



Research Article

Retrograde phases of former bridgmanite inclusions in superdeep diamonds

Dmitry Zedgenizov^{a,b,*}, Hirioyuki Kagi^c, Eiji Ohtani^d, Tatsuki Tsujimori^{e,d}, Kazuki Komatsu^c

^a V.S.Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia

^b Novosibirsk State University, Novosibirsk, Russia

^c Geochemical Research Center, Graduate School of Science, University of Tokyo, Japan

^d Department of Earth Science, Graduate School of Science, Tohoku University, Aoba, Sendai 980-8578, Japan

^e Center for Northeast Asian Studies, Tohoku University, Aoba, Sendai 980-8576, Japan

ARTICLE INFO

Article history:

Received 20 March 2020

Received in revised form 21 June 2020

Available online 27 June 2020

Keywords:

Bridgmanite

Superdeep diamonds

Lower mantle

Jeffbenite

ABSTRACT

(Mg,Fe)SiO₃ bridgmanite is the dominant phase in the lower mantle; however no naturally occurring samples had ever been found in terrestrial samples as it undergoes retrograde transformation to a pyroxene-type structure. To identify retrograde phases of former bridgmanite single-phase and composite inclusions of (Mg,Fe)SiO₃ in a series of superdeep diamonds have been examined with electron microscopy, electron microprobe, Raman spectroscopy and X-ray diffraction techniques. Our study revealed that (Mg,Fe)SiO₃ inclusions are represented by orthopyroxene. Orthopyroxenes in single-phase and composite inclusions inherit initial chemical composition of bridgmanites, including a high Al and low Ni contents. In composite inclusions they coexist with jeffbenite (ex-TAPP) and olivine. The bulk compositions of these composite inclusions are rich in Al, Ti, and Fe, which are similar but not fully resembling Al-rich bridgmanite produced in experiments on the MORB composition. The retrograde origin of composite inclusions due to decomposition of Al-rich bridgmanite may be doubtful because each of observed minerals may represent coexisting HP phases, i.e. bridgmanite or ringwoodite.

© 2020 Elsevier B.V. All rights reserved.

1. Introduction

Bridgmanite (Mg,Fe)SiO₃, a high pressure mineral with a perovskite structure (MgSi-perovskite), is a dominant material in the lower mantle at the depths from 660 to 2700 km and therefore is probably the most abundant mineral in the Earth (Irfune, 1994; Ringwood, 1962; Stixrude and Lithgow-Bertelloni, 2007). The minimum pressure of stability of bridgmanite is ~20 GPa (Hirose et al., 2001) and it increases to 25 GPa with the incorporation of alumina (Kubo and Akaogi, 2000). Although synthetic analogues of this mineral have been well studied (e.g. O'Neill and Jeanloz, 1990; Kesson et al., 1994; Hirose et al., 1999; Ono et al., 2001; Hirose and Fei, 2002; Litasov and Ohtani, 2004; Litasov and Ohtani, 2005; Kojitani et al., 2007; Shatskiy et al., 2007; Ricolleau et al., 2010; Inoue et al., 2010), no naturally occurring samples have ever been found in a rock on the planet's surface except from some shocked meteorites (Tomioka and Fujino, 1997; Tschauner et al., 2014). In other available natural environments bridgmanite undergoes retrograde transformation to a pyroxene-type structure. So-called superdeep diamonds carry mineral inclusions which belong to

associations formed at the depth of sublithospheric upper mantle and lower mantle (Harte and Hudson, 2013; Kaminsky, 2017). The identification of the retrograde phase as bridgmanite in superdeep diamonds is based on the association with ferropericlase (Mg,Fe)O and other lower-mantle minerals predicted from theoretical models and HP-HT experiments.

The inclusions of (Mg,Fe)SiO₃ associated with ferropericlase have first been found in diamonds from the Kofffontein kimberlite pipe (South Africa) and Orroroo dyke (South Australia) (Moore et al., 1986; Scott Smith et al., 1984). At present (Mg,Fe)SiO₃ inclusions suggested as bridgmanite (MgSi-perovskite) are described in super-deep diamonds from several worldwide localities: placer deposits and kimberlite pipes in the Juina and Machado areas in Brazil (Wilding et al., 1991; Harte et al., 1999; Kaminsky et al., 2001, 2009; Hayman et al., 2005; Bulanova et al., 2010; Thomson et al., 2014; Zedgenizov et al., 2014, 2015), Kankan placer deposit in Guinea (Stachel et al., 2000), kimberlitic pipes in the Northwest Territories of Canada (Davies et al., 2004; Tappert et al., 2005), kimberlites and ancient placer deposits from the Orroroo area in South Australia (Tappert et al., 2009). In this study, single-phase and composite inclusions of (Mg,Fe)SiO₃ have been analyzed in a series of superdeep diamonds from São-Luis river deposits (Juina, Brazil) to identify retrograde phase of former bridgmanite. The definition of nature of single-phase and composite inclusions is

* Corresponding author at: V.S.Sobolev Institute of Geology and Mineralogy, Novosibirsk, Russia.

E-mail address: zed@igm.nsc.ru (D. Zedgenizov).

becoming more apparent from analysis of data from electron microscopy, electron microprobe, Raman spectroscopy and X-ray diffraction techniques. These data are used to specify chemical and structural features of retrograde phase of bridgmanite and associated minerals.

2. Samples and methods

The majority of diamonds from São-Luis collection are shown to contain inclusions which belong to minerals formed at the depth of transition zone and lower mantle (Zedgenizov et al., 2014). The presence of inclusions of $(\text{Mg,Fe})\text{SiO}_3$ have been detected in samples SL-13, SL-14 and SL-80 (Fig. 1). These inclusions are associated with individual inclusions of breyite (walstromite-structured CaSiO_3 ; Brenker et al., 2018) in diamond SL-13, ferropericlasite in diamond SL-14, majoritic garnet and breyite in diamond SL-80. The morphology of these diamonds was twinned octahedral crystals (SL-13 – Fig. 1a), rounded crystal of irregular shape (SL-14 – Fig. 1d), and rounded crystal of octahedral-to-dodecahedral transition form (SL-80 – Fig. 1g). Each diamond was polished to expose inclusions on the same plane.

