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Letter

Merwinite in diamond from São Luiz, Brazil: A new mineral of the Ca-rich mantle environment

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Abstract

Diamonds from Juina province, Brazil, and some others localities reveal the existence of a deep, Ca-rich carbonate-silicate source different from ultramafic and eclogite compositions. In this study, we describe the first observation of merwinite ($Ca_{2.85}Mg_{0.96}Fe_{0.11}Si_{2.04}O_8$) in a diamond; it occurs as an inclusion in the central growth domain of a diamond from the São Luiz river alluvial deposits (Juina, Brazil). In addition, the diamond contains inclusions of walstromite-structured $CaSiO_3$ in the core and $(Mg_{0.86}Fe_{0.14})_2SiO_4$ olivine in the rim. According to available experimental data, under mantle conditions, merwinite can only be formed in a specific Ca-rich and Mg- and Si-depleted enviroment that differs from any known mantle lithology (peridotitic or eclogitic). We suggest that such chemical conditions can occur during the interaction of subduction-derived calcium carbonatite melt with peridotitic mantle. The partial reduction of the melt could cause the simultaneous crystallization of Ca-rich silicates ($CaSiO_3$ and merwinite) and diamond at an early stage, and $(Mg_{0.86}Fe_{0.14})_2SiO_4$ olivine and diamond at a later stage, after the Ca-Mg exchange between carbonatite melt and peridotite has ceased. This scenario is supported by the presence of calcite microinclusions within merwinite.

Keywords: Merwinite, diamond, Earth's mantle, calcic lithology, carbon

Introduction

The São Luiz river alluvial deposits (Juina, Brazil) are a well-known source of sublithospheric diamonds as identified by their mineral inclusions (Harte et al. 1999; Hutchison et al. 2001; Kaminsky et al. 2001; Araujo et al. 2003; Hayman et al. 2005). The studies of mineral inclusions within diamonds from São Luiz and some others localities have revealed the existence of a deep, Ca-rich carbonate-silicate reservoir different from ultramafic and eclogite compositions, and the absence of several common mantle minerals, such as olivine, garnet, and low-Ca pyroxene (Brenker et al. 2005). The following polyphase inclusions have been reported: $CaSiO_3 + CaSi_2O_5 \pm Ca_2SiO_4$, $CaSiO_3 + CaTiO_3$, $CaSiO_3 + CaCO_3$, $CaMgSi_2O_6 + CaCO_3$ (Joswig et al. 1999; Stachel et al. 2000; Kaminsky et al. 2001; Brenker et al. 2005, 2007; Hayman et al. 2005; Walter et al. 2008; Bulanova et al. 2010; Harte 2010; Zedgenizov et al. 2014). These inclusions suggest the presence of a chemically distinct reservoir in the sublithospheric, convecting mantle. Several aspects, e.g., the C-isotopic composition of the host diamonds (Bulanova et al. 2010; Walter et al. 2011; Zedgenizov et al. 2014) or Eu-anomalies of $CaSiO_3$ (Harte et al. 1999; Stachel et al. 2000, 2005), link the Ca-rich lithology to subduction processes. Additionally, some of the Ca-rich inclusions originate from the transition zone and even the lower mantle (Joswig et al. 1999; Kaminsky et al. 2001; Walter et al. 2008). In this study, we provide the first report of a new Ca-rich inclusion in diamond, merwinite, from a diamond discovered in the São Luiz river alluvial deposits.

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Method

The morphology of the diamond crystal was studied using a LEO 1430 VPSEM scanning electron microscope (SEM). The diamond was subsequently polished to expose its mineral inclusions. The polished plate was carbon-coated and put into a JEOL JXA-8100 electron microprobe (EMP) at IGM SB RAS (Novosibirsk, Russia). The samples were imaged in the electron backscattered (EBS) mode, and the inclusions were analyzed using a quantitative EMP analyzer at 15 kV accelerating voltage, 20 nA sample current, and 2 μm beam diameter. The internal uncertainty of each EMP analysis did not exceed 5%.

