	11.74	11.7	11.62	10.84	11.43	10.61
Cr <sub>2</sub> O <sub>3</sub>	15.82	15.16	15.10	15.59	14.94	14.92	16.23	15.28	16.09
FeO	3.38	3.48	3.55	3.38	3.41	3.44	3.22	3.52	3.67
MnO	0.08	0.07	0.09	0.08	0.08	0.09	0.1	0.08	0.08
MgO	23.46	23.58	23.67	23.38	21.99	21.84	21.34	21.23	19.73
CaO	3.00	3.26	2.83	3.21	5.15	5.21	5.47	6.10	7.49
Na <sub>2</sub> O	0.01	0	0.03	0.01	0.04	0.01	0.02	0.03	0.03
total	99.47	99.46	99.42	99.78	99.47	99.29	99.30	99.66	99.50
<sup>IV</sup> Si	3.066	3.057	3.061	3.074	3.079	3.084	3.089	3.074	3.084
<sup>VI</sup> Ti	0.005	0.005	0.005	0.004	0.005	0.006	0.007	0.007	0.009
<sup>VI</sup> Al	0.995	1.021	1.032	1.005	1.009	1.004	0.941	0.989	0.927
<sup>VI</sup> Cr	0.912	0.874	0.870	0.895	0.865	0.865	0.945	0.887	0.943
<sup>VIII</sup> Fe <sup>++</sup>	0.206	0.212	0.216	0.205	0.209	0.211	0.198	0.216	0.227
<sup>VIII</sup> Mn	0.005	0.004	0.006	0.005	0.005	0.006	0.006	0.005	0.005
<sup>VIII</sup> Mg	2.550	2.563	2.570	2.532	2.400	2.388	2.342	2.323	2.179
<sup>VIII</sup> Ca	0.234	0.255	0.221	0.250	0.404	0.409	0.432	0.480	0.595
<sup>VIII</sup> Na	0.001	0.000	0.004	0.001	0.006	0.001	0.003	0.004	0.004
S_Cat	7.976	7.991	7.985	7.972	7.981	7.976	7.963	7.984	7.974
Fe#	7.48	7.65	7.76	7.50	8.00	8.12	7.80	8.51	9.45
Cr#	47.82	46.12	45.73	47.11	46.14	46.28	50.11	47.28	50.43



**Table 3.** Representative chemical composition of olivine after the experiments (wt.%).

sample	1	2	3	4	5	6	7
SiO <sub>2</sub>	42.31	42.02	42.21	42.25	42.1	41.88	42.12
TiO <sub>2</sub>	0	0	0	0	0	0	0
Al <sub>2</sub> O <sub>3</sub>	0	0	0	0	0	0	0
Cr <sub>2</sub> O <sub>3</sub>	0.12	0.22	0.2	0.14	0.26	0.17	0.27
FeO	2.86	2.98	2.71	2.74	2.88	3.11	2.63
MnO	0	0	0	0	0	0	0
MgO	54.07	54.05	54.45	54.03	54.11	53.83	54.21
CaO	0	0	0	0	0	0	0
total	99.36	99.27	99.57	99.16	99.35	98.99	99.23
Si	1.009	1.004	1.004	1.009	1.005	1.004	1.005
Ti	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Al	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Cr	0.002	0.004	0.004	0.003	0.005	0.003	0.005
Fe <sup>++</sup>	0.057	0.060	0.054	0.055	0.057	0.062	0.053
Mn	0.000	0.000	0.000	0.000	0.000	0.000	0.000
Mg	1.922	1.926	1.932	1.923	1.925	1.924	1.929
Ca	0.000	0.000	0.000	0.000	0.000	0.000	0.000
S_Cat	2.990	2.994	2.994	2.990	2.993	2.994	2.992
#Fe <sup>++</sup>	2.88	3.00	2.72	2.77	2.90	3.14	2.65

**Table 4.** Representative chemical composition of orthopyroxene after the experiments (wt.%).

sample	1	2	3	4	5
SiO <sub>2</sub>	59.15	59.03	59.10	59.22	59.30
TiO <sub>2</sub>	0	0	0	0	0
Al <sub>2</sub> O <sub>3</sub>	0.55	0.62	0.67	0.39	0.46
Cr <sub>2</sub> O <sub>3</sub>	0.56	0.85	0.64	0.56	0.43
FeO	1.59	1.50	1.85	1.72	1.64
MnO	0	0	0	0	0
MgO	37.86	37.97	37.64	37.86	38.04
CaO	0	0	0	0	0
total	99.71	99.97	99.90	99.75	99.87
Si	1.997	1.990	1.994	2.000	1.999
Ti	0.000	0.000	0.000	0.000	0.000
Al	0.022	0.025	0.027	0.016	0.018
Cr	0.015	0.023	0.017	0.015	0.011
Fe	0.045	0.042	0.052	0.049	0.046
Mn	0.000	0.000	0.000	0.000	0.000
Mg	1.906	1.908	1.894	1.906	1.912
Ca	0.000	0.000	0.000	0.000	0.000
S_Cat	3.984	3.987	3.984	3.985	3.986
Fe#	2.30	2.17	2.68	2.49	2.36
Mg#	40.58	47.91	39.05	49.06	38.54

**Table 5.** Representative chemical composition of spinel after the experiments (wt.%).

sample	1	2	3	4	5
TiO <sub>2</sub>	0	0	0	0	0
Al <sub>2</sub> O <sub>3</sub>	9.18	7.22	7.70	10.37	4.26
Cr <sub>2</sub> O <sub>3</sub>	65.96	67.36	66.44	60.57	70.04
FeO	7.63	7.47	9.63	14.45	8.96
MnO	0	0.31	0	0	0
MgO	17.10	16.94	16.01	14.04	15.97
total	99.87	99.30	99.78	99.43	99.23
Ti	0.000	0.000	0.000	0.000	0.000
Al	0.343	0.274	0.292	0.397	0.165
Cr	1.651	1.712	1.690	1.555	1.817
Fe	0.202	0.201	0.259	0.392	0.246
Mn	0.000	0.008	0.000	0.000	0.000
Mg	0.807	0.812	0.768	0.680	0.781
S_Cat	3.003	3.007	3.009	3.024	3.009
Fe#	20.02	19.83	25.23	36.60	23.94
Cr#	82.82	86.22	85.27	79.67	91.69