Raman spectra of mineral inclusions were collected using a Horiba Jobin Yvon LabRAM HR800 Raman micro-spectrometer equipped with a 532 nm Nd:YAG laser and an Olympus BX41 microscope with 50 $\times$ magnification at V.S. Sobolev Institute of Geology and Mineralogy (Novosibirsk, Russia). Crystallographic identification of phases was performed with Oxford Aztec EBSD on a JEOL JSM-7001F FE-SEM at Tohoku

University (Sendai, Japan). Electron back-scattered diffraction (EBSD) maps were obtained out on samples tilted to 70° with accelerating voltages of 15 kV, work distances of 25 mm and step sizes of 0.3 μm . The obtained crystallographic data were processed with Channel 5 analysis software from HKL technology. Noise reduction included the removal of wild spikes, extrapolation of zero solutions by iteration to 6 neighbours and application of Kuwahara filter with the grid size of 3×3 , smoothing angle of 2° and artefact angle of 1°.

The X-ray diffraction (XRD) patterns of inclusions were obtained using a microfocused X-ray generator (MicroMax-007; Rigaku, Japan) with a Mo rotating target ($\lambda = 0.7107 \text{ \AA}$, 50 kV, 24 mA) and confocal mirror optics (Varimax-Mo; Rigaku). The incident X-ray was collimated by a single pinhole collimator with a hole diameter of $\phi 0.05 \text{ mm}$. The sample for X-ray diffraction was mounted on a glass fiber with glue, and the position of the sample was aligned using a goniometer under a microscope to the rotation center of the goniometer and the X-ray beam was pre-aligned to the rotation center. Diffraction images of the samples with totally 180 images with 1 deg. oscillation per image were collected. The obtained images were analyzed by a software CrystalClear (Rigaku) to identify respective diffraction spots, and converted them to reciprocal lattices.

Major element compositions of minerals were analyzed by a FE-SEM, JEOL JSM-7001F, equipped with an EDS, Oxford INCA X-act energy dispersive X-ray spectrometer at Tohoku University (Sendai, Japan). The quantitative analyses were conducted using a 15 kV acceleration

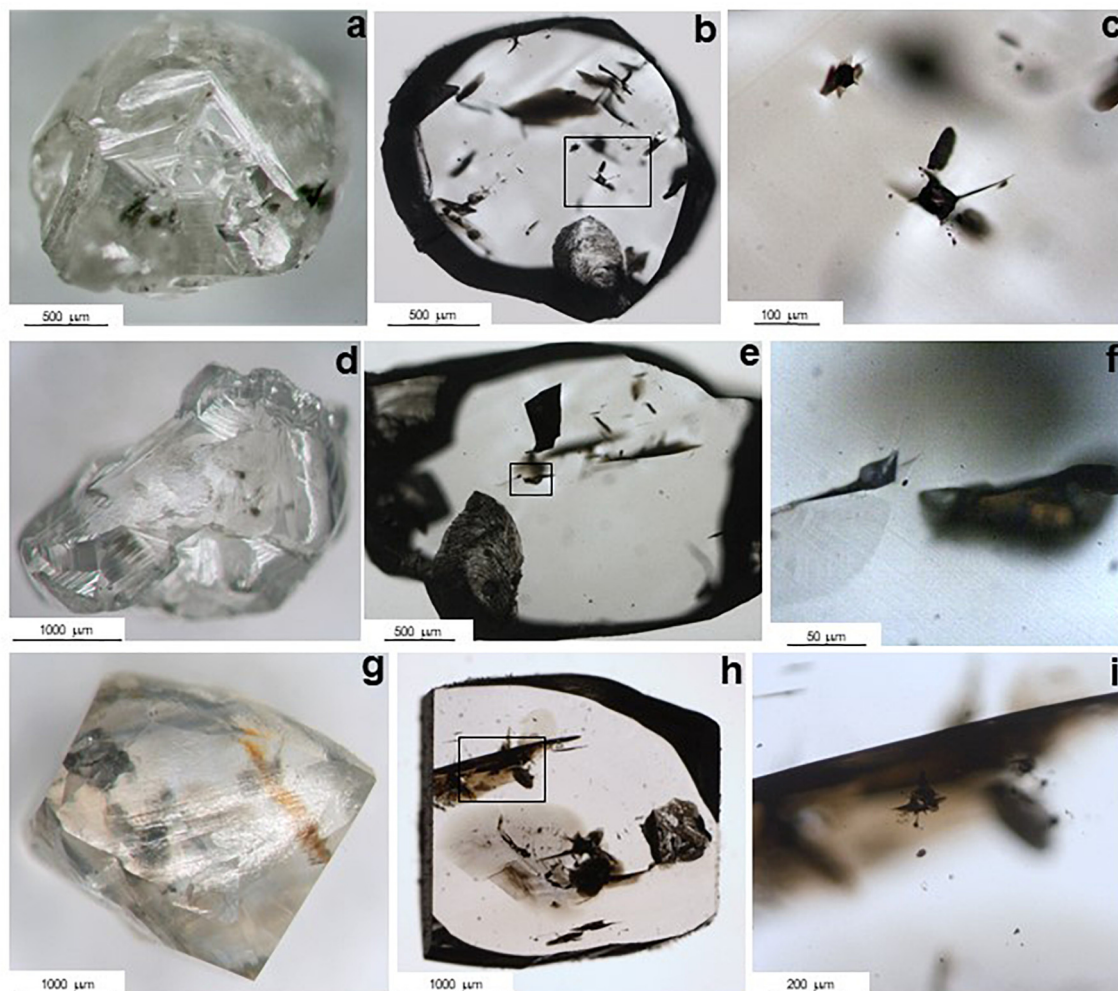


Fig. 1. Diamonds with inclusions of MgSiO_3 (a – SL-13; d – SL-14; g – SL-80; reflected light) and their polished plates (b – SL-13; e – SL-14; h – SL-80; transmitted light). c, f and i are details displaying the MgSiO_3 inclusions.

voltage, a 1.4 nA beam current, and a 75 s integration time. We have also estimated the bulk composition of combined (composite) inclusions by averaging relatively large areal quantitative analyses.

3. Results

The inclusions of (Mg,Fe)SiO₃ in studied diamonds are 20 to 50 μm in size. They show the textures from flat-faced, sharp octahedral to more ragged-looking irregular shapes. All inclusions have large decompression cracks around them and possess small droplet-like satellite inclusions localized along these cracks (Fig. 2 a, c, e). Raman observation has revealed that inclusions of (Mg,Fe)

SiO₃ in all studied samples is represented by rhombic pyroxene (orthopyroxene - Opx). The most prominent vibrational modes in each Raman spectrum are marked of Fig. 2 b, d, f. The two main modes at 236–237 cm^{-1} and at 340–344 cm^{-1} are characterized by metal-oxygen stretching vibrations. The modes at 661–663 cm^{-1} and at 683–684 cm^{-1} are related to Si-O-Si bending, and the ones at 1008–1011 cm^{-1} are generally assigned to Si—O stretching vibrations. These peaks are consistent with the orthopyroxene end-member enstatite with a minor amount of ferrosilite (Huang et al., 2000). No shift of peak at 236–237 cm^{-1} and the appearance of lines at 369 and 431 cm^{-1} indicating clinoenstatite (Ulmer and Stalder, 2001) were observed in each spectrum.

