Hydrous fluid as the growth media of natural polycrystalline diamond, carbonado: Implication from IR spectra and microtextural observations

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ABSTRACT

Carbonado, a variety of natural polycrystalline diamond whose origin remains unknown, differs notably in the properties from common diamonds of mantle origin. In this study, infrared spectroscopic and microscopic analyses were conducted on carbonado from the Central African Republic. Stepwise heating followed by infrared spectroscopic measurements indicated that liquid H2O is enclosed within diamond single crystals in carbonado. Transmission electron microscope observation revealed a negative crystal that is interpreted as a primary fluid inclusion in a diamond single crystal. Observations by field-emission scanning electron microscope and electron backscatter diffraction analysis show an absence of lattice preferred orientation of diamond crystals, {111} growth steps along grain boundaries, and the crystal-size distribution of diamond similar to those of crystals formed in liquid media. In addition, the redox conditions of carbonado formation is inferred to be ~3 log units below the quartz-magnetite-fayalite buffer, which is the prevailing condition in cratonic upper mantle. These lines of evidence suggest that the carbonado crystallized in C-O-H fluid, supporting the hypothesis of a mantle-depth origin of carbonado.

Keywords: Carbonado, diamond, fluid inclusion, IR spectroscopy, TEM, crystal-size distribution

INTRODUCTION

Carbonado is a variety of natural polycrystalline diamond whose origin is enigmatic (Heaney et al. 2005; McCall 2009). Carbonado possesses peculiar characteristics, including low 13C/12C isotope ratios, high porosity, absence from kimberlites, and lack of mantle-derived mineral inclusions (Heaney et al. 2005 and references therein), making it extremely different from common diamonds of mantle origin. Consequently, non-mantle origins have been proposed for carbonado, including an origin by impact-induced phase transition from organic carbon (Smith and Dawson 1985), an irradiation-induced phase transition from coal (Ozima et al. 1991), and chemical vapor deposition in interstellar space (Garai et al. 2006). In contrast, a mantle-depth origin has been proposed in previous studies (Robinson 1978; Nadolinny et al. 2003; Kagi and Fukura 2008; Petrovsky et al. 2009), as is commonly accepted for other natural polycrystalline diamonds, but this hypothesis is not widely accepted. No conclusive evidence has been proposed to confirm or refute any of these hypotheses, despite the fact that carbonado has been studied for nearly 30 years; consequently, its origin remains debated.

It is generally accepted that the growth media of diamond forming in the mantle and crustal environments are volatile-saturated melts or fluids (Haggerty 1986; Sobolev and Shatsky 1990; Pal’yanov et al. 1999, 2007). Fibrous or cloudy mantle diamonds contain K-rich fluid inclusions whose composition belongs to one of the three main types: a hydrous silicic end-member rich in water, a carbonatitic end-member rich in carbonate, and brine (e.g., Schrauder and Navon 1994; Izrae1 et al. 2001; Zedgenizov et al. 2004; Pal’yanov et al. 2007). Potassium-enriched C-O-H fluid inclusions have also been found in metamorphic microdiamonds (e.g., Hwang et al. 2005). Experimental studies have revealed that coexisting fluids promote the formation of diamond and influence its morphology (e.g., Pal’yanov and Sokol 2009); indeed, fluid composition has a strong influence on diamond growth (Sokol et al. 2009).

The composition of C-O-H fluid provides information on the redox conditions of carbonado formation, because the composition varies significantly with oxygen fugacity (fO2) under diamond-saturated conditions (e.g., Woodland and Koch 2003; Sokol et al. 2009; Zhang and Duan 2009). Therefore, evidence for the coexistence of a fluid phase would provide a critical constraint on the origin of carbonado. No previous study has presented clear evidence of primary fluid inclusions in carbonado.

Kagi and Fukura (2008) measured the infrared (IR) absorption spectra of crushed carbonado grains after acid leaching and detected absorption bands assignable to liquid water and carbonate. Based on the observations, Kagi and Fukura (2008) proposed that liquid water and carbonate may exist as primary inclusions in carbonado grains. However, this proposal remains speculative because it is difficult to completely eliminate volatile-bearing impurities from grain boundaries by acid leaching, and water may be contaminated during the procedure.

