

SiO₂ Inclusions in Sublithospheric Diamonds

D. A. Zedgenizov^{a, b, *}, A. L. Ragozin^{a, b}, H. Kagi^c, H. Yurimoto^d, and V. S. Shatsky^{a, b}

^a*Sobolev Institute of Geology and Mineralogy, Siberian Branch, Russian Academy of Sciences, Novosibirsk, 630090 Russia*

^b*Novosibirsk State University, Novosibirsk, 630090 Russia*

^c*Geochemical Research Center (GRC), Graduate School of Science, Tokyo University, Tokyo, 113-0032 Japan*

^d*Department of Natural History Sciences, Hokkaido University, Sapporo, Hokkaido, 060-0810 Japan*

*e-mail: zed@igm.nsc.ru

Received January 29, 2019; revised February 2, 2019; accepted February 25, 2019

Abstract—The paper describes mineralogical characteristics of SiO₂ inclusions in sublithospheric diamonds, which typically have complicated growth histories showing alternating episodes of growth, dissolution, and postgrowth deformation and crushing processes. Nitrogen contents in all of the crystals do not exceed 71 ppm, and nitrogen is detected exclusively as B-defects. The carbon isotope composition of the diamonds varies from $\delta^{13}\text{C} = -26.5$ to -6.7% . The SiO₂ inclusions occur in association with omphacitic clinopyroxenes, majoritic garnets, CaSiO₃, jeffbenite, and ferropicriase. All SiO₂ inclusions are coesite, which is often associated with micro-blocks of kyanite in the same inclusions. It was suggested that these phases have been produced by the retrograde dissolution of primary Al-stishovite, which is also evidenced by the significant internal stresses in the inclusions and by deformations around them. The oxygen isotope composition of SiO₂ inclusions in sublithospheric diamonds ($\delta^{18}\text{O}$ up to 12.9‰) indicates a crustal origin of the protoliths. The negative correlation between the $\delta^{18}\text{O}$ of the SiO₂ inclusions and the $\delta^{13}\text{C}$ of their host diamonds reflects interaction processes between slab-derived melts and reduced mantle rocks at depths greater than 270 km.

Keywords: diamonds, inclusions, stishovite, coesite, sublithospheric mantle, subduction, carbon, oxygen

DOI: 10.1134/S0016702919090131

INTRODUCTION

Natural diamonds are unique geological material, which was brought from the greatest depths, so far available for geological studies. They have long been used in solving problems related to the nature of the Earth's mantle and chemical processes in deep zones of the Earth. One of the key indicators of the genesis of diamonds is the mineralogy and composition of inclusions in them, most of which suggest that diamonds were formed mostly in ultramafic (peridotite, P-type) and mafic (eclogite, E-type) rocks in the bottom part of the lithospheric mantle of ancient cratons (Sobolev, 1974; Meyer, 1987; Harris, 1992). It is also thought that a small percentage (<5%) of diamonds could be formed under much higher pressures in the transition zone of the upper mantle (>410 km) or even in the lower mantle (>660 km) (Harte et al., 1999; Stachel et al., 2005; Walter et al., 2011; Kaminsky, 2012). It is thereby emphasized that diamonds are produced in the sublithospheric mantle and transition zone mostly in relation to subducted mafic rocks of the oceanic lithosphere but not to ultramafic material of the primitive mantle, in which most diamonds in the lower mantle are produced (Harte, 2010).

According to current geodynamic models, subduction of the oceanic lithosphere is able to transfer the

material of the Earth's upper shells (bottom sediments, altered lavas, and depleted mantle rocks) from Earth's upper zones to deep levels of its mantle. The subducted rocks can be accumulated in the bottom part of the subcratonic mantle, as is inferred from mantle xenoliths and diamond-hosted inclusions found worldwide in kimberlites (Jacob, 2004; Taylor et al., 2005; Shatsky et al., 2015, 2016; Zedgenizov et al., 2016), or these rocks can be brought to the depths of the seismically determined boundary between the upper and lower mantle and even into the lower mantle (Fukao et al., 2001).

Silica phases (coesite and stishovite) have never been found in peridotitic rocks in the upper mantle but are quite common in the mafic (eclogite) association. Although coesite eclogites are only infrequently found in kimberlites worldwide, coesite inclusions were identified in diamonds from practically all primary and placer deposits around the world. It was determined that diamond-hosted mineral assemblages with coesite correspond to a broad series of mafic compositions from magnesian websterites to kyanite eclogites, grosspyrites, and calc-silicate rocks, which were produced in the bottom part of the subcratonic lithospheric mantle (Sobolev, 2006). Inclusions of a supposedly high-pressure SiO₂ phase (stishovite) were

also documented in many diamonds, which were also thought to crystallize at greater depths: in the asthenosphere, transition zone, and lower mantle (Kaminsky, 2012). Keen interest is attracted by diamonds from different sources (kimberlites and alluvial placers) in the Juina area, Brazil, because these diamonds typically host inclusions of mineral assemblages of the sublithospheric mantle (Harte et al., 1999; Kaminsky et al., 2001, 2009; Hutchison et al., 2001; Hayman et al., 2005; Brenker et al., 2007; Walter et al., 2008; Bulanova et al., 2010; Araujo et al., 2013; Zedgenizov et al., 2014; Thomson et al., 2014; Burnham et al., 2015). This paper presents new data on the distinguishing mineralogical features of SiO₂ inclusions in sublithospheric diamonds from São Luís placers, Brazil. These data are then used in discussing the conditions of the origin (in the sublithospheric mantle) and the possible protoliths of rocks with diamonds hosting SiO₂ phases.

CHARACTERISTICS OF THE SUPERDEEP DIAMONDS WITH SiO₂ INCLUSIONS

The diamonds with inclusions of a SiO₂ phase are colorless or pale brown crystals, which have a geometrically distorted shape or are euhedral. They show evidence of intense dissolution, etching channels, and numerous cracks and chippings. We used parallel double-sided polished plates to study the internal structure, impurity defects, and carbon isotope composition of the diamonds and inclusions in them.