The internal structure of diamond was imaged using cathodoluminescence (CL) coupled with SEM. The carbon isotope composition of the different diamond zones was determined using a CAMECA IMS 1270 secondary ion mass spectrometer (SIMS) at the University of Edinburgh (U.K.). The uncertainty of each internal carbon isotopic analysis did not exceed 0.2‰. Infrared absorption spectra of the studied diamonds were recorded on an FTIR Bruker VERTEX 70 equipped with a HYPERION 2000 microscope. Local spectra with resolution of 4 cm^{-1} over the range the range 600–4500 cm^{-1}, were recorded by averaging 50 scans from an area of 50 × 50 μm. The contents of N-centers were calculated following a standard procedure (Mendelssohn and Milledge 1995). The intrinsic absorption of diamonds (12.3 at 2030 cm^{-1}) was taken to be the internal standard (Zaitsev 2001). The decomposition of the spectrum from 1100 to 1350 cm^{-1} made it possible to determine the contribution of different N-defects with characteristic absorptions of specified shapes.

Results

The diamond (~1.7 mm in size) is a colorless, with rounded tetrahexahedroid morphology (Figs. 1a and 1b), whereas its internal structure, as visualized by the CL images, reveals octahedral growth zones (Fig. 1c). The CL images reveal a dark core and a brighter rim (Figs. 1c and 1d). The brighter rim shows parallel lines intersecting the octahedral growth zones (Figs. 1c and 1d). Generally this feature is considered as a sign of plastic deformation (Lang 1977), which is very common in Juina diamonds (Hutchison et al. 1999).

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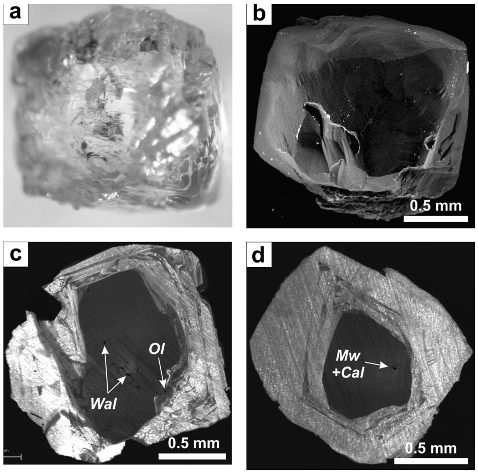

FIGURE 1. The external and internal morphology of diamond no. 88 from São Luiz river alluvial deposits. (**a**) Optical photomicrograph and (**b**) BSE image of the diamond before polishing. (**c**, **d**) Cathodoluminescence images of both sides of a (110) diamond plate (~300 μm in thickness) mounted into epoxy (black). Wal = $CaSiO_3$ walstromite, Mw+Cal = $Ca_{2.85}Mg_{0.96}Fe_{0.11}Si_{2.04}O_8$ merwinite inclusion containing calcite, Ol = $(Mg_{0.86}Fe_{0.14})_2SiO_4$ olivine.

TABLE 1. Composition (EMP-analysis) of inclusions in diamond 88 from São Luiz river alluvial deposits

	Walstromite		Merwinite		Olivine	
	wt%	mol%	wt%	mol%	wt%	mol%
SiO_2	51.6	50.3	36.8	34.2	39.8	33.4
TiO_2	0.04	0.03	0.02	0.01	0.0	0.0
Al_2O_3	0.01	0.01	0.10	0.05	0.0	0.0
Cr_2O_3	0.0	0.0	0.02	0.01	0.09	0.03
FeO	0.31	0.26	2.32	1.80	13.6	9.62
MnO	0.00	0.00	0.04	0.03	0.04	0.03
MgO	0.00	0.00	11.7	16.1	45.4	56.8
CaO	47.3	49.4	47.9	47.6	0.12	0.10
Na_2O	0.03	0.03	0.24	0.22	0.0	0.0
K_2O	0.00	0.00	0.01	0.00	0.0	0.0
NiO	n.d.	n.d.	n.d.	n.d.	0.25	0.17
Total	99.3	100.0	99.1	100.0	99.3	100.0

