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Evidence for phase transitions in mineral inclusions in superdeep diamonds of the São Luiz deposit (*Brazil*)

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Abstract

Evidence for phase transitions in mineral inclusions in superdeep diamonds of alluvial placers in the São Luiz River deposits (Brazil) is obtained by the electron backscatter diffraction technique. It has been shown that the crystal structure of superdeep diamonds is significantly deformed around inclusions of MgSi-, CaSi-, and CaTiSi-perovskites, SiO_2 (stishovite?), and Mg_2SiO_4 (ringwoodite?). On the contrary, significant deformations around inclusions of olivine, ferropericlase, and majoritic garnet are not detected. The absence of deformation near these minerals reveals the lack of phase transitions with dramatic volume changes. The present study suggests that the formation of superdeep diamonds proceeds at different levels of the sublithospheric mantle, transition zone, and lower mantle.

Keywords: diamond; inclusions; deformation; superdeep minerals; upper mantle; transition zone; lower mantle

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Introduction

Natural diamonds have been studied intensely for many years as carriers of information about the geochemistry, mineralogy, and PTf_{O_2}-conditions of the Earth's mantle. Analysis of the properties of diamonds and trapped inclusions provides important information about the formation of diamonds. Many-year studies of diamond-hosted crystal inclusions, summarized in a detailed review (Shirey et al., 2013), showed that the formation of diamonds in subcontinental lithospheric mantle takes place in peridotite (P-type) and eclogite (E-type) substrates (Harris, 1992; Meyer, 1987; Sobolev, 1974). Between these two main parageneses, there are much more rare intermediate assemblages of mineral inclusions—pyroxenite and websterite assemblages. Studies of mineral equilibria suggest that the formation of diamonds in all these assemblages takes place at 900–1400 ℃ at depths of 150–200 km (Boyd and Finnerty, 1980; Dawson and Smith, 1975; Nechaev and Khokhryakov, 2013; Ragozin et al., 2014; Rudnick et al., 1998; Sobolev, 1974; Stachel and Harris, 2008).

In recent years, data have been obtained on diamonds from the asthenosphere (250–410 km), transition zone (410–670 km), and lower mantle (>670 km). An assemblage of ferropericlase (Mg,Fe)O and the $(Mg,Fe)SiO_3$ phase, which was interpreted as Mg(Fe)Si-perovskite, was detected in diamond of the Koffiefontein pipe (Scott Smith et al., 1984). Experimental data demonstrate that olivine, the principal mantle mineral, transforms into wadsleyite—a high-pressure modification—at 12–16 GPa and into ringwoodite at 18–22 GPa. At more than 24 GPa, ringwoodite breaks up into ferropericlase and $(Mg,Fe)SiO_3$ with a perovskite structure (Chudinovskikh and Boehler, 2001; Ringwood and Irifune, 1988). Somewhat later, majoritic garnet was detected in diamond of the Monastery pipe (South Africa), and its composition suggests formation at depths of 250 to 400 km (Moore and Gurney, 1985, 1989; Moore et al., 1991). Diamonds containing superdeep assemblages have been described from 12 deposits worldwide: Slave Craton (Canada)

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(Davies et al., 1999; Pokhilenko et al., 2004), Brazil (Harte et al., 1999a,b; Hutchison et al., 1999, 2001; Kaminsky et al., 2001; McCammon, 1997; Wilding et al., 1991), West Africa (Joswig et al., 1999; Stachel et al., 2000, 2002), Kaapvaal Craton (South Africa) (Deines et al., 1991; McDade and Harris, 1999; Moore and Gurney, 1985), Arkhangel'sk kimberlite province (Sobolev et al., 1997), and Siberian Platform (Shatskii et al., 2010; Sobolev et al., 2004).

Ferropericlase is the most widespread inclusion of the superdeep assemblage in such diamonds (Kaminsky, 2012). However, the presence of ferropericlase alone is not an indicator of the superdeep origin of host diamond. Only the assemblage of ferropericlase with the MgSi and CaSi phases and quartz/coesite is evidence for the lower-mantle origin of host diamond (Stachel et al., 2000). These phases are low-pressure polymorphs or polyphase products of decomposition of high-pressure minerals $MgSiO_3$ and $CaSiO_3$ with a perovskite structure and SiO_2 with a stishovite structure. Besides, a high-pressure tetragonal almandine–pyrope phase (TAPP) is known in the superdeep assemblage of diamond-hosted inclusions (Harris et al., 1997; Harte et al., 1999b). The fact that inclusions of $MgSiO_3$-perovskite at equilibrium with ferropericlase have an order of magnitude higher Ni content than ordinary enstatite of this composition hosted by upper-mantle diamonds is a typomorphic feature of all lower-mantle inclusions of $MgSiO_3$ (Stachel et al., 2000). Also, inclusions of corundum in an assemblage with $MgSiO_3$-perovskite and ferropericlase confirmed the existence of a free-alumina phase in the lower mantle (Hutchison et al., 2001).