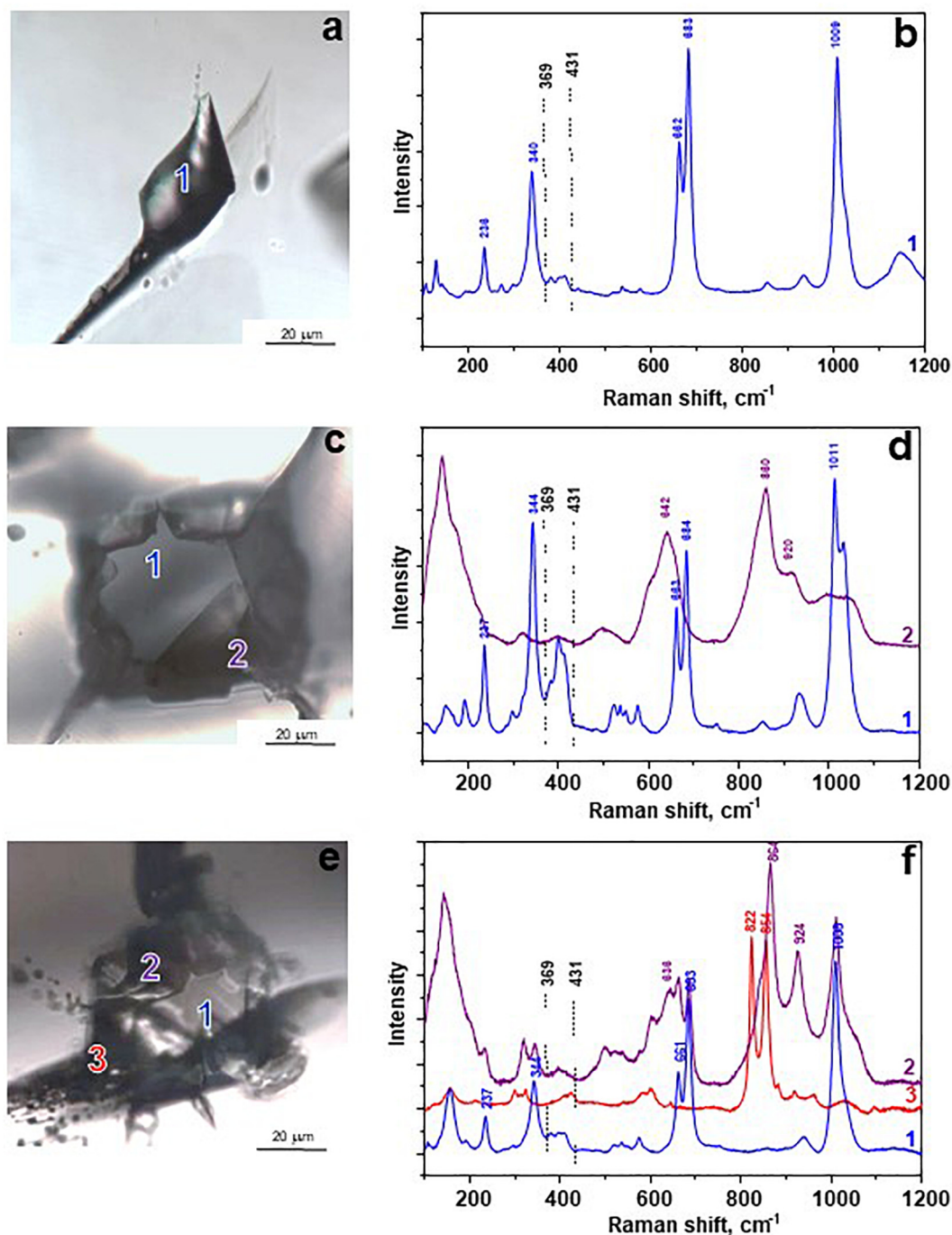


Fig. 2. Single-phase and composite inclusions of MgSiO₃ and Raman spectra of each detected phase (a, b - SL-14; c, d - SL-13; e, f - SL-80). 1 - orthopyroxene; 2 - jeffbenite; 3 - olivine.

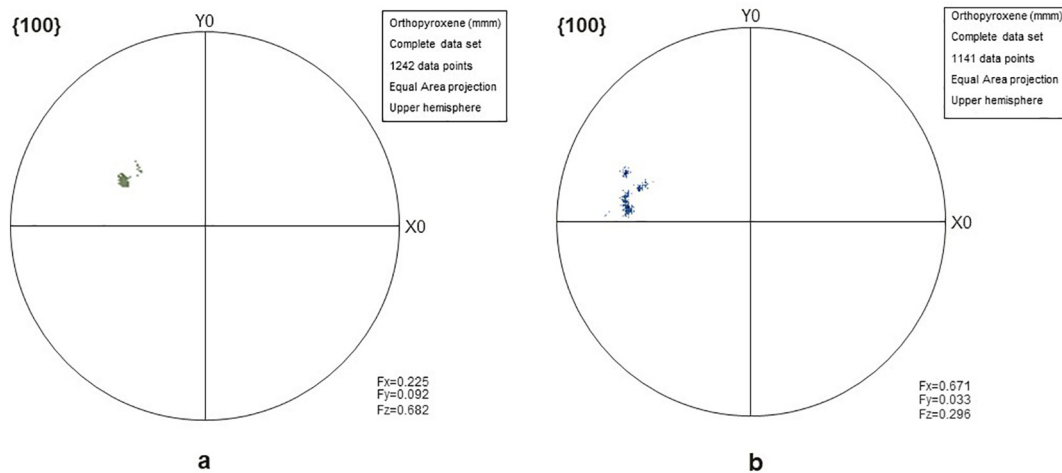


Fig. 3. {100} pole figures of the EBSD orientations of MgSiO₃ inclusions in diamonds SL-13 (a) and SL-80 (b).

