

# Carbonatite metasomatism of peridotite lithospheric mantle: implications for diamond formation and carbonatite-kimberlite magmatism

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## Abstract

Mineral inclusions in diamond record its origin at different depths, down to the lower mantle. However, most diamonds entrained with erupting kimberlite magma originate in lithospheric mantle. Lithospheric U-type diamonds crystallize during early metasomatism of reduced ( $f_{O_2}$  at the IW oxygen buffer) depleted peridotite in the roots of Precambrian cratons. Evidence of the metasomatic events comes from compositions of garnets in peridotitic xenoliths and inclusions in diamonds. On further interaction with carbonatitic melt, peridotite changes its composition, while diamond no longer forms in a more oxidized environment ( $f_{O_2}$  near the CCO buffer). Silicate metasomatism of depleted peridotite (by basanite-like melts) does not induce diamond formation but may participate in generation of group I kimberlite. Low-degree (below 1%) partial melting of metasomatized peridotite produces a kimberlite-carbonatite magmatic assemblage, as in the case of the Snap Lake kimberlite dike. Occasionally, mantle metasomatism may occur as reduction reactions with carbonates and  $H_2O$  giving rise to hydrocarbon compounds, though the origin of hydrocarbons in the deep mantle remains open to discussion. Melting experiments in carbonate systems show hydrous carbonated melts with low  $H_2O$  to be the most plausible agents of mantle material transport. An experiment-based model implies melting of carbonates in subducting slabs within the mantle transition zone, leading to formation of carbonatitic diapirs, which can rise through the mantle by buoyancy according to the dissolution-precipitation mechanism. These processes, in turn, can form oxidized channels in the mantle and maintain diamond growth at the back of diapirs by reducing carbon from carbonated melts. When reaching the lithospheric base, such diapirs form a source of kimberlite and related magmas. The primary composition of kimberlite often approaches carbonatite with no more than 10–15%  $SiO_2$ .

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## Introduction

Metasomatism may control the composition trends of lithospheric mantle, diamond formation, and petrogenesis of kimberlitic and other within-plate magmas, as follows from analyses of carbonatite and kimberlite samples and mantle xenoliths in kimberlite pipes. Metasomatism of peridotitic lithospheric mantle has been largely studied (Agashev et al., 2013; Pearson et al., 1995a,b, 2003; Pokhilenko et al., 1999; Shirey et al., 2013; Simon et al., 2003, 2007; Sobolev, 1974). The traditional chemical classification distinguishes carbonatitic and silicate types of mantle metasomatism. Carbonatite metasomatism is most evident in depleted (including diamond-

bearing) dunite-harzburgite in the middle part of mantle section and provides its high enrichments in incompatible elements without notable changes to mineralogy. Silicate metasomatism occurs mostly in lithospheric roots (Agashev et al., 2013) or in the upper lithospheric mantle (Tychkov et al., 2014) and increases percentages of garnet and clinopyroxene in peridotite. Inclusions in diamond reveal its metasomatic origin (Klein-BenDavid et al., 2007; Liu et al., 2009; Navon, 1999), while the chemistry of fluid inclusions records mainly carbonatitic environments of diamond growth (Klein-BenDavid et al., 2009; Zedgenizov et al., 2007).

Metasomatic carbonated lherzolite at the base of lithospheric mantle may be responsible, for instance, for the origin of the Snap Lake kimberlite dike system (Agashev et al., 2008; Pokhilenko et al., 2004). Namely, the Snap Lake kimberlite may be originally evolved from carbonatitic magma that produced by low-degree partial melting of metasomatized

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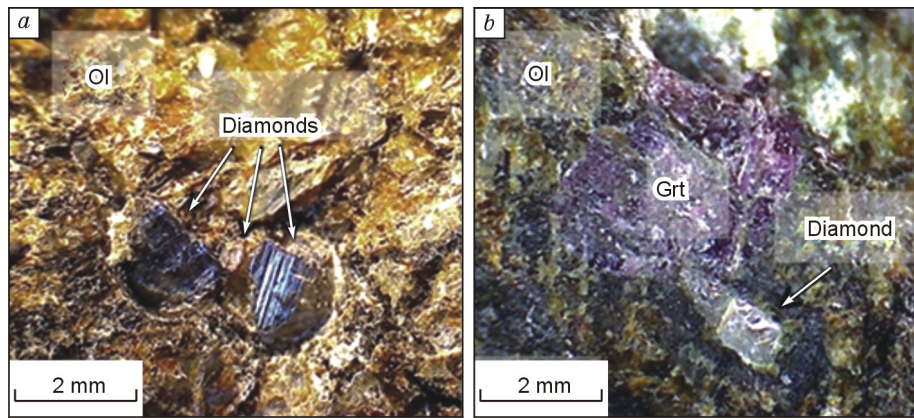


Fig. 1. Representative microphotographs of diamondiferous peridotite xenoliths from Udachnaya kimberlite (Pokhilenko et al., 2014). Ol, olivine; Grt, garnet; a, sample Uv-177/89; b, sample Uv 465/86.

carbonated mantle (Agashev et al., 2001a, 2008). During further ascent and melting progress to higher degrees, such melts acquire a more kimberlitic composition as silicate minerals from lithospheric mantle become assimilated in the melt. This hypothesis has been used in many recent models (Kamenetsky et al., 2009a,b; Sharygin et al., 2014).