Polyphase inclusions in sublithospheric diamonds are often viewed as originally homogeneous silicate phases which decomposed during the rise of the diamonds in a mantle plume (Bulanova et al., 2010; Harte, 2010; Hayman et al., 2005; Kaminsky et al., 2010; Walter et al., 2011). The movement of sublithospheric diamonds to higher mantle levels is evidenced by the presence of polymineral inclusions of garnet and clinopyroxene, which are interpreted as decomposed majoritic garnet (Harte and Cayzer, 2007). Inclusions in lower-mantle diamonds must experience phase transformations with a considerable increase in volume with decreasing pressure (Harte et al., 1999b; Hutchison et al., 2001; Kaminsky et al., 2001). As a result, phase transitions for diamond-hosted inclusions of lower-mantle minerals must cause stress around the inclusions and generate excess residual pressure within them. Almost all the inclusions in diamonds of placers in the Juina province, Brazil (São Luiz, Mutum, Vermelho, and Corrigo Chicoria), belong to superdeep assemblages (Kaminsky et al., 2001). Therefore, to prove the existence of phase transitions, we studied residual stress around inclusions in superdeep diamonds of alluvial placers in the basin of the São Luiz River (Brazil).

Samples and methods

In the present paper, an assessment of strain around inclusions by reflection-electron diffraction was used for an attempt to analyze possible phase transitions in mineral inclusions in diamonds of the São Luiz deposit, Brazil, which belong to superdeep phases based on a whole range of features. The previous studies show that many diamonds of this deposit contain inclusions of minerals which formed at the depth of the seismically detectable transition zone and lower mantle (Zedgenizov et al., 2014a). Most of the studied crystals are rounded and have traces of partial dissolution. Also, a considerable part of the diamonds of this deposit are irregularly shaped aggregates. The São Luiz diamonds in many cases show an internal zoning. According to IR spectroscopy data, nitrogen content within one crystal can vary from 0 to 500 ppm. The studied diamonds are distinguished by an extremely high degree of aggregation of nitrogen defects (90–100% *B* centers).

Diamonds with mineral inclusions were polished so that the inclusions were on the same plane as host diamond. The major elements of the exposed mineral inclusions were determined by electron-probe microanalysis. The measurements were taken with a JEOL JXA 8100 electron microprobe at the Analytical Center of the Sobolev Institute of Geology and Mineralogy with a 2-μm beam at 20 nA and 15 kV.

The study of the mineral inclusions from the São Luiz diamonds showed the predominance of phases typical of the minerals of the sublithospheric upper mantle, transition zone, and lower mantle. In the previously studied diamonds, we detected majoritic garnet; clinopyroxene; ferropericlase; CaSi-, CaTiSi-, and MgSi-perovskites; TAPPs; the SiO_2 and Al_2SiO_5 phases; olivine; K-feldspar (K-hollandite?); merwinite; grossular; magnesite; iron sulfides; and native Fe (Zedgenizov et al., 2014a,b). Table 1 shows the compositions of the diamond-hosted mineral inclusions for which the misorientation of lattice was studied.

The São Luiz diamonds were studied with the use of equipment from the Tomsk Materials Science Center of Common Use. The deviation from the basic orientation in the grain for a diamond-hosted inclusion was mapped by electron backscatter diffraction (EBSD) (Humphreys, 2001). The EBSD analysis was performed with the use of a Pegasus attachment to a Quanta 200 3D SEM with a tungsten hot cathode at 20 and 30 kV. Kikuchi patterns formed by back-scattered electrons were automatically indexed by the TSL OIM (Orientation Imaging Microscopy) data collection software. The accuracy of determination of the angles of misorientation by this method was 0.5°–1.0° (Adams et al., 1993).

Results

The figures below show the results of mapping of misorientation of the diamond lattice around inclusions with the use of reflection-electron diffraction. All the images have the same spectrum of colors, in which each color corresponds to crystallographic misorientation with respect to a fixed standard spot at the longest distance from the inclusion. Small (<0.5°) or absent misorientations are marked blue. Misorientations of