Although the inclusion of (Mg,Fe)SiO₃ in diamond SL-14 is single phase, the inclusions of (Mg,Fe)SiO₃ are combined with jeffbenite in diamond SL-13 and with jeffbenite and olivine in diamond SL-80. Jeffbenite in diamond SL-13 have main Raman peaks centered at 860, 920 and 642 cm⁻¹ (Fig. 2 d). Raman spectrum of jeffbenite in diamond SL-80 show main peaks at 864, 924 and 636 cm⁻¹ and lower intensity peaks at 320 and 498 cm⁻¹ (Fig. 2 f). The configuration of these spectra and positions of main peaks are similar to that described previously in a jeffbenite inclusion extracted from a super-deep diamond (Nestola et al., 2016). The spectra of jeffbenite do not show the intense peaks at 360–365 and 550–560 cm⁻¹ caused by rotational vibrations of SiO₄ tetrahedron (R[SiO₄]) and internal Si—O bending vibrations (ν_2) observed in all pyrope garnet inclusions in diamonds (Kalugina and Zedgenizov, 2019).

Olivine in combined inclusion in diamond SL-80 show coupled strong peaks at 822 and 853 cm⁻¹ which can be attributed to internal stretching vibrational modes ν_1 and ν_3 of the SiO₄ tetrahedron (Kuebler et al., 2006). The positions of these peaks correspond to olivine with 85–90% of forsterite component (Fo) assuming released pressure effect. This estimate however may be even lower as each peak position may be upshifted by residual internal pressure of olivines in diamond inclusions (Izraeli et al., 1999; Yasuzuka et al., 2009).

XRD patterns of inclusions with (Mg,Fe)SiO₃ have been analyzed in all three samples. The diffraction spots obtained from the inclusions were indexed to single phase orthopyroxene in diamond SL-14, two phases, orthopyroxene and jeffbenite, in diamond SL-13 and three phases, orthopyroxene, jeffbenite and olivine, in diamond SL-80. It is

noted that orthopyroxene show several orientations suggesting that it consists of subgrains.

Similarly, EBSD mapping of studied exposed inclusion has revealed the presence of orthopyroxene in diamond SL-14, orthopyroxene and jeffbenite in diamond SL-13 and orthopyroxene, jeffbenite and olivine in diamond SL-80. No one of detected phase have orientational correlation with the host diamond implying that there is no epitaxial growth (Nestola et al., 2017). Crystallographic orientations of orthopyroxene inclusions, determined using EBSD, revealed that they have not a homogeneous orientation and record small angular deviations (Fig. 3). At least three slightly misorientated orthopyroxene grains are detected in diamond SL-80 and two orthopyroxene grains in diamonds SL-13. At that, BSE images of composite inclusions show linear crystallographic boundaries between different mineral phases (Fig. 4).

The compositions of mineral inclusions in studied diamonds are presented in Table 1. All found orthopyroxenes have a variable content of FeO from 5.02 to 10.5 wt% and high concentration of Al₂O₃ from 1.34 to 3.22 wt%. The lowest amount of these components is detected in the single-phase orthopyroxene inclusion in diamond SL-14. This diamond also contain inclusion of ferropericlase with Mg# 67.4 and high content of NiO (1.15 wt%) and Cr₂O₃ (0.28 wt%). The higher amount of Al₂O₃ in orthopyroxenes is detected in diamond SL-80: 3.22 wt% in single-phase orthopyroxene and 2.98 wt% in orthopyroxene in composite inclusion with jeffbenite and olivine (Fig. 4 a). Jeffbenite is significantly enriched with Al₂O₃ (21.8 wt%) and TiO₂ (1.41 wt%). Olivine in composite inclusion has high FeO (17.9 wt%) and a low NiO content (0.16 wt%). Two other exposed inclusions in this diamond are

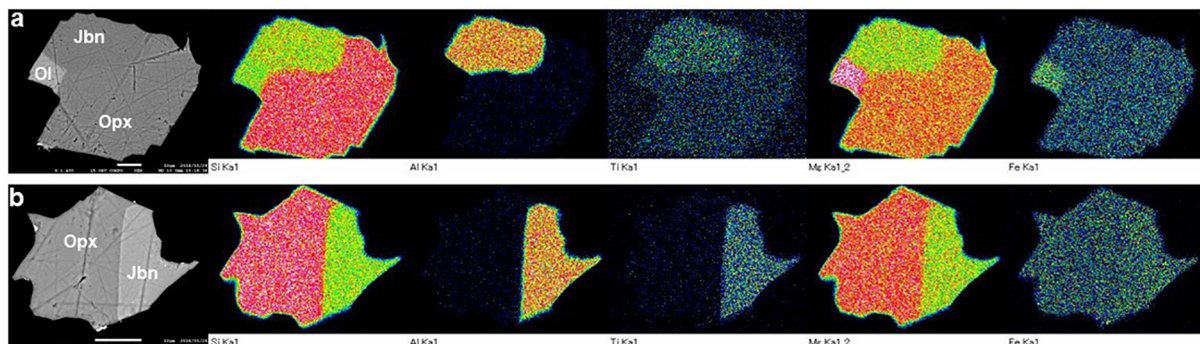


Fig. 4. A back-scattered electron image and elemental distribution maps of polished composite inclusions in diamonds SL-13 (a) and SL-80 (b).

Table 1The composition of MgSiO₃ and associated inclusions in studied diamonds (in wt%).

	SL-14		SL-13				SL-80						
	1	2	1		2		1				2	3	4
	Opx	fPer	Opx	Jbn	Bulk	CaSiO ₃	Opx	Jbn	Ol	Bulk	MgSiO ₃	CaSiO ₃	Maj
SiO ₂	57.7	0.06	56.5	39.9	51.4	47.3	55.1	41.9	39.4	50.9	54.9	50.4	42.1
TiO ₂	0.09	0.03	0.19	5.37	1.82	6.54	0.09	1.41	0.02	0.39	0.18	3.56	0.77
Al ₂ O ₃	1.34	0.08	2.03	18.8	7.10	0.32	2.93	21.8	0.14	7.79	3.22	0.50	20.4
Cr ₂ O ₃	0.46	0.28	0.08	1.31	0.53	0.03	0.04	0.25	0.02	0.09	0.05	0.00	0.12
FeO	5.02	27.5	8.10	9.00	8.34	0.09	10.5	10.1	17.9	10.8	10.4	0.16	9.56
MnO	0.18	0.19	0.17	0.16	0.26	bdl	0.17	0.12	0.08	0.14	0.17	0.01	0.18
MgO	33.9	69.8	32.8	25.4	30.3	bdl	30.8	24.4	42.4	29.6	30.6	0.0	12.5
CaO	1.23	bdl	0.09	0.07	0.03	45.1	0.09	0.05	bdl	0.12	0.06	44.5	14.0
Na ₂ O	0.08	0.05	0.09	0.05	0.10	0.02	0.06	0.02	0.05	0.05	0.04	0.10	0.39
K ₂ O	0.03	bdl	0.04	0.01	0.01	0.01	0.01	0.03	0.01	bdl	0.07	0.02	bdl
NiO	0.10	1.15	0.02	0.03	0.06	bdl	0.16	0.07	0.16	0.13	bdl	bdl	bdl
Total	100.02	99.17	100.05	100.06	100.01	99.42	99.93	100.09	100.16	100.00	99.61	99.24	100.02
bdl - > detection limit													