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The present study is aimed at establishing the growth conditions of carbonado from detailed spectroscopic and microtextural observations. We describe an analysis of carbonado from the Central African Republic (CAR) using IR spectroscopy, field-emission scanning electron microscopy (FE-SEM), electron backscatter diffraction (EBSD), and transmission electron microscopy (TEM).

SAMPLES AND METHODS

The carbonado samples studied here were mined from alluvial deposits in the CAR and were sourced from a commercial dealer; the average grain size was 5–10 mm. The carbonado grains are from the same suite of samples as those examined in our previous studies (Fukura et al. 2005; Kagi and Fukura 2008).

To measure IR absorption spectra, a carbonado grain was crushed to fragments of several millimeters in size. The crushed sample was then incrementally heated at 700, 900, 950, and 1100 °C for 30 min at each temperature under vacuum. IR absorption spectra were measured at room temperature in air after each heating step, using a Fourier transform infrared spectrometer equipped with an IR microprobe (Spectrum 2000; Perkin-Elmer Inc.).

TEM observations were performed on a foil of carbonado (0.1 μm thick) made from a crushed fragment of carbonado after Au-coating. The foil was fabricated with a Ga ion beam at an accelerating voltage of 30 kV under a vacuumed condition using a focused ion beam (FIB) instrument (JOEL JEM-9301FIB). The foil was observed with a TEM (JEOL JEM-2010) under an accelerating voltage of 200 kV.

To observe the microtextures of carbonado, one face of a CAR carbonado grain was polished to optical grade for FE-SEM and EBSD analyses. The polished surface was observed by FE-SEM (JOEL JSM-700F) under analytical conditions of 15 kV accelerating voltage and 7.5 nA load current. The crystallographic orientations of carbonado-forming diamonds were analyzed by EBSD using HKL Channel 5 software. In addition to the point analysis, we obtained EBSD maps under conditions of 0.5 and 0.2 μm/step for the areas of 280 × 350 and 64 × 80 μm, respectively. Distributions of crystallographic orientation and crystal size were analyzed from the EBSD mapping data. The 2D crystal-size distribution (CSD) of carbonado-forming diamonds was stereologically converted to the 3D crystal-size distribution using CSD Corrections software (Higgins 2000).

RESULTS AND DISCUSSION

Infrared absorption spectra

Figure 1 shows the IR absorption spectra of a crushed carbonado fragment before heating and after heating at 700, 900, and 950 °C. At 1100 °C, the transparent diamond became opaque due to graphitization and the IR spectrum could not be measured. Our attention is focused on the spectral region of 3000–3800 cm\(^{-1}\), which corresponds to OH stretching vibrations. The absorption at around 3400 cm\(^{-1}\) is attributed to liquid water and the band around 3250 cm\(^{-1}\) is assigned to water that is adsorbed along the diamond–diamond grain boundaries within carbonado. The assignment was based on the fact that OH stretching vibration of water thinly adsorbed on a solid is observed at significantly lower frequencies in comparison with that of liquid water (e.g., Foster et al. 2005). However, the assignment is not straightforward. We have to mention that the 3250 cm\(^{-1}\) band could be also assignable to a N–H related vibration (Anderson et al. 1998; Garai 2012). However, the intensity of the N–H absorption is considerably low in natural diamond samples (Anderson et al. 1998) and it is difficult to conclude that the 3250 cm\(^{-1}\) band is resulted exclusively from the N–H related vibrations. Sharp absorption bands at around 3600–3700 cm\(^{-1}\) are generally attributed to OH stretching in hydrous minerals (Beran 2002; Madejova 2003). The broad absorption component at around 3250 cm\(^{-1}\) observed from a non-heated sample disappeared after heating at 700 °C, indicating dehydration from grain boundaries. Absorption bands at around 3600–3700 cm\(^{-1}\) disappeared above 900 °C, indicating the dehydration of hydrous minerals. The absorption bands at around 3400 and 1640 cm\(^{-1}\), which are, respectively, attributed to OH stretching and H–O–H bending modes of liquid H\(_2\)O, remained after heating above 900 °C and persisted until diamond graphitization, at which point both hydrous minerals and water trapped in grain boundary were lost. The presence of these absorption bands after heating strongly suggests that liquid water was present, enclosed within single crystals of diamond as primary fluid inclusions. It is noteworthy that the IR absorption spectrum after heating at 950 °C showed a very similar pattern with that of a cratonic diamond, which has hydrous fluid inclusions (Zedgenizov et al. 2004). The spectroscopic observations raise the possibility that a main component of the diamond-growth media of carbonado was H\(_2\)O.