The two growth domains differ in N content: the core is N-free (type IIa) while the rim contains 20–25 ppm of N with a low aggregation state (21–30% IaB). In addition, an absorption band at 3107 cm^{-1} is evident in the infrared absorption spectrum of the N-bearing rim. This band is related to a C-H bond stretching mode (Woods and Collins 1983).

Four individual inclusions were exposed in different growth zones. Two inclusions of $CaSiO_3$ and a single inclusion of $Ca_{2.85}Mg_{0.96}Fe_{0.11}Si_{2.04}O_8$ are located in the central growth domain (Figs. 1c and 1d). A single inclusion of $(Mg_{0.86}Fe_{0.14})_2SiO_4$ was observed in the outer growth domain (Fig. 1c). The size of the inclusions ranges from 5 to 12 μm. The inclusions compositions are given in Table 1. The Raman spectra of the inclusions were consistent with those of walstromite (Brenker et al. 2007), merwinite (Piriou and McMillan 1983), and olivine (Chopelas 1991) (Fig. 2). The Raman spectrum of the merwinite-containing inclusion has additional peaks assignable to calcite (Fig. 2b). Although the specimen was heated to 300–400 °C during polishing, the Raman spectra of the mineral inclusions show no evidence of amorphization, as expected for high-pressure phases such as Mg-Si-perovskite.

The studied diamond has a relatively heavy carbon isotope composition $\delta^{13}C$ = –1.8 to –3.4 ‰, in comparison with the average mantle $\delta^{13}C$ ~ –5 ‰ (Harte 2010); the $\delta^{13}C$ values show no correlation to the growth zones.

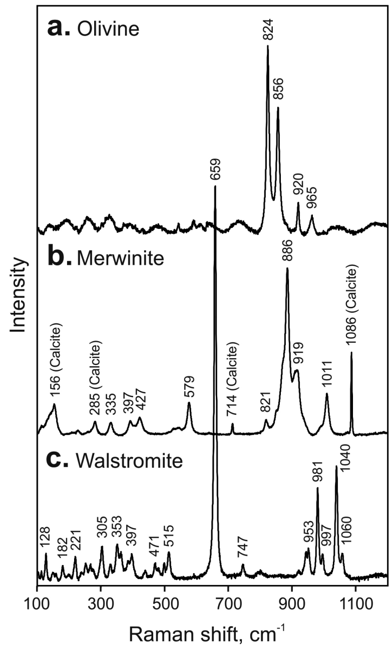

FIGURE 2. Raman spectra of mineral inclusions in diamond no. 88 from São Luiz river alluvial deposits: $(Mg_{0.86}Fe_{0.14})_2SiO_4$ olivine (**a**), $Ca_{2.85}Mg_{0.96}Fe_{0.11}Si_{2.04}O_8$ merwinite and calcite (**b**), and $CaSiO_3$ walstromite (**c**).

DISCUSSION

It was pointed out that the heavier $\delta^{13}C$ values correspond well to those of marine carbonate sediments (Stachel et al. 2005; Tappert et al. 2005). Harte (2010) also argued that the formation of many superdeep diamonds was probably triggered by the dehydration of deeply subducted material. Walter et al. (2008) have provided experimental and geochemical evidence that Ca-silicate mineral inclusions in some diamonds from Juina, Brazil, crystallized from primary and evolved carbonate melts in the mantle transition zone. They suggest a process whereby subducted carbonated oceanic crust undergoes low-degree partial melting to produce carbonate melts. Metasedimentary carbon in altered oceanic crust consists of a mixture of organic components ($\delta^{13}C$ ≈ –27‰) and marine carbonates ($\delta^{13}C$ ≈ 0‰) (Shilobreeva et al. 2011).