represented by breyite and majoritic garnet. The specific feature of breyite is elevated concentration of TiO₂ (3.56 wt%). Majoritic garnet have the excess of Si 3.08 pfu and by high CaO (14 wt%) and low Cr₂O₃ (0.12 wt%) content may be attributed to eclogitic paragenesis (Grutter et al., 2004; Sobolev, 1977). Orthopyroxene from composite inclusion with jeffbenite in diamond SL-13 (Fig. 4 b) has Al₂O₃ (2.03 wt%) and FeO (8.10 wt%). Jeffbenite in this inclusion is enriched with Al₂O₃ (18.8 wt%), TiO₂ (5.37 wt%) and has elevated chromium content (1.31 wt% of Cr₂O₃). The inclusion of breyite found in the same diamond also show high concentration of TiO₂ (6.54 wt%).

4. Discussion

Bridgmanite (MgSiO₃) represents the most abundant lower-mantle mineral, but the least common of these minerals included in superdeep diamonds from Lower Mantle (Harte, 2010; Kaminsky, 2012). In this study, (Mg,Fe)SiO₃ phases in one single-phase and two composite inclusions in diamonds from Juina (Brazil), have been analyzed to identify retrograde phases of former bridgmanite. XRD and Raman spectra have revealed that they are represented by orthopyroxene (Opx). XRD patterns and EBSD mapping of orthopyroxenes in these inclusions indicate that they are not single crystals. These polycrystalline textures together with high lattice strain of host diamond around these inclusions may be an evidence for the retrograde phase transition of former bridgmanite (Zedgenizov et al., 2015). Significant volume expansion expected at this phase transition on ascent from lower mantle depths had been retained due to internal fracturing and plastic deformation of the diamond (Anzolini et al., 2016; Hutchison et al., 2001).

The specific feature of studied orthopyroxenes is an elevated Al₂O₃ content (1.34–3.22 wt%). Kaminsky (2012) have suggested that

retrograde phase fully inherits its initial bridgmanite chemical composition, including a high Al content, which is not characteristic for orthopyroxenes occurring as inclusions in diamonds from lithospheric mantle (e.g. Stachel and Harris, 2008). In comparison with lithospheric orthopyroxenes, bridgmanite show very low Ni contents because of preferential partitioning of Ni into associated ferropericlase (Harte et al., 1999; Stachel et al., 2000). The partitioning of Fe and Ni between associated inclusions of orthopyroxene and ferropericlase in diamond SL-14 (Fe-Mg Kd ~0.38; D_{Ni} ~ 0.09) correspond well to experimentally determined values between bridgmanite and ferropericlase at the lower mantle conditions (Auzende et al., 2008; Kesson and FitzGerald, 1991; Muir and Brodholt, 2016; Prescher et al., 2014).

Most previously reported bridgmanites from diamond inclusions have an Al₂O₃ content ranging from 0.55 to 3.37 wt%, but rare bridgmanites show much higher contents (Harte and Hudson, 2013). In several cases, bridgmanite is recorded in composite inclusions with jeffbenite, olivine and spinel (Hayman et al., 2005; Thomson et al., 2014; Walter et al., 2011; Zedgenizov et al., 2015). Walter et al. (2011) and Thomson et al. (2014) have interpreted these composite inclusions as a product of retrograde decomposition of original aluminous bridgmanite. The bulk compositions of these inclusions are very similar to bridgmanites produced in experiments on basaltic compositions at lower-mantle P-T parameters (Ono et al., 2001; Ricolleau et al., 2010; Hirose et al., 2001; Litasov and Ohtani, 2005). They are much richer in Al, Ti, and Fe than are bridgmanites that form in experiments on mantle peridotite. Two composite inclusions in studied diamonds are represented by associations of orthopyroxene with jeffbenite (SL-13) and with jeffbenite and olivine (SL-80). These constituents may represent an original equilibrium mineral assemblage or may be the multi-phase decompression product of an original single-phase inclusion. The bulk compositions of these composite inclusions are also significantly enriched in Al, Ti, and Fe, but not fully resemble the composition of Al-rich bridgmanites produced in HP-HT experiments on basaltic compositions (Fig. 5). The orthopyroxenes in studied single-phase and composite inclusions by composition correspond to bridgmanites produced in experiments modelling mantle peridotites whereas associated jeffbenite are similar to Al-rich bridgmanites formed in eclogitic systems.

The jeffbenite was considered to originate in upper/lower mantle boundary and lower mantle assemblages because it was found in association with ferropericlase and bridgmanite inclusions in the same diamond, and sometimes appeared to occur as a single-phase inclusion (Armstrong and Walter, 2012; Bulanov et al., 2010; Harris et al., 1997; Kaminsky, 2012; Zedgenizov et al., 2014). Although jeffbenite has been found in inclusions in many superdeep diamonds, it had never been produced in HP-HT experiments resembling lower mantle

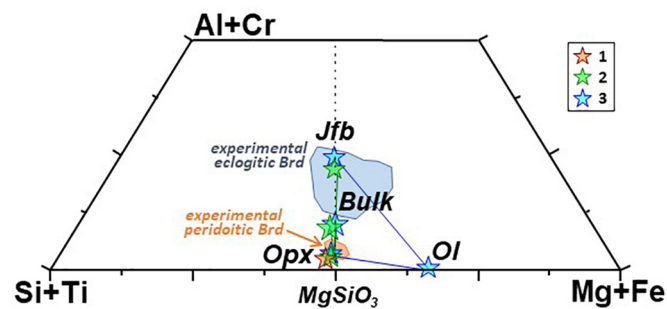


Fig. 5. Portion of ternary plot illustrating the compositions of single phase (SL-14-1) and composite inclusions (SL-13-2; SL-80-3) with MgSiO₃.

conditions. Armstrong and Walter (2012) have suggested that jeffbenite must be a retrograde product, forming mainly from Al-bridgmanite, but possibly also from garnet, because it is stable only at relatively low pressures (up to 13 GPa at 1973 °C). This observation makes enigmatic the association of jeffbenite with ferropericlasite and bridgmanite in some superdeep diamond. However, the stability field of jeffbenite has been extended to ~23 GPa (~660 km), demonstrating that this mineral may represent one of the most reliable markers for diamonds super-deep origin (Anzolini, 2018).