The internal structure of the diamonds with SiO₂ inclusions, which was detected by studying the polished plates in cathodoluminescence, suggests complex growth histories of the diamonds (Fig. 1). The crystals typically show a number of contrasting growth zones, which sometimes have thin concentric zoning. The boundaries of the growth zones are of irregular shape, which indicates that the crystals originally had distorted morphologies. Various zones of the crystals show traces of plastic deformations in the form of thin intersecting lines. These features of internal structure are also typical of many other superdeep diamonds described earlier in the Juina area (Hutchison et al., 1999; Kaminsky et al., 2001; Araujo et al., 2013; Hayman et al., 2005; Bulanova et al., 2010; Zedgenizov et al., 2014; Thomson et al., 2014; Burnham et al., 2015). These and our newly acquired data thus confirm that superdeep diamonds, and those with SiO₂ inclusions among others, are characterized by complicated growth histories with alternating growth and dissolution episodes and those of overprinted deformation and crushing processes.

Using FTIR spectroscopy, we have analyzed local variations in the nitrogen and hydrogen defects of the diamonds with SiO₂ inclusions. These data indicate that none of the crystals contains more than 71 ppm nitrogen (Fig. 1 shows these values for discrete zones). Many diamonds or their zones contain <10 ppm nitro-

gen and can thus be classified with nitrogen-free diamonds of type IIa. A high percentage of nitrogen-free diamonds is an inherent feature of the population of superdeep diamonds (Hayman et al., 2005; Hutchison et al., 1999; Kaminsky et al., 2001; Bulanova et al., 2010). Thereby the percentage of diamond crystals containing statistically significant nitrogen concentrations are characterized by its maximum aggregation, i.e., the presence of nitrogen in the IR spectra is identified exclusively in B defects (four nitrogen atoms substituting carbon around a vacancy; Zaitsev, 2001) in the absolute absence of absorption related to the specific structural platelets.

Six diamonds with SiO₂ inclusions were analyzed by SIMS for carbon isotope composition in their discrete zones. Figure 1 shows the corresponding $\delta^{13}\text{C}$ values in the zones. The carbon isotope composition broadly varies from -26.5% in diamond SL-2 (Fig. 1a) to -6.7% in diamond SL-48 (Fig. 1h). Such characteristics of carbon isotope composition were also determined in other superdeep diamonds with SiO₂ inclusions (Burnham et al., 2015). Significant variations (by more than 10‰ in diamond SL-16, Fig. 1b) were also detected between discrete zones in single crystals. The variations in the crystals are associated with a shift in the $\delta^{13}\text{C}$ values toward heavier compositions. According to their relationships between the carbon isotope composition and defect-admixture composition (Fig. 2), diamonds with SiO₂ inclusions from the Juina province plot within a region whose parameters are typical only of a small percentage (<10%) of all currently known diamonds (Cartigny et al., 2001), and the great majority of these diamonds affiliates with the eclogite assemblage.

Assemblages of SiO₂ Inclusions in Superdeep Diamonds

SiO₂ inclusions hosted in various zones of the diamonds often occur in association with inclusions of other minerals: omphacitic clinopyroxene (*Omph*) in diamond SL-55; majoritic garnet (*Maj-Grt*) in diamonds SL-16, SL-28, SL-31, and SL-36; a CaSiO₃ phase in diamonds SL-28, SL-31, and SL-42; and jeffbenite (*Jfbn*) in diamond C-40 (Zedgenizov et al., 2014). SiO₂ inclusions in association with a CaSiO₃ phase were described in other superdeep diamonds (Stachel et al., 2000; Bulanova et al., 2010). It was suggested that inclusions of a CaSiO₃ phase of perovskite structure can be produced in mantle rocks at pressures above 14–16 kbar, i.e., in the thermodynamic stability field of stishovite (Walter et al., 2011; Kaminsky, 2012; Thomson et al., 2016). In the diamonds in question, such inclusions are usually low-pressure polymorphs (Zedgenizov et al., 2016). The garnet shows broad compositional variability and concentration of the majorite end member and is poor in Cr₂O₃ (<0.3 wt %). The jeffbenite is also poor in Cr₂O₃ (<0.1 wt %) and rich in TiO₂ (4.5 wt %). Composi-