The internal texture of the studied diamond exhibits a primary octahedral growth morphology (Fig. 1c); this is reminiscent of experiments performed at 6 GPa in which diamonds were grown from hydrous carbonatite melts upon gradual reduction by hydrogen-containing fluids (Pal'yanov et al. 2002). The external shape of the studied crystal exhibits a rounded dissolution morphology, similar to the rounded tetrahexahedroid. This habit suggests that the original octahedron lost about 50% of its initial weight as a result of dissolution in the water-bearing $CaCO_3$ or kimberlite melt (Khokhryakov and Pal'yanov 2007, 2010). The $CaSiO_3$ inclusions found in the same growth zone as the merwinite inclusion can be interpreted as former Ca-Si perovskite, i.e., a mineral of the transition zone or the lower mantle (Harte 2010). Yet, under mantle conditions, merwinite is unusual and can be only formed in specific Ca-rich and Mg- and Si-depleted environments (Yoder 1968; Sharp et al. 1986; Moriyama et al. 1992; Safonov et al. 2007; Luth 2009), which differs from any known mantle lithology (peridotitic, eclogitic, or pelitic). Such chemical conditions can occur during interaction of subduction-derived, calcio-carbonatite melt with peridotitic mantle. Carbonatite melts are very mobile and rapidly infiltrate peridotite wall-rock by a dissolution-precipitation mechanism (Hammouda and Laporte 2000), because the dihedral angle at the contacts between silicate minerals and melt is lower than 60° (Hunter and McKenzie 1989; Minarik and Watson 1995), and because the diffusivity of silicate solute in the carbonatite melt is high (Shatskiy et al. 2013b). According to the experimental studies of Hammouda (2003) and Grassi and Schmidt (2011), partial melting of the uppermost part of the subducted slab (i.e., carbonated eclogite and pelite) yields a $CaCO_3$-rich carbonatite melt. This melt differs from the magnesio-dolomitic carbonatite melt that can coexist with the peridotitic mantle (Dasgupta and Hirschmann 2007; Brey et al. 2008). Therefore, subduction-derived calcio-carbonatite melt must react with overlying host mantle to form Ca-bearing silicates and a Ca-dolomite carbonatite melt. The following reactions between alkali-bearing $CaCO_3$ melt and peridotite were experimentally established at 6.5 GPa (Sharygin et al. 2012):

$$4Mg_2Si_2O_6(OPx) + 8CaCO_3(Liq) = Mg_2SiO_4(Ol) + CaMgSi_2O_6(CPx) + Ca_3MgSi_2O_8(Mw) + 3SiO_2(Liq) + 4CaMg(CO_3)_2(Liq) \quad (1)$$

$$2Mg_2SiO_4(Ol) + 6CaCO_3(Liq) = Ca_3MgSi_2O_8(Mw) + 3CaMg(CO_3)_2(Liq) \quad (2)$$

In short (<6 h) experiments, merwinite was found at the melt-olivine interface at 1400 °C, and at the melt-orthopyroxene interface at 1300 °C. However, once the infiltrated melt approaches an equilibrium (Ca-dolomitic) composition during re-equilibration with peridotite mantle, merwinite crystallization terminates and CPx replaces merwinite. At higher temperatures, the merwinite-forming reactions do not occur, and the interaction of $CaCO_3$ melt with the OPx + Ol assemblage yields direct formation of the CPx + Ol assemblage (Sharygin et al. 2012). That is, the finding of a merwinite inclusion in diamond is consistent with the above experimental evidence, and indicates its crystallization from a $CaCO_3$-rich carbonatite melt infiltrated into peridotite mantle.