Bridgmanite becomes stable after breakdown of garnet or olivine polymorphs at the depth of upper/lower mantle boundary around 660 km. Experiments have demonstrated very narrow and flat loop with coexisting Mg-perovskite, ferropericlasite and ringwoodite (spinel-structured olivine polymorph) near that boundary (Ishii et al., 2019). It was earlier suggested that ringwoodite with Mg# 80 would coexist with ferropericlasite with Mg# 71 and perovskite with Mg# 85 (Brey et al., 2004). Olivine and orthopyroxene in composite inclusion in diamond SL-80 have Mg# 81 and 84, which is very similar to the predicted values. Their protoliths must be rich in Fe and could be a hybrid rocks of peridotite plus subducted eclogite or sediments at the depth of upper/lower mantle boundary (Brey et al., 2004). High-Ca and low-Cr majoritic garnet in the same diamond, however, corresponds to the depth of upper mantle (Stachel, 2001). Thus the presence of this garnet suggests that this diamond undergoes polybaric growth in the mantle.

5. Conclusions

In this study, one single-phase (sample SL-14) and two composite inclusions of (Mg,Fe)SiO₃ coexisting with (Mg,Fe)₃Al₂Si₃O₁₂ jeffbenite (sample SL-13), and with (Mg,Fe)₃Al₂Si₃O₁₂ jeffbenite and (Mg,Fe)₂SiO₄ olivine (sample SL-80) have been analyzed to identify retrograde phases of former bridgmanite in superdeep diamonds from Juina (Brazil). Raman spectra, XRD and EBSD have revealed that (Mg,Fe)SiO₃ are represented by orthopyroxene. (Mg,Fe)₃Al₂Si₃O₁₂ and (Mg,Fe)₂SiO₄ in composite inclusions are identified as jeffbenite (TAPP) and olivine. These inclusions are associated with inclusions of ferropericlasite (SL-14), breyite (SL-13), single-phase (Mg,Fe)SiO₃ (Opx), breyite and majoritic garnet (SL-80). XRD patterns of (Mg,Fe)SiO₃ inclusions indicate that they are not single crystals. These data, together with high lattice strain of host diamond around these inclusions observed from EBSD (Zedgenizov et al., 2015) it may be an evidence for the retrograde phase transition of former bridgmanite.

Single-phase inclusions of (Mg,Fe)SiO₃ in superdeep diamonds are suggested to represent a retrograde phase of bridgmanite and fully inherit its initial chemical composition, including a high Al and low Ni contents (Harte and Hudson, 2013; Kaminsky, 2017). The composite inclusions of (Mg,Fe)SiO₃ with jeffbenite and other silicate and oxide phases may be interpreted as exsolution products from originally homogeneous bridgmanite (Walter et al., 2011). The bulk compositions of composite inclusions in studied diamonds are rich in Al, Ti, and Fe, which are similar but not fully resembling Al-rich bridgmanite produced in experiments on the MORB composition. However, the retrograde origin of these composite inclusions due to decomposition of Al-rich bridgmanite may be doubtful because each of observed phases may represent single-phase inclusions, i.e. bridgmanite (SL-14), with similar compositional features.

Acknowledgements

This work was supported by Russian Science Foundation (grant no. 16-17-10067 of DZ). EDS and EBSD study of inclusions was provided by CNEAS of Tohoku University. We extend our appreciation to Jun Muto and Naoko Takahashi for their assistance on the EBSD analyses. EO and TT appreciate their support from JSPS (Kakenhi Grant JP15H05748 and JP18H01299, respectively).