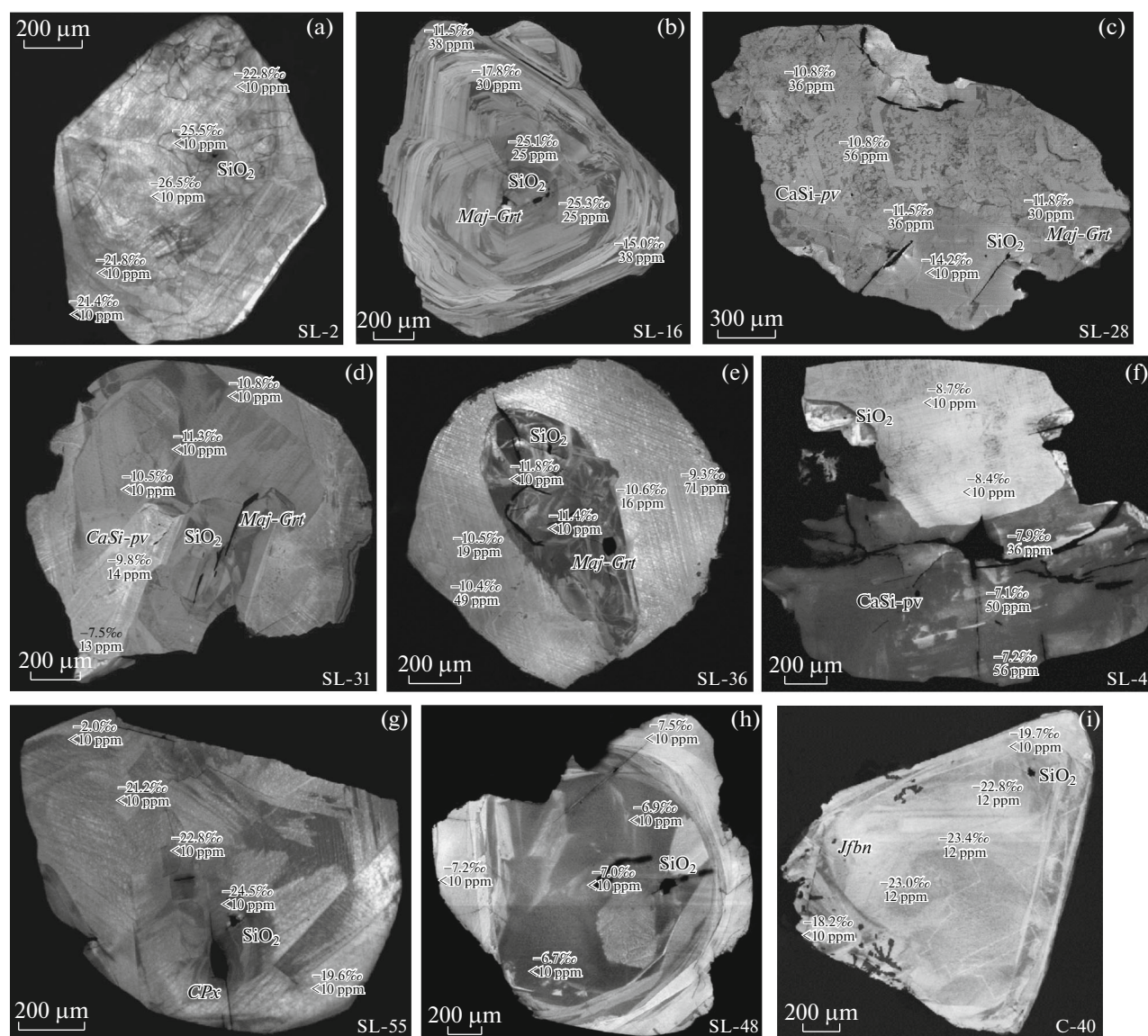


Fig. 1. Cathodoluminescence images of polished sections of superdeep diamond platelets with inclusions of SiO_2 and other minerals from the Juina deposit, Brazil: (a) SL-2; (b) SL-16; (c) SL-28; (d) SL-31; (e) SL-36; (f) SL-42; (g) SL-55; (h) SL-48; (i) C-40. The images show the associations of the inclusions and the variations in the carbon isotope composition ($\delta^{13}\text{C}$) and nitrogen concentrations of the diamonds.

tional traits of the inclusions found in association with the SiO_2 inclusions seem to suggest that they were formed in mafic rocks (Zedgenizov et al. 2014).

In addition to minerals that can be attributed to mafic associations of the sublithospheric mantle, SiO_2 inclusions were also found in the diamonds that hosted ferropericlase inclusions (Harte et al., 1999; Kaminsky et al., 2001; Stachel et al., 2000; Davies et al., 2004). Theoretical models and experimental data suggest that ferropericlase can be produced only in ultramafic rocks at depths corresponding to the boundary between the transition zone and lower mantle (Harte, 2010). According to F.V. Kaminsky (2017), the presence of free silica in the lower mantle is explained by that its composition differs from pyrolite. It was

hypothesized that silica may have come to the lower mantle from the core (Hirose et al. 2017; Helffrich et al. 2018). An equilibrium association of ferropericlase and a high-pressure SiO_2 phase (stishovite) can be produced by a peritectic reaction involving bridgmanite, another typical mineral of the lower mantle, as has been experimentally established for FeO-enriched compositions, the so-called *stishovite paradox* (Litvin et al., 2017).

Characteristics of SiO_2 Inclusions in Superdeep Diamonds

To characterize structural–chemical features of SiO_2 inclusions in superdeep diamonds, we have ana-

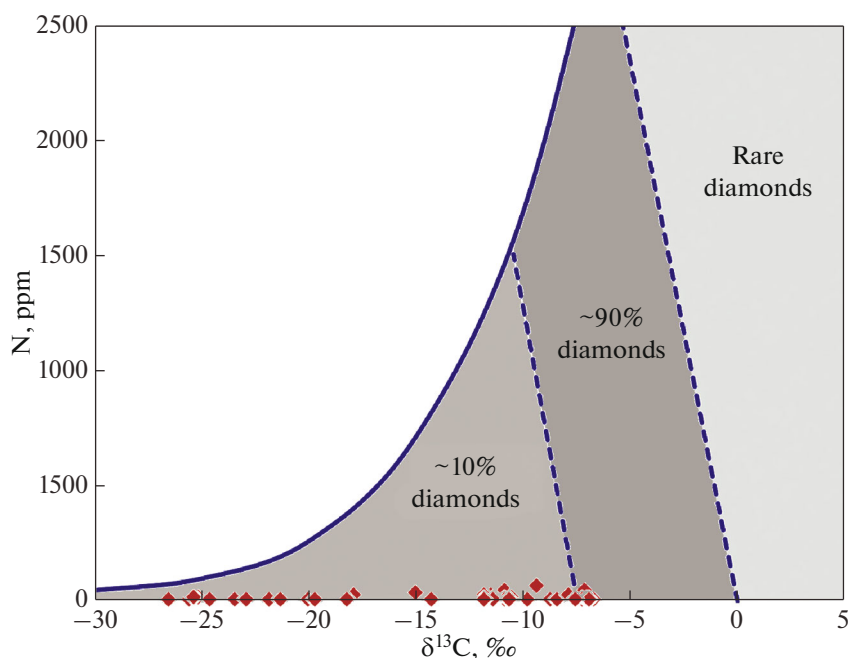


Fig. 2. Correlation between the carbon isotope composition ($\delta^{13}\text{C}$, ‰) and nitrogen concentration (N, ppm) in superdeep diamonds with SiO₂ inclusions from the Juina deposit, Brazil.

lyzed them using Raman spectroscopy. The spectra of the inclusions show lines of coesite with a characteristic more intense line with a maximum at 525–531 cm^{-1} (Fig. 3). The shift of this line toward higher frequencies suggests residual strain in the inclusions. The shift of this coesite line relative to its “normal” (without strain) position at 521 cm^{-1} is $2.9 \pm 0.1 \text{ cm}^{-1}/\text{GPa}$ (Hemley, 1987). Based on this calibration, we estimated the residual strain in the inclusions at 1.6–3.4 GPa, with different values acquired even for inclusions hosted in a single crystal (for example, 1.8 and 3.4 GPa for diamond SL-42), which obviously indicates that some of the inclusions have relaxed their strain via plastic and brittle deformations. We have found extensive deformations around SiO₂ inclusions in superdeep diamonds based on electron backscatter diffraction (EBSD) data (Zedgenizov et al., 2015). Deformations induced by strain around the inclusions were also identified using the 4- cm^{-1} shift of the diamond peak at 1332 cm^{-1} in the Raman spectra (Fig. 4).

In addition to lines of coesite, the spectra of many of the inclusions show a series of less intense bands of another phase (Fig. 3). Comparison with reference spectra from the RRUFF database led us to suggest that this phase is always kyanite. Kyanite microblocks (5–10 μm) were also identified in the BSE images of some of the polished inclusions (Fig. 5), and their identification was confirmed by chemical analyses, which corresponded to the stoichiometry of Al₂SiO₅. We have not detected any significant admixtures in either the coesite or the kyanite.