An absorption band at 1450 cm\(^{-1}\), attributable to carbonate, was observed before heating and after heating at 900 °C, but it disappeared after heating at 950 °C. These temperatures are consistent with the thermal decomposition of CaCO\(_3\) (e.g., Criado and Ortega 1992). The thermal decomposition of carbonate minerals at grain boundaries and subsequent loss of volatile component explain the band disappearance. The present IR spectroscopic results suggest that the carbonate absorption found in previous studies (Kagi and Fukura 2008; Garai et al. 2006) was attributed to carbonate minerals at grain boundaries that survived acid leaching and that the major component of fluid inclusions within diamond crystals of the carbonado was H\(_2\)O.
TEM observation of a single crystal of diamond in carbonado

Figure 2a shows a bright-field image of a carbonado film, revealing several voids of various sizes without any systematic arrangement. The [110] incident electron diffraction pattern obtained from the entire area of the film (inset in Fig. 2b) indicates that the film is composed of a single grain of diamond. Figure 2b shows a magnified image around a void in the film. The void is hexagonal in shape, and the diffraction pattern shown in the inset of Figure 2b determines the crystallographic direction of the hexagonal void. Four of the six sides of the hexagon are parallel to [111] and two are parallel to [101] (Fig. 2b). A striped thickness fringe indicates a progressive upward increase in film thickness. The image clearly shows that this hexagonal outline is a cross-section of an octahedral void surrounded by [111] planes, intersected by a plane parallel to the (110) plane. This octahedral void, controlled by the crystallographic structure of the host diamond, is unambiguously a negative crystal of diamond, which may have been filled by a H₂O-bearing fluid before cutting.

Fluid inclusions generally form by one of two mechanisms: (1) the entrapment of neighboring fluid during growth of the host crystal, or (2) crack formation and fluid infiltration followed by healing of the host crystal. Fluid inclusions that form by the former mechanism (primary inclusions) tend to be found as isolated inclusions, whereas those that form by the latter mechanism almost always occur as a trail of inclusions (van der Kerkhof and Hein 2001). In the present case, the negative crystal was found as an isolated inclusion (Fig. 2a). In addition, FE-SEM observations of polished surfaces also revealed many isolated voids in single diamond crystals, which may be evidence of fluid inclusions (see later). Therefore, we interpret the inclusion to be a negative crystal that formed during crystal growth of the host diamond, and its smooth surfaces indicate that near-equilibrium was attained between the fluid and the host diamond.

The presence of a coexisting fluid phase during growth indicates that the host mineral phase is thermodynamically stable and even supersaturated in the coexisting liquid phase. Therefore, it is concluded that the carbonado-forming diamond was crystallized from a highly carbon-oversaturated H₂O-bearing fluid under thermodynamic conditions in which diamond is stable; i.e., at the depth of Earth’s mantle. This result is consistent with previous spectroscopic observations that the residual pressure in a CAR carbonado corresponds to the stability field of diamond at high temperatures (Fukura et al. 2005; Kagi and Fukura 2008). Our observations are also consistent with the description of Rondeau et al. (2008) of the texture of a carbonado sample overgrown by columnar polycrystals of coarse diamonds up to several millimeters in length; such a coarse diamond would only be able to grow under diamond-stable conditions.

Microtextures

Figure 3 shows a misorientation angle distribution for diamond crystals in the CAR carbonado. The result quantitatively indicates that crystallographic orientations of diamond crystals are random; this is consistent with previous results (e.g., Trueb and Buttermann 1969; De et al. 1998).

Crystal-size distribution (CSD) of diamond crystals of carbonado is shown in Figure 4. This study first presents quantitative CSD data for natural polycrystalline diamonds. Crystal size varies significantly from several tens of micrometers to submicrometers. Number density (number of crystals per unit volume divided by the size interval) increases almost monotonously with decreasing crystal size; no depletion in the number density for fine crystals was detected in the observed size range. Because a decrease in the number density of fine crystals is attributed to Ostwald ripening (driven by annealing and characteristic of annealed polycrystalline bodies; e.g., Cashman and Ferry 1988), the absence of such a decrease suggests that the polycrystalline structure underwent no notable annealing resulting in the grain growth after its formation. It is noteworthy that the CSD pattern of the carbonado is similar in shape to those of rapidly formed crystals in silicate and carbonatitic melts (e.g., Cashman and Marsh 1988; Mattsson and Caricchi 2009) and in aqueous solution (e.g., Kile et al. 2000). These CSD patterns characterized by an exponential decrease of crystal number density with respect to size were interpreted as a result of nucleation and growth processes (Marsh 1998). This process is consistent with the random crystallographic orientations of diamond crystals.