References

- Anzolini, C., 2018. Depth of formation of super-deep diamonds. *Plinius* 44. <https://doi.org/10.19276/plinius.2018.01001>.
- Anzolini, C., Angel, R.J., Merlini, M., Derzsi, M., Tokár, K., Milani, S., Krebs, M.Y., Brenker, F.E., Nestola, F., Harris, J.W., 2016. Depth of formation of CaSiO₃-walsstromite included in super-deep diamonds. *Lithos* 265, 138–147.
- Armstrong, L.S., Walter, M.J., 2012. Tetragonal almandine pyrope phase (TAPP): retrograde Mg-perovskite from subducted oceanic crust? *Eur. J. Mineral.* 24, 587–597.
- Auzende, A.-L., Badro, J., Ryerson, F.J., Weber, P.K., Fallon, S.J., Addad, A., Siebert, J., Fiquet, G., 2008. Element partitioning between magnesium silicate perovskite and ferropericlasite: new insights into bulk lower-mantle geochemistry. *Earth Planet. Sci. Lett.* 269 (1–2), 164–174.
- Brenker, F., Nestola, F., Brenker, L., Peruzzo, L., Secco, L., Harris, J.W., 2018. Breyite, IMA 2018–062, CNMNC Newsletter No. 45, October 2018. *Mineral. Mag.* 82, 1225–1232.
- Brey, G.P., Bulatov, V., Girs, A., Harris, J.W., Stachel, T., 2004. Ferropericlasite - a lower mantle phase in the upper mantle. *Lithos* 77, 655–663.
- Bulanova, G.P., Walter, M.J., Smith, C.B., Kohn, S.C., Armstrong, L.S., Blundy, J., Gobbo, L., 2010. 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.
- Davies, R.A., Griffin, W.L., O'Reilly, S.Y., McCandless, T.E., 2004. Inclusions in diamonds from the K14 and K10 kimberlites, Buffalo Hills, Alberta, Canada: diamond growth in a plume? *Lithos* 77 (1–4), 99–111.
- Grueter, H.S., Gurney, J.J., Menzies, A.H., Winter, F., 2004. An updated classification scheme for mantle-derived garnet, for use by diamond explorers. *Lithos* 77, 841–857.
- Harris, J.W., Hutchison, M.T., Hursthouse, M., Light, M., Harte, B., 1997. A new tetragonal silicate mineral occurring as inclusions in lower mantle diamonds. *Nature* 387, 486–488.
- Harte, B., 2010. Diamond formation in the deep mantle: the record of mineral inclusions and their distribution in relation to mantle dehydration zones. *Mineral. Mag.* 74 (2), 189–215.
- Harte, B., Hudson, N.F.C., 2013. Mineral associations in diamonds from the lowermost upper mantle and uppermost lower mantle. In: Pearson, D.G., et al. (Eds.), *Proceedings of 10th International Kimberlite Conference*. vol. 1, pp. 235–253 Special Issue of the *Journal of the Geological Society of India*.
- Harte, B., Harris, J.W., Hutchison, M.T., Watt, G.R., Wilding, M.C., 1999. Lower mantle mineral associations in diamonds from Sao Luiz, Brazil. 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 Publication No. 6, pp. 125–153.
- Hayman, P.C., Kopylova, M.G., Kaminsky, F.V., 2005. Lower mantle diamonds from Rio Soriso (Juina, Brazil). *Contrib. Mineral. Petrol.* 149 (4), 430–445.
- Hirose, K., Fei, Y., 2002. Subsolidus and melting phase relations of basaltic composition in the uppermost lower mantle. *Geochim. Cosmochim. Acta* 66 (12), 2099–2108.
- Hirose, K., Fei, Y., Ma, Y., Mao, H.-K., 1999. The fate of subducted basaltic crust in the Earth's lower mantle. *Nature* 397, 53–56.
- Hirose, K., Komabayashi, T., Murakami, M., Funakoshi, K., 2001. In situ measurements of the majorite-akimotoite-perovskite phase transition boundaries in MgSiO₃. *Geophys. Res. Lett.* 28, 4351–4354.
- Huang, E., Chen, C.H., Huang, T., Lin, E.H., Xu, J., 2000. Raman spectroscopic characteristics of Mg-Fe-Ca pyroxenes. *Am. Mineral.* 85, 473–479.
- Hutchison, M.T., Hursthouse, M.B., Light, M.E., 2001. Mineral inclusions in diamonds: associations and chemical distinctions around the 670-km discontinuity. *Contrib. Mineral. Petrol.* 142 (2), 119–126.
- Inoue, T., Wada, T., Sasaki, R., Yurimoto, H., 2010. Water partitioning in the Earth's mantle. *Phys. Earth Planet. Inter.* 183, 245–251.
- Irifune, T., 1994. Absence of an aluminous phase in the upper part of the Earth's lower mantle. *Nature* 370, 131–133.
- Ishii, T., Huang, R., Myhill, R., Fei, H., Koemets, I., Liu, Z., Maeda, F., Yuan, L., Wang, L., Druzhbin, D., Yamamoto, T., Bhat, S., Farla, R., Kawazoe, T., Tsujino, N., Kulik, E., Higo, Y., Tange, Y., Katsura, T., 2019. Sharp 660-km discontinuity controlled by extremely narrow binary post-spinel transition. *Nat. Geosci.* 12, 869–872.
- Izraeli, E.S., Harris, J.W., Navon, O., 1999. Raman barometry of diamond formation. *Earth Planet. Sci. Lett.* 173, 351–360.
- Kalugina, A.D., Zedgenizov, D.A., 2019. Raman discrimination of garnet inclusions in Siberian diamonds. *J. Raman Spectrosc.* 1–7.
- Kaminsky, F.V., 2012. Mineralogy of the lower mantle: a review of 'super-deep' mineral inclusions in diamond. *Earth Sci. Rev.* 110 (1), 127–147.
- Kaminsky, F.V., 2017. *The Earth's Lower Mantle*. Springer International Publishing AG (331 p).
- Kaminsky, F.V., Zakharchenko, O.D., Davies, R., Griffin, W.L., Khachatryan-Blinova, G.K., Shiryayev, A.A., 2001. Superdeep diamonds from the Juina area, Mato Grosso State, Brazil. *Contrib. Mineral. Petrol.* 140 (6), 734–753.
- Kaminsky, F.V., Khachatryan, G.K., Andreazza, P., Araujo, D., Griffin, W.L., 2009. Superdeep diamonds from kimberlites in the Juina area, Mato Grosso State, Brazil. *Lithos* 112S(2), 833–842.
- Kesson, S.E., FitzGerald, J.D., 1991. Partitioning of MgO, FeO, NiO, MnO and Cr₂O₃ between magnesian silicate perovskite and magnesio-wüstite: implications for the origin of inclusions in diamond and the composition of the lower mantle. *Earth Planet. Sci. Lett.* 111, 229–240.
- Kesson, S.E., FitzGerald, J.D., Shelley, J.M.G., 1994. Mineral chemistry and density of subducted basaltic crust at lower-mantle pressures. *Nature* 372, 767–769.
- Kojitani, H., Katsura, T., Akaogi, M., 2007. Aluminum substitution mechanisms in perovskite-type MgSiO₃: an investigation by Rietveld analysis. *Phys. Chem. Miner.* 34 (4), 257–267.