To determine the nature and possible sources of the protoliths of the rocks in which the superdeep diamonds crystallized, we have analyzed the oxygen isotope composition of the SiO₂ inclusions by SIMS. In five of the samples, $\delta^{18}\text{O}$ values ranged from 10.4 to 12.6‰, except a single sample (SL-31) whose $\delta^{18}\text{O}$ = 6.4‰ and which most closely approached the hypothetical mantle average values of $\delta^{18}\text{O}$ = $5.5 \pm 0.4\text{‰}$ (Mattey et al., 1994). The diamonds whose inclusions have a heavy oxygen isotope composition typically have a relatively light carbon isotope composition of $\delta^{13}\text{C}$ = –25.4 to –20.6‰ (Fig. 6). An exception is sample SL-31, having $\delta^{13}\text{C}$ = –7.5‰, with inclusions in it having $\delta^{18}\text{O}$ = 10.4‰. Data on the oxygen isotope composition of SiO₂ phases ($\delta^{18}\text{O}$ from 8.3 to 12.9‰) and the carbon isotope composition of the host superdeep diamonds from the Juina province ($\delta^{13}\text{C}$ from –26.1 to –6.4‰) were also published in (Burnham et al., 2015). Our data reported herein show similar tendencies, which are also typical of many coesite inclusions in lithospheric diamonds (Schulze et al., 2013) (Fig. 6).

DISCUSSION

The presence of a free SiO₂ phase (coesite or stishovite) in crustal rocks subducted to significant depths has been demonstrated by extensive natural and experimental data. It was determined that the upper-mantle coesite-bearing mineral assemblages extremely widely vary in composition and, according to isotope–

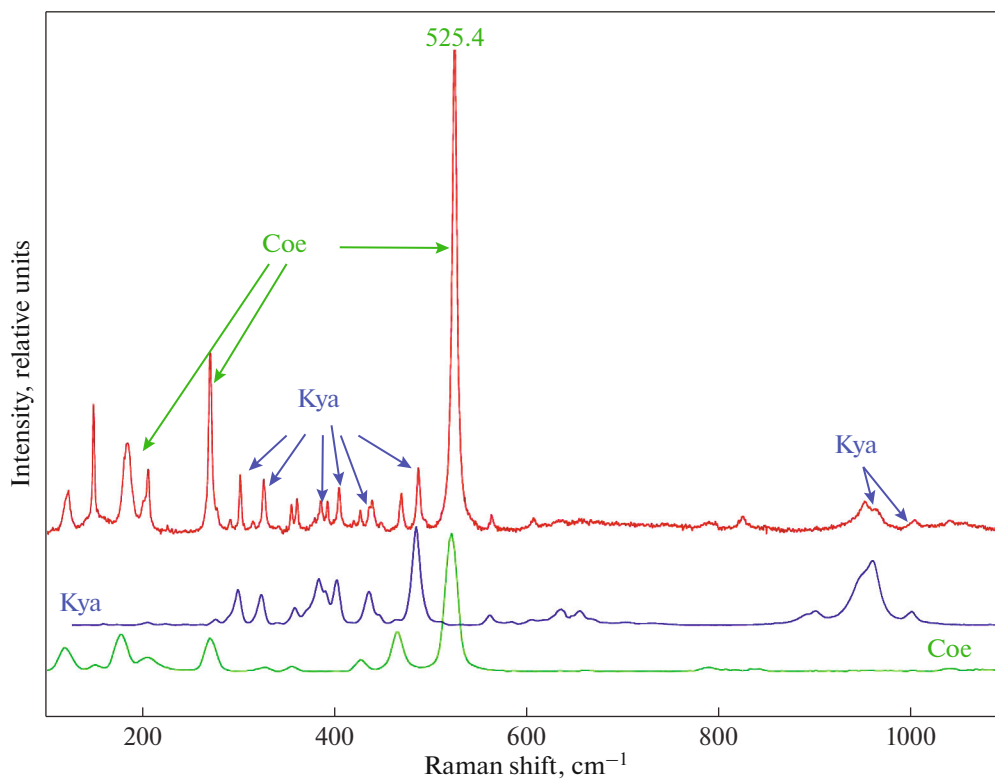


Fig. 3. In-situ Raman spectrum of a SiO_2 inclusion in diamond SL-55 in comparison with the reference spectra of coesite and kyanite from the RRUFF database.

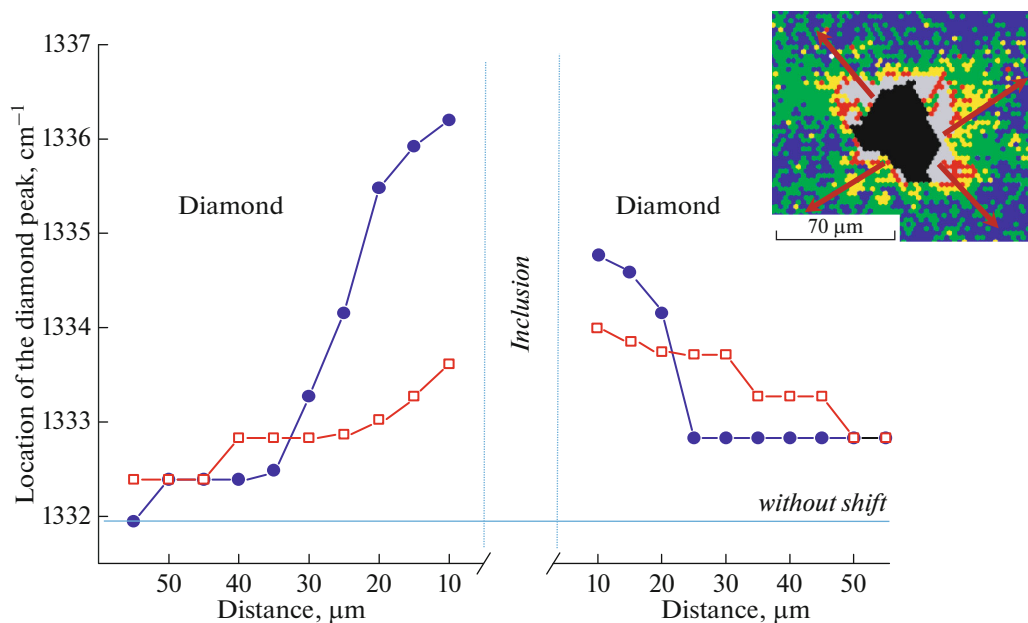


Fig. 4. Raman shift of (1) diamond around (2) a SiO_2 inclusion in sample SL-48. The inset in the top right-hand corner shows an image of deformations around the inclusion (EBSD data) and spectrum-recording profiles.