Figure 5a is a secondary electron image of the polished surface of the CAR carbonado. It shows that both the diamond...
crystals and interstitial voids vary in size, and voids are in multi-
angular shapes. Figure 5b shows the boundary between two
independent diamond grains. The grain boundary has a zigzag
shape on the submicrometer scale and fine triangular voids occur
between adjacent diamond crystals. In addition, a sub-micro-
meter rectangular bulge intrudes a neighboring crystal. Similar
textures were found over the entire polished surface.

Crystallographic orientation data, obtained from EBSD
patterns, indicate that the zigzag boundaries are oriented per-
pendicular to <110> axes of diamond (see Fig. 5b), suggesting
in turn, that the boundary represents the line of intersection
between {110} or {111} planes and the polished surface of the
sample. The zigzag boundary is more likely to be defined by
{111} faces, because these are the main growth faces of natural
diamonds (Sunagawa 1990). In addition, previous experiments
have reported the growth of {111} faces during the formation
of polycrystalline diamond in C-O-H fluid and melt (e.g., Akai-
shi and Yamaoka 2000; Sokol et al. 2009; Spivak and Litvin
2004). Furthermore, {111} faces have been reported from SEM
observations of the crushed surfaces of carbonado (Petrovsky
et al. 2009). Consequently, we conclude that the zigzag shaped
interfaces are {111} growth steps of diamonds. The fact that the
growth steps were also found at diamond–diamond boundaries
indicates that they existed during the intergrowth of diamond
grains; i.e., the {111} growth steps are a primary texture of the
carbonado. Therefore, the voids surrounded by the {111} growth
steps were also a primary texture that compensated crystal-
lographic orientation mismatch among neighboring crystals
and were filled by the coexisting fluid. We conclude that fluid
coexisted with the carbonado during the period of intergrowth.
The observations of the {111} growth steps and the voids are
also consistent with the nucleation and growth process suggested
from the CSD pattern (Fig. 4).

Because of high-interfacial energy for submicrometer-scale
textures, primary textures (e.g., absence of number density
depletion for fine crystals, the zigzag grain boundary and submi-
crometer-scale voids observed in the present study) are unstable
and would presumably disappear during protracted annealing.

Thus, the survival of such textures indicates that the present
carbonado sample underwent little or no annealing after diamond
formation. The lack of a protracted annealing period is consistent
with a previous IR spectroscopic study that reported immature
nitrogen aggregates in carbonado samples from CAR (Kagi and
Fukura 2008). We conclude that the carbonado examined in this

![Figure 3](image3.png)

**Figure 3.** Misorientation angle distribution of diamond crystals in the CAR carbonado. The line indicates the distribution of randomly oriented cubic crystals.

![Figure 4](image4.png)

**Figure 4.** CSD plots of diamond crystals in the CAR carbonado. Bars indicate 1σ errors. Note that the number density (number of crystals per unit volume divided by the size interval) shows a monotonous increase with decreasing crystal size. No depletion of fine grains is observed.

![Figure 5](image5.png)

**Figure 5.** (a) Field-emission scanning electron microscope image of a polished surface of carbonado. Scale bar is 10 μm. (b) Magnified image of the area indicated by the white square in a. Scale bar is 5 μm. The white octahedrons indicate the orientations of {111} planes for each diamond crystal.
study was transported to the surface and quenched shortly after the formation of its primary texture. This result does not mean that all of carbonado grains underwent no annealing because: (1) it may be difficult to explain the coarse columnar texture of diamond crystals grown on the surface of carbonado (Rondeau et al. 2008) without annealing; and (2) nitrogen aggregation state varies significantly in the carbonado suite (Kagi et al. 1994). We think annealing duration can vary with respect to each carbonado sample and our sample may be one that is the least annealed.