Diamond formation requires a continuous carbon supply to the growing crystals, i.e., supersaturation of the solution with carbon (e.g., as with a carbonatite melt; Pal'yanov et al. 1999a). It requires continuous reduction of carbonatite melt (Pal'yanov et al. 2002), which should inevitably occur during its interaction with reduced surrounding mantle (Frost and McCammon 2008). The partial reduction of $CaCO_3$-rich, SiO_2-bearing melt should cause precipitation of silicate solutes simultaneously with diamond crystallization. Therefore, at the early stage, the diamond entraps the Ca-rich silicates: $CaSiO_3$ (walstromite or perovskite) and $Ca_3MgSi_2O_8$ (merwinite), as we found in the central growth domain of this specimen. This scenario is supported by the presence of calcite as microinclusions within the merwinite inclusion, as is evident from the Raman spectra (Fig. 2b). At a later stage, the carbonatite melt becomes a Ca-dolomitic in composition due to Ca-Mg exchange with peridotitic mantle. The reduction of this melt could also cause precipitation of $(Mg_{0.86}Fe_{0.14})_2SiO_4$, which has been found as an inclusion in the outer growth domain. The relatively high Fe-content in this inclusion may suggest an Fe enrichment of the parental carbonatite melt. Indeed, subduction-derived carbonatite melts formed as a result of partial melting of carbonated eclogite or pelite are Fe-rich (Hammouda 2003; Grassi and Schmidt 2011).

Alternatively, the carbonatite melt can be partially reduced, and continuous carbon supply could occur via carbonate-silicate reactions, which proceed slightly below the CCO ($C + O_2 = CO_2$) oxygen buffer (Ogasawara et al. 1997; Palyanov et al. 2005). One of these reactions, previously suggested by Luth (1993), has been experimentally established at 6.5 GPa and 1400 °C in a long-duration experiment (16 h) (Sharygin et al. 2012):

$$3Mg_2Si_2O_6(OPx) + 2CaCO_3(Liq) = 2Mg_2SiO_4(Ol) + 2CaMgSi_2O_6(CPx) + 2C + 2O_2 \quad (3)$$

Based on the available experimental data on the merwinite-forming carbonate-silicate reactions (Sharygin et al. 2012), kinetics of diamond crystallization in the carbonatite melt (Pal'yanov et al. 1999b, 2002), and melting phase relations in the carbonate and carbonate-silicate systems (Hammouda 2003; Grassi and Schmidt 2011; Litasov et al. 2013; Shatskiy et al. 2013a, 2013c, 2013d), the most probable growth conditions of the studied diamond are 1150–1400 °C and pressures exceeding 6 GPa. According to the phase relations in the $CaO-SiO_2$ system, the $CaSiO_3$ compounds can stabilize as walstromite in the pressure range of 4–10 GPa, and as perovskite above 12–14 GPa (Huang and Wyllie 1975; Gasparik et al. 1994; Akaogi et al. 2004). Merwinite has been found to be a stable phase at least up to 16 GPa and 2000 °C (Moriyama et al. 1992). Thus, we can conclude that the inner growth zone of the studied diamond could form either under the upper mantle conditions ($6 < P < 10$ GPa) or in the transition zone ($14 < P \leq 16$ GPa). Depending on the upper-pressure limit of the merwinite stability field (which is unknown), this pressure range may extend to that of the lower mantle. The outer, olivine-hosting zone could crystallize at a later time at the same or shallower depth in the upper mantle.

The presence of merwinite in the studied diamond from the São Luiz river alluvial deposits suggests a process whereby subduction-derived Ca-carbonatite melt reacts with host peridotitic mantle to form Ca-rich silicates ($CaSiO_3$ and merwinite) to cause diamond formation. Under mantle conditions, merwinite can only be formed in a specific Ca-rich and Mg- and Si-depleted enviroment that differs from any known mantle lithology (peridotitic or eclogitic). Thus, merwinite could be an apparent evidence of Ca-carbonatite metasomatism in the deep mantle.

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