geochemical evidence, were formed in relation to the subduction of the ancient oceanic crust (Sobolev, 2006). As the pressure increases (>9 GPa), stishovite

becomes the stable SiO_2 phase. The minimum depth of stishovite crystallization in the mantle was estimated at 270 km (Zhang et al., 1993). We have not

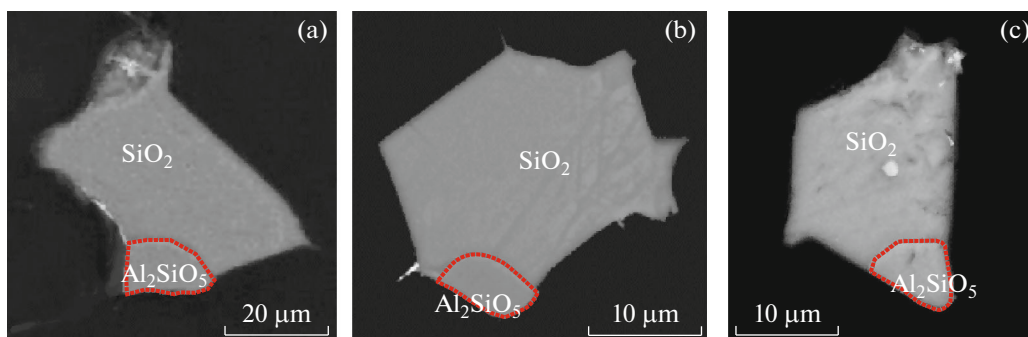


Fig. 5. BSE images of polished SiO₂ inclusions with Al₂SiO₅ blocks in superdeep diamonds: (a) SL-16; (b) SL-48; (c) SL-2. The composition of the phases is confirmed by EDS microprobe analyses.

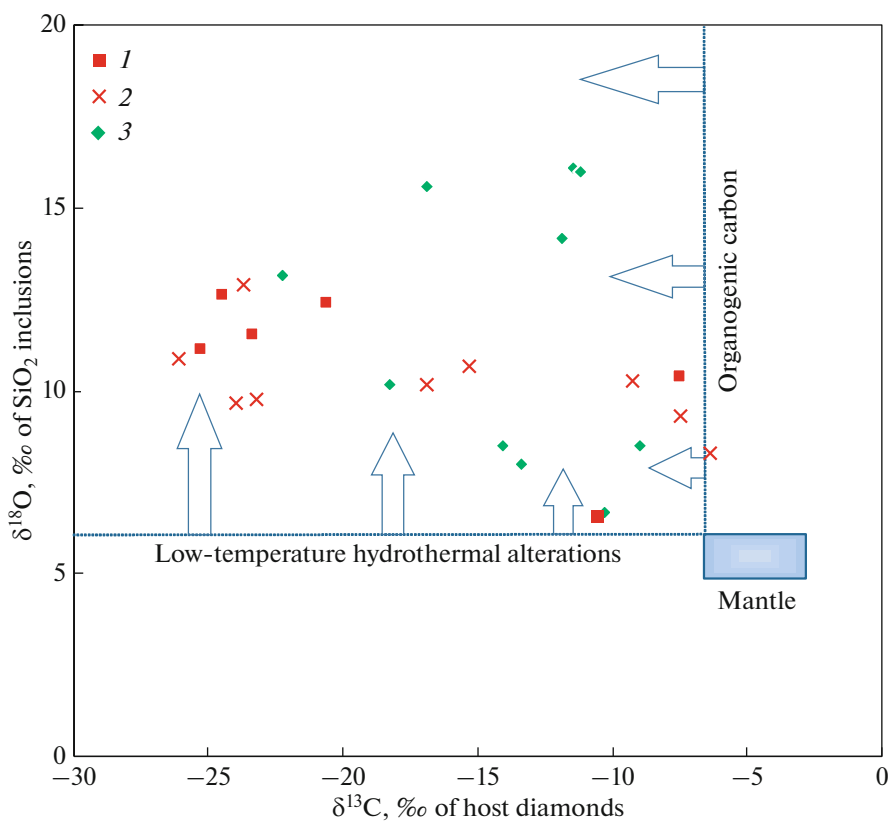


Fig. 6. Correlation of the oxygen isotope composition ($\delta^{18}\text{O}$, ‰) of SiO₂ inclusions and the carbon isotope composition ($\delta^{13}\text{C}$, ‰) of the host diamonds: (1) superdeep diamonds from the Juina deposit, Brazil (newly obtained data); (2) superdeep diamonds from the Juina deposit, Brazil (Burnham et al., 2015); (3) diamonds with coesite inclusions from the lithospheric mantle (Schulze et al., 2013). The diagram shows the range of the average mantle ratios and the variations related to low-temperature hydrothermal alterations of oceanic crustal rocks and introduction of organogenic carbon.

identified stishovite in the superdeep diamonds. According to Raman spectroscopic data, all of the SiO₂ inclusions are the lower pressure modification coesite. It was hypothesized that coesite hosted in superdeep diamonds was produced by the retrograde transformation of stishovite, which was originally captured by the diamonds within the stability fields of minerals coexisting with it (Kaminsky et al., 2012).

This transformation should have obviously been associated with large volume effects (~32%) and should have brought about internal strain in the inclusions and deformations of the host diamond around them.

In many of the inclusions, coesite was determined to occur in association with kyanite. Experimental data indicate that stishovite can contain much Al, and its concentration in the mineral increases with

increasing pressure (Pawley et al., 1993). This led us to suggest that composite coesite inclusions with kyanite hosted in the superdeep diamonds were originally Al-bearing stishovite, which underwent phase transition at decompression. Aluminum is accommodated in stishovite via the substitution $\text{Si}^{4+} \rightarrow \text{Al}^{3+} + \text{H}^+$ (Pawley et al., 1993). As was demonstrated in (Litasov et al., 2007), hydrogen concentration in stishovite increases with increasing pressure, and this makes it possible to regard this mineral as a potential transporter of water with subducted oceanic crustal metabasite rocks into the lower mantle.