- Kubo, A., Akaogi, M., 2000. Post-garnet transitions in the system $\text{Mg}_4\text{Si}_4\text{O}_{12}\text{-Mg}_3\text{Al}_2\text{Si}_3\text{O}_{12}$ up to 28 GPa: phase relations of garnet, ilmenite and perovskite. *Phys. Earth Planet. Inter.* 121 (1–2), 85–102.
- Kuebler, K.E., Jolliff, B.L., Wang, A., Haskin, L.A., 2006. Extracting olivine (Fo-Fa) compositions from Raman spectral peak positions. *Geochim. Cosmochim. Acta* 70, 6201–6222.
- Litasov, K.D., Ohtani, E., 2004. Relationship between Al-bearing phases NAL and CF in the lower mantle. *Russ. Geol. Geophys.* 45 (11), 1313–1325.
- Litasov, K.D., Ohtani, E., 2005. Phase relations in hydrous MORB at 18–28 GPa: implications for heterogeneity of the lower mantle. *Phys. Earth Planet. Inter.* 150 (4), 239–263.
- Moore, R.O., Otter, M.L., Rickard, R.S., Harris, J.W., Gurney, J.J., 1986. The occurrence of moissanite and ferro-periclase as inclusions in diamond. 4th International Kimberlite Conference Extended Abstracts, Perth. vol. 16. Geological Society of Australia Abstracts, pp. 409–411.
- Muir, J.M.R., Brodholt, J.P., 2016. Ferrous iron partitioning in the lower mantle. *Phys. Earth Planet. Inter.* 257, 12–17.
- Nestola, F., Burnham, A.D., Peruzzo, L., Tauro, L., Alvaro, M., Walter, M.J., Gunter, M., Anzolini, C., Kohn, S.C., 2016. Tetragonal almandine-pyrope phase, TAPP: finally a name for it, the new mineral jeffbenite. *Mineral. Mag.* 80, 1219–1232.
- Nestola, F., Jung, H., Taylor, L.A., 2017. Mineral inclusions in diamonds may be synchronous but not syngenetic. *Nat. Commun.* 8, 14168.
- O'Neill, B., Jeanloz, R., 1990. Experimental petrology of the lower mantle: a natural peridotite taken to 54 GPa. *Geophys. Res. Lett.* 17, 1477–1480.
- Ono, S., Ito, E., Katsura, T., 2001. Mineralogy of subducted basaltic crust (MORB) from 25 to 37 GPa, and chemical heterogeneity of the lower mantle. *Earth Planet. Sci. Lett.* 190, 57–63.
- Prescher, C., Langenhorst, F., Dubrovinsky, L.S., Prakapenka, V.B., Miyajima, N., 2014. The effect of Fe spin crossovers on its partitioning behavior and oxidation state in a pyrolytic Earth's lower mantle system. *Earth Planet. Sci. Lett.* 399, 86–91.
- Ricolleau, A., Perrillat, J.-P., Fiquet, G., Daniel, I., Matas, J., Addad, A., Menguy, N., Cardon, H., Mezouar, M., Guignot, N., 2010. Phase relations and equation of state of a natural MORB: implications for the density profile of subducted oceanic crust in the Earth's lower mantle. *J. Geophys. Res. Solid Earth* 115, B08202.
- Ringwood, A.E., 1962. A model for the upper mantle. *J. Geophys. Res.* 67, 857–867.
- Scott Smith, B.H., Danchin, R.V., Harris, J.W., Stracke, K.J., 1984. Kimberlites near Orroroo, South Australia. In: Kornprobst, J. (Ed.), *Kimberlites I: Kimberlites and Related Rocks*. Elsevier, Amsterdam, pp. 121–142.
- Shatskiy, A., Fukui, H., Matsuzaki, T., Shinoda, K., Yoneda, A., Yamazaki, D., Ito, E., Katsura, T., 2007. Growth of large (1 mm) MgSiO_3 perovskite single crystals: a thermal gradient method at ultrahigh pressure. *Am. Mineral.* 92, 1744–1749.
- Sobolev, N.V., 1977. *Deep-Seated Inclusions in Kimberlites and the Problem of the Composition of the Upper Mantle* (Translated from the Russian Edition, 1974). AGU, Washington.
- Stachel, T., 2001. Diamonds from the asthenosphere and the transition zone. *Eur. J. Mineral.* 13 (5), 883–892.
- Stachel, T., Harris, J.W., 2008. The origin of cratonic diamonds - constraints from mineral inclusions. *Ore Geol. Rev.* 34, 5–32.
- Stachel, T., Harris, J.W., Brey, G., Joswig, W., 2000. Kankan diamonds (Guinea) II: lower mantle inclusion paragenesis. *Contrib. Mineral. Petrol.* 140, 16–27.
- Stixrude, L., Lithgow-Bertelloni, C., 2007. Influence of phase transformations on lateral heterogeneity and dynamics in Earth's mantle. *Earth Planet. Sci. Lett.* 263 (1–2), 45–55.
- Tappert, R., Stachel, T., Harris, J.W., Muehlenbachs, K., Ludwig, T., Brey, G.P., 2005. Diamonds from Jagersfontein (South Africa): Messengers from the sublithospheric mantle. *Contrib. Mineral. Petrol.* 150, 505–522.
- Tappert, R., Foden, J., Stachel, T., Muehlenbachs, K., Tappert, M., Wills, K., 2009. Deep mantle diamonds from South Australia; a record of Pacific subduction at the Gondwanan margin. *Geology* 37, 43–46.
- Thomson, A.R., Kohn, S.C., Bulanova, G.P., Smith, C.B., Araujo, D., Walter, M.J., 2014. Origin of sub-lithospheric diamonds from the Juina-5 kimberlite (Brazil): constraints from carbon isotopes and inclusion compositions. *Contrib. Mineral. Petrol.* 168, 1081.
- Tomioka, N., Fujino, K., 1997. Natural $(\text{Mg,Fe})\text{SiO}_3$ -ilmenite and -perovskite in the Tenham meteorite. *Science* 277, 1084–1086.
- Tschauner, O., Ma, C., Beckett, J.R., Prescher, C., Prakapenka, V.B., Rossman, G.R., 2014. Discovery of bridgmanite, the most abundant mineral in Earth, in a shocked meteorite. *Science* 346, 1100–1102.
- Ulmer, P., Stalder, R., 2001. The $\text{Mg}(\text{Fe})\text{SiO}_3$ orthoenstatite-clinoenstatite transitions at high pressures and temperatures determined by Raman-spectroscopy on quenched samples. *Am. Mineral.* 86 (10), 1267–1274.
- Walter, M.J., Kohn, S.C., Araujo, D., Bulanova, G.P., Smith, C.B., Gaillou, E., Wang, J., Steele, A., Shirey, S.B., 2011. Deep mantle cycling of oceanic crust: evidence from diamonds and their mineral inclusions. *Science* 334, 54–57.
- Wilding, M.C., Harte, B., Harris, J.W., 1991. Evidence for a deep origin for the Sao Luiz diamonds. Fifth International Kimberlite Conference Extended Abstracts, Araxa, pp. 456–458.
- Yasuzuka, T., Ishibashi, H., Arakawa, M., Yamamoto, J., Kagi, H., 2009. Simultaneous determination of Mg# and residual pressure in olivine using micro-Raman spectroscopy. *J. Mineral. Petrol. Sci.* 104 (6), 395–400.
- Zedgenizov, D.A., Kagi, H., Shatsky, V.S., Ragozin, A.L., 2014. Local variations of carbon isotope composition in diamonds from Sao-Luis (Brazil): evidence for heterogeneous carbon reservoir in sublithospheric mantle. *Chem. Geol.* 363, 114–124.
- Zedgenizov, D.A., Shatsky, V.S., Panin, A.V., Evtushenko, O.V., Ragozin, A.L., Kagi, H., 2015. Evidence for phase transitions in mineral inclusions in superdeep diamonds of the Sao Luiz deposit (Brazil). *Russ. Geol. Geophys.* 56, 296–305.