Experimental studies of peridotite, eclogite, and kimberlite systems with CO<sub>2</sub> (Dasgupta and Hirschmann, 2006; Dasgupta et al., 2013; Ghosh et al., 2009, 2014; Litasov, 2011; Litasov et al., 2011a) show the presence of carbonated melt with no more than 5–10% SiO<sub>2</sub> at the pressures and temperatures of lithospheric mantle and asthenosphere (Dasgupta et al., 2013; Sharygin et al., 2014; Shatskiy et al., 2015). Other inferences from experimental results mean that carbonates consumed during subduction are recycled mostly within the mantle transition zone and can become a source of plume carbonatitic magma (Grassi and Schmidt, 2011; Litasov et al., 2013b). Many recent melting experiments shed light on liquidus phase relations in kimberlitic systems and melt compositions at pressures to 3–8 GPa (Litasov et al., 2010; Sharygin et al., 2013, 2014; Sokol et al., 2013b; Sokol and Kruk, 2015).

In this paper we discuss models of metasomatism in lithospheric mantle roots with implications for diamond formation, origin of kimberlite magma at the lithospheric base, and sources of carbon and hydrogen that come from the mantle transition zone (stagnant slabs) or from the core-mantle boundary. The discussion bases upon earlier published evidence and new analytical data for xenoliths and lithospheric mantle minerals and for kimberlite and carbonatite samples, as well as upon recent high-pressure experimental studies of carbonate-bearing systems.

## Materials and data

We use a large collection of kimberlites, peridotitic xenoliths and xenocryst minerals of lithospheric mantle analyzed for many years. Some reported results are new and some were published before, such as data on xenoliths (Agashev et al.,

2013; Howarth et al., 2014; Pokhilenko, 2009; Pokhilenko et al., 1993, 1999, 2004, 2014; Shimizu et al., 1999) and on kimberlites and carbonatites from the Siberian craton and the Snap Lake dike (Slave craton, Canada) (Agashev et al., 2000, 2001b, 2008). New results include compositions of diamond-related high-Cr garnets and clinopyroxenes from coarse granular peridotite xenoliths, including diamond-bearing megacrystalline ones (Fig. 1), found in the Udachnaya kimberlite pipe (Pokhilenko et al., 2014).

## Chemistry of high-Cr garnets

Major- and trace-element compositions of Cr-rich garnets from coarse granular and megacrystalline peridotitic xenoliths from the Udachnaya kimberlite have been studied (Table 1) with implications for effects of carbonatite metasomatism. Most of the analyzed garnets fall into the dunite-harzburgite field in the Cr<sub>2</sub>O<sub>3</sub>–CaO diagram (Sobolev et al., 1969, 1973), while some garnets with greater CaO enrichment correspond to wherlitic compositions (Fig. 2). The Cr<sub>2</sub>O<sub>3</sub> and CaO ranges, respectively, are 6.4–12.4 wt.% and 0.86–7.53 wt.% for harzburgite garnets and 4.5–7.4 and 6.1–7.1 for wherlitic varieties. All garnets are highly magnesian (Mg# 81.0–85.4) and strongly depleted in TiO<sub>2</sub> (0–0.33 wt.%). Garnets from sheared peridotite (Agashev et al., 2013) have compositions with broadly varying CaO within the lherzolitic trend (Fig. 2).

High-Cr garnets have large ranges of incompatible elements and are more or less strongly enriched in LREE, MREE and Nb, but are depleted in HREE and Y. The chondrite-normalized REE patterns of harzburgite garnets (Fig. 3) split into two groups: garnets with (i) highest LREE enrichment and Ce and Pr peaks (Hz1) and those with (ii) MREE enrichment and a Nd peak. The earlier studied compositions of garnets from sheared lherzolite (Agashev et al., 2013) likewise fall into two groups: (i) Lz1 garnets with sine-shaped REE spectra (Sm/Er,  $n > 1$ ) and (ii) garnets with normal REE patterns. Although the two groups overlap in some elements, the spectra differ in both curve shapes and element abundances.

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