Experimental studies of systems that model the composition of mid-oceanic ridge basalts (MORB) show that, at 10–15 GPa, the redistribution of pyroxene components into garnet with increasing pressure leads to that eclogite is gradually transformed into a rock consisting only of majoritic garnet and stishovite (10–20 vol %) (Irfune and Ringwood, 1993). At pressures higher than 20 GPa, majoritic garnet starts to decompose and produce a CaSiO_3 phase of perovskite structure. The associations *Maj-Grt* + CaSiO_3 + SiO_2 and CaSiO_3 + SiO_2 , which were identified in some of the studied and previously described diamonds, seem to reflect these and deeper environments. Experiments modeling the average composition of the continental crust have demonstrated higher (25–35 vol %) stishovite contents in association in majoritic garnet, K-hollandite (KAlSi_3O_8), and clinopyroxene (>24 GPa) (Irfune et al., 1994). The likely stability of this association in the mantle was confirmed by finds of supposed K-hollandite inclusions in superdeep diamonds from the Juina province (Bulanova et al., 2010; Zedgenizov et al., 2014).

Note that neither coesite nor stishovite are expected in ultramafic (metaperidotite) associations at various depth levels in the upper and lower mantle. Nevertheless, the identified association of SiO_2 inclusions in ferropericlase, a typical mineral of the lower-mantle metaperidotite association, in a few superdeep diamonds may reflect the unusual parameters of their crystallization, including the composition of the lower-mantle material different from pyrolite (Kaminsky, 2017). The crystallization of new association with ferropericlase and stishovite was experimentally demonstrated at 24 and 26 GPa in both the metaperidotite and the metabasite systems at their interaction with carbonate melts (Litvin et al., 2016). However, it was experimentally demonstrated that ferropericlase can be formed in reactions between carbonatite melt and reduced rocks at deep levels of the upper mantle (>270 km) and should not necessarily crystallize in the lower mantle (Brey et al., 2004). Ferropericlase inclusions in association with a SiO_2 phase are notably enriched in Fe compared to ferropericlase expected in lower-mantle metaperidotite association. The ferropericlase composition series in superdeep diamonds, which are enriched in Fe, likely documents a prograde

reaction between carbonate melts and mantle rocks. This interaction may result in new mineral associations crystallizing at pressures of 10–16 GPa, which shall be intermediate between metaperidotites and metabasites (Thomson et al., 2016). A possible source of the carbonate melts in the mantle is thought to be both peridotites (Kaminsky et al. 2016; Ryabchikov and Kogarko, 2016) and subducted rocks of the oceanic lithosphere (Walter et al., 2008).

The oxygen isotope composition of the silicate inclusions (SiO_2 phases among them) and the carbon isotope composition of the diamonds are considered to be major evidence of their subduction-related genesis (Schulze et al., 2013; Ickert et al., 2013). Currently available data show that the oxygen isotope composition of the SiO_2 inclusions and the carbon isotope composition of superdeep diamonds broadly vary. It is thought that $\delta^{18}\text{O}$ values higher or lower than the mantle average ones reflect near-surface low- and high-temperature hydrothermal alterations of the rocks in the oceanic crust (Taylor et al., 2005). When these rocks are brought to significant depths, the isotope composition is not modified any significantly. Hence, the high $\delta^{18}\text{O}$ values of SiO_2 inclusions in the superdeep diamonds definitely suggest that the rocks in which the diamonds crystallized were crustal. A crustal origin of superdeep diamonds hosting SiO_2 inclusions also follows from their relatively light carbon isotope composition, which reflects isotope fractionation in a biogenic or abiogenic cycle of organic carbon on the Earth's surface (Kirkley et al., 1991; Shilobreeva et al., 2011). The aforementioned correlation between the $\delta^{18}\text{O}$ of the SiO_2 inclusions and the $\delta^{13}\text{C}$ of their host superdeep diamonds may be explained by re-equilibration of the subduction-related carbonate melts with reduced mantle rocks at depths greater than 270 km (Burnham et al., 2015).

CONCLUSIONS

Data of long-term studies showed that SiO_2 phases (quartz and coesite) are indicators of the mafic (eclogite) association of the lithospheric upper mantle. The occurrence of the higher pressure phase stishovite is inferred from results of studies of diamond-hosted inclusions from deeper levels of the sublithospheric mantle. In the course of this study, we have analyzed mineralogical characteristics of SiO_2 inclusions in sublithospheric diamonds from the widely known Juina deposit in Brazil.

The diamonds hosting SiO_2 inclusions typically show evidence of intense dissolution, etching channels, numerous internal cracks, and chippings. The inner structure of these diamond crystals provides evidence of their complicated growth histories, with alternating growth and dissolution episodes and overprinted plastic and brittle deformation processes. Nitrogen concentrations in all of the analyzed crystals

are no higher than a few tens ppm, and this element was identified only as B defects, in the complete absence of platelets. The carbon isotope composition of superdeep diamonds with SiO₂ inclusions broadly varies from $\delta^{13}\text{C} = -26.5$ to -6.7% . The relationships between the carbon isotope composition and nitrogen contents indicate that these diamonds were produced in a region in which relatively little (<10%) of all previously studied diamonds were formed. The latter diamonds affiliate mostly to the eclogite assemblage.

Inclusions of SiO₂ occur in superdeep diamonds in association with omphacitic clinopyroxene, majoritic garnet, a CaSiO₃ phase, jeffbenite, and ferropericlae. We failed to identify any stishovite relics. It was determined that all of the SiO₂ inclusions are coesite, which often occurs in association with minor kyanite grains. We suggest that these phases were produced by retrograde transition of primary Al-stishovite. The significant internal strain in the inclusions and deformations around them may be indicators of these transformations. Al-stishovite is regarded as a potential H₂O transporter in deeply subducted mafic rocks of the oceanic crust into the lower mantle. The oxygen isotope composition of SiO₂ inclusions in superdeep diamonds ($\delta^{18}\text{O}$ up to 12.9‰) indicates that their protoliths were of crustal nature. The correlation between the $\delta^{18}\text{O}$ of the SiO₂ inclusions and the $\delta^{13}\text{C}$ of their host diamonds seems to reflect interaction between subduction-related melts and reduced mantle rocks at depths greater than 270 km.

FUNDING

This study was carried out under government-financed project 0330-2016-0007 and was supported by the Russian Foundation for Basic Research, project no. 17-55-50062, under agreement 14.Y26.31.0018 with the Ministry of Education and Science of the Russian Federation.

REFERENCES

- D. P. Araujo, J. C. Gaspar, G. P. Bulanova, C. B. Smith, S. C. Kohn, M. J. Walter, and E. H. Hauri, "Juina diamonds from kimberlites and alluvials: a comparison of morphology, spectral characteristics and carbon isotope composition," *Proceed. X Intern. Kimberlite Conf.* Springer, India, 255–269 (2013).
- F. E. Brenker, C. Vollmer, L. Vincze, B. Vekemans, A. Szymanski, K. Janssens, I. Szaloki, L. Nasdala, W. Joswig, and F. Kaminsky, "Carbonates from the lower part of transition zone or even the lower mantle," *Earth Planet. Sci. Lett.* **260**, 1–9 (2007).
- G. P. Brey, V. Bulatov, A. Girmis, J. W. Harris, and T. Stachel, "Ferropericlae—a lower mantle phase in the upper mantle," *Lithos* **77**, 655–663 (2004).
- G. P. Bulanova, M. J. Walter, C. B. Smith, S. C. Kohn, L. S. Armstrong, J. Blundy, and L. Gobbo, "Mineral inclusions in sublithospheric diamonds from Collier 4 kimberlite pipe, Juina, Brazil: subducted protoliths, carbonated melts and primary kimberlite magmatism," *Contrib. Mineral. Petrol.* **160**, 489–510 (2010).
- A. Burnham, A. Thomson, G. Bulanova, S. Kohn, C. Smith, and M. Walter, "Stable isotope evidence for crustal recycling as recorded by superdeep diamonds," *Earth Planet. Sci. Lett.* **432**, 374–380 (2015).
- P. Cartigny, J. W. Harris, and M. Javoy, "Diamond genesis, mantle fractionations and mantle nitrogen content: a study of delta C-13-N concentrations in diamonds," *Earth Planet. Sci. Lett.* **185**, 85–98 (2001).
- R. M. Davies, W. L. Griffin, S. Y. O'Reilly, and B. J. Doyle, "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**, 39–55 (2004).
- Y. Fukao, S. Widiyantoro, and M. Obayashi, "Stagnant slabs in the upper and lower mantle transition region," *Rev. Geophys.* **39**, 291–323 (2001).
- J. W. Harris, "Diamond geology," *The Properties of Natural and Synthetic Diamond*, Ed. by J. E. Field (Academic Press, London, 1992), pp. 345–393.
- B. Harte, "Diamond formation in the deep mantle: the record of mineral inclusions and their distribution in relation to mantle dehydration zones," *Mineral. Mag.* **74**, 189–215 (2010).
- B. Harte, J. Harris, M. Hutchison, G. Watt, and M. Wilding, "Lower mantle mineral associations in diamonds from Sao Luiz, Brazil," *Mantle Petrology: Field Observations and High-Pressure Experimentation: A Tribute to Francis R. (Joe) Boyd* **6**, 125–153 (1999).
- P. C. Hayman, M. G. Kopylova, and F. V. Kaminsky, "Lower mantle diamonds from Rio Soriso (Juina area, Mato Grosso, Brazil)," *Contrib. Mineral. Petrol.* **149**, 430–445 (2005).
- G. Helffrich, M. Ballmer, and K. Hirose, "Core-exsolved SiO₂ dispersal in the Earth's mantle," *J. Geophys. Res. Solid Earth* **123** (1), 176–188 (2018).
- R. J. Hemley, "Pressure dependence of Raman spectra of SiO₂ polymorphs: quartz, coesite, and stishovite," *High-Pressure Research in Mineral Physics*, Ed. by M. H. Manghnani and Y. Syono (Terra Scientific Publishing Co., Tokyo, 1987), pp. 347–359.
- K. Hirose, G. Morard, R. Sinmyo, K. Umemoto, J. Hernlund, G. Helffrich, and S. Labrosse, "Crystallization of silicon dioxide and compositional evolution of the Earth's core," *Nature* **543**, 99–102 (2017).
- M. Hutchison, P. Cartigny, and J. Harris, "Carbon and nitrogen compositions and physical characteristics of transition zone and lower mantle diamonds from Sao Luiz, Brazil. Proceed," *VII Intern. Kimberlite Conf.* (Red Roof Design, Cape Town, 1999), Vol. 1, pp. 372–382.
- M. Hutchison, M. Hursthouse, and M. Light, "Mineral inclusions in diamonds: associations and chemical distinctions around the 670-km discontinuity," *Contrib. Mineral. Petrol.* **142**, 119–126 (2001).
- R. B. Ickert, T. Stachel, R. A. Stern, and J. W. Harris, "Diamond from recycled crustal carbon documented by coupled $\delta^{18}\text{O}$ - $\delta^{13}\text{C}$ measurements of diamonds and their inclusions," *Earth Planet. Sci. Lett.* **364**, 85–97 (2013).
- T. Irifune and A. E. Ringwood, "Phase transformations in subducted oceanic crust and buoyancy relationships at depths of 600–800 km in the mantle," *Earth Planet. Sci. Lett.* **117**, 101–110 (1993).

- T. Irifune, A. E. Ringwood, and W. O. Hibberson, "Subduction of continental crust and terrigenous and pelagic sediments: an experimental study," *Earth Planet. Sci. Lett.* **126**, 351–368 (1994).
- D. Jacob, "Nature and origin of eclogite xenoliths from kimberlites," *Lithos* **77**, 295–316 (2004).
- F. Kaminsky, "Mineralogy of the lower mantle: a review of 'super-deep' mineral inclusions in diamond," *Earth Sci. Rev.* **110**, 127–147 (2012).
- F. V. Kaminsky, *The Earth's Lower Mantle: Composition and Structure* (Springer Geology, 2017).
- F. V. Kaminsky, O. D. Zakharchenko, R. Davies, W. L. Griffin, G. K. Khachatryan-Blinova, and A. A. Shiryaev, "Super-deep diamonds from the Juina area, Mato Grosso State, Brazil," *Contrib. Mineral. Petrol.* **140**, 734–753 (2001).
- F. Kaminsky, R. Wirth, S. Matsyuk, A. Schreiber, and R. Thomas, "Nyerereite and nahcolite inclusions in diamond: evidence for lower-mantle carbonatitic magmas," *Mineral. Mag.* **73**, 797–816 (2009).
- F. V. Kaminsky, I. D. Ryabchikov, and R. Wirth, "A primary natrocarbonatitic association in the deep," *Earth. Mineral. Petrol.* **110** (2–3), 387–398 (2016).
- M. B. Kirkley, J. J. Gurney, M. L. Otter, S. J. Hill, and L. R. Daniels, "The application of C isotope measurements to the identification of the sources of C in diamonds: a review," *Appl. Geochem.* **6**, 477–494 (1991).
- K. D. Litasov, H. Kagi, A. Shatskiy, E. Ohtani, D. L. Lakshtanov, J. D. Bass, and E. Ito, "High hydrogen solubility in Al-rich stishovite and water transport in the lower mantle," *Earth Planet. Sci. Lett.* **262**, 620–634 (2007).
- Yu. A. Litvin, A. V. Spivak, and A. V. Kuzyura, "Fundamentals of the mantle carbonatite concept of diamond genesis," *Geochem. Int.* **54** (10), 839–857 (2016).
- Yu. A. Litvin, A. V. Spivak, L. S. Dubrovinsky, and D. A. Simonova, "The stishovite paradox in the evolution of lower mantle magmas and diamond-forming melts (experiment at 24 and 26 GPa)," *Dokl. Earth Sci* **473** (2), 444–448 (2017).
- D. Matthey, D. Lowry, and C. Macpherson, "Oxygen isotope composition of mantle peridotite," *Earth Planet. Sci. Lett.* **128**, 231–241 (1994).
- H. O. A. Meyer, "Inclusions in diamond," *Mantle Xenoliths*, Ed. by P. H. Nixon (Wiley, Chichester, 1987), pp. 501–522.
- A. R. Pawley, P. F. Mcmillan, and J. R. Holloway, "Hydrogen in stishovite, with implications for mantle water-content," *Science* **261**, 1024–1026 (1993).
- I. D. Ryabchikov and L. N. Kogarko, "Deep differentiation of alkali ultramafic magmas: formation of carbonatite melts," *Geochem. Int.* **54** (9), 739–747 (2016).
- D. J. Schulze, B. Harte, EIMF staff, F. Z. Page, J. W. Valley, D. M. D. R. Channer, and A. L. Jaques, "Anticorrelation between low $\delta^{13}\text{C}$ of eclogitic diamonds and high $\delta^{18}\text{O}$ of their coesite and garnet inclusions requires a subduction origin," *Geology* **41**, 455–458 (2013).
- V. S. Shatsky, D. A. Zedgenizov, A. L. Ragozin, and V. V. Kalinina, "Diamondiferous subcontinental lithospheric mantle of the northeastern Siberian Craton: Evidence from mineral inclusions in alluvial diamonds," *Gondwana Res.* **28**, 106–120 (2015).
- V. S. Shatsky, D. A. Zedgenizov, and A. L. Ragozin, "Evidence for subduction component in the diamond-bearing mantle of the Siberian craton," *Russ. Geol. Geophys.* **57** (1), 111–126 (2016).
- S. Shilobreeva, I. Martinez, V. Busigny, P. Agrinier, and C. Laverne, "Insights into C and H storage in the altered oceanic crust: results from ODP/IODP Hole 1256D," *Geochim. Cosmochim. Acta* **75**, 2237–2255 (2011).
- N. V. Sobolev, *Deep Seated Inclusions in Kimberlites and Composition of Upper Mantle* (Nauka, Novosibirsk, 1974) [in Russian].
- N. V. Sobolev, "Coesite as indicator of ultrahigh pressures in continental lithosphere," *Russ. Geol. Geophys.* **47** (1), 94–104 (2006).
- T. Stachel, J. W. Harris, G. P. Brey, and W. Joswig, "Kankan diamonds (Guinea) II: lower mantle inclusion parageneses," *Contrib. Mineral. Petrol.* **140**, 16–27 (2000).
- T. Stachel, G. P. Brey, and J. W. Harris, "Inclusions in sublithospheric diamonds: glimpses of deep Earth," *Elements* **1** (2), 73–78 (2005).
- L. A. Taylor, Z. V. Spetsius, R. Wiesli, M. Spicuzza, and J. W. Valley, "Diamondiferous peridotites from oceanic protoliths: crustal signatures from Yakutian kimberlites," *Russ. Geol. Geophys.* **46** (12), 1176–1184 (2005).
- A. Thomson, S. Kohn, G. Bulanova, C. Smith, D. Araujo, and M. Walter, "Origin of sub-lithospheric diamonds from the Juina-5 kimberlite (Brazil): constraints from carbon isotopes and inclusion compositions," *Contrib. Mineral. Petrol.* **168**, 1081 (2014).
- A. R. Thomson, M. J. Walter, S. C. Kohn, and R. A. Brooker, "Slab melting as a barrier to deep carbon subduction," *Nature* **529**, 76–79 (2016).
- M. J. Walter, G. P. Bulanova, L. S. Armstrong, S. Keshav, J. D. Blundy, G. Gudfinnsson, O. T. Lord, A. R. Lennie, S. M. Clark, C. B. Smith, and L. Gobbo, "Primary carbonatite melt from deeply subducted oceanic crust," *Nature* **454**, 622–630 (2008).
- M. Walter, S. Kohn, D. Araujo, G. Bulanova, C. Smith, E. Gaillou, J. Wang, A. Steele, and S. Shirey, "Deep mantle cycling of oceanic crust: evidence from diamonds and their mineral inclusions," *Science* **334**, 54–57 (2011).
- A. M. Zaitsev, *Optical Properties of Diamond: a Data Handbook* (Springer Verlag, Berlin, 2001).
- D. A. Zedgenizov, H. Kagi, V. S. Shatsky, and A. L. Ragozin, "Local variations of carbon isotope composition in diamonds from São Luiz (Brazil): evidence for heterogeneous carbon reservoir in sublithospheric mantle," *Chem. Geol.* **363**, 114–124 (2014).
- D. V. Zedgenizov, S. Shatsky, A. V. Panin, O. V. Evtushenko, A. L. Ragozin, and H. Kagi, "Evidence for phase transitions in mineral inclusions in superdeep diamonds of the Sao Luiz deposit, Brazil," *Russ. Geol. Geophys.* **56** (1–2), 295–305 (2015).
- D. A. Zedgenizov, A. L. Ragozin, V. V. Kalinina and H. Kagi, "The mineralogy of Ca-rich inclusions in sublithospheric diamonds," *Geochem. Int.* **54** (10), 890–900 (2016).
- D. Zedgenizov, D. Rubatto, V. Shatsky, A. Ragozin, and V. Kalinina, "Eclogitic diamonds from variable crustal protoliths in the northeastern Siberian craton: trace elements and coupled $\delta^{13}\text{C}$ – $\delta^{18}\text{O}$ signatures in diamonds and garnet inclusions," *Chem. Geol.* **422**, 46–59 (2016).
- J. Zhang, R. C. Liebermann, T. Gasparik, and C. T. Herzberg, "Melting and subsolidus relations of SiO_2 at 9–14 GPa," *J. Geophys. Res.* **98**, 19785–19793 (1993).

Translated by E. Kurdyukov