The formation process of carbonado

Our results suggest that the CAR carbonado was formed under thermodynamically diamond-stable and H₂O-rich fluid coexistent conditions. Previous hypotheses of impact-induced origin (Smith and Dawson 1985) and chemical vapor deposition origin (Garai et al. 2006) are both inconsistent with our results. The first reason is that C-O-H fluid is not likely to be present during impact or in interstellar space where chemical vapor deposition occurred. The second reason is that it is difficult to form a smooth interface between diamond and fluid during impact-induced rapid crystallization or chemical vapor deposition of diamond. In addition, previous studies (e.g., McCall 2009) pointed out that it is difficult to form coarse diamond crystals by mechanisms suggested by these hypotheses; in fact, interstellar diamonds are ca. 2–3 orders of magnitude smaller in crystal size (e.g., Lewis et al. 1989).

Based on the present observations, we propose the formation process of carbonado as follows; C-O-H fluid was highly oversaturated in carbon under the diamond-stable conditions, and then diamond crystals crystallized rapidly to form a porous polycrystalline body of carbonado. This process explains all of our observations such as presence of fluid inclusions, random crystallographic orientation, CSD, the {111} growth steps found as the zigzag grain boundary, and multi-angular voids surrounded by the {111} steps.

Oversaturation of carbon in C-O-H fluid is realized by several ways. Figure 6 shows the isobaric and isothermal phase diagram for the C-O-H system calculated using the G-Fluid program (Zhang and Duan 2009). The phase relation in Figure 6 was calculated for conditions of 1673 K and 6 GPa; no notable shift was found in the phase boundary by changes in pressure and temperature. The figure suggests that the redox reaction causes the C-O-H fluid to be oversaturated in carbon. The redox reaction includes: (1) oxidation of relatively reduced fluid chiefly composed of CH₄ and H₂O (arrow 1 in Fig. 6); (2) reduction of relatively oxidized fluid chiefly composed of CO₂ and H₂O (arrow 2 in Fig. 6); and (3) mixing between the oxidized and reduced C-O-H fluids (arrow 3 in Fig. 6). The first option may be realized by ascent of highly reduced lower mantle-derived fluid into more oxidized upper mantle. On the other hand, the second option may be realized when subduction-related, relatively oxidized C-O-H fluid infiltrated into more reduced upper mantle. The third option may occur in both the first and second cases. Reaction with metastable carbonaceous matter also induces carbon-oversaturation of C-O-H fluid. This may occur when C-O-H fluid encountered metastable carbon and/or when kinetically sluggish reactions in the mixture of metastable carbon and C-O-H fluid are activated by heating. This may be similar to the formation of subduction-related metamorphic diamonds.

In addition, we cannot exclude the possibility of cooling as a cause of carbon oversaturation in C-O-H fluid. Thus, diamond crystallization from C-O-H fluid in the mantle where diamond is thermodynamically stable is a reasonable process for formation of polycrystalline diamond.

Redox conditions and location for carbonado formation

The redox conditions of diamond formation can be constrained from the composition of coexisting C-O-H fluid because it significantly depends on fO₂ under diamond-saturated conditions (e.g., Sokol et al. 2009; Zhang and Duan 2009; Woodland and Koch 2003). Figure 7 shows the relations between ΔQMF (the difference of log fO₂ from that of the quartz-magnetite-fayalite buffer) and mole fractions of H₂O, CO₂, and CH₄ (XH₂O, XCO₂, and XCH₄, respectively) in C-O-H fluid under carbon-saturated, various fO₂ conditions at 1673 K and 6 GPa calculated using the G-Fluid program (Zhang and Duan 2009). Under oxidized conditions (ΔQMF = 0), C-O-H fluid is chiefly composed of CO₂ and H₂O is minor. XCO₂ decreases and XH₂O increases with reduction. XH₂O reaches a maximum (~0.9) near the fO₂ condition of ca. 3 log unit below the QMF buffer. Under this condition, both CO₂ and CH₄ are minor. Under more reduced conditions, XH₂O decreases and XCH₄ increases. Hereafter, we denote the fO₂ at which XH₂O reaches a maximum as the maximum H₂O condition. Our results suggest that the fO₂ condition of carbonado formation was near the fO₂ where the mole fraction of H₂O was at a maximum.

In Figure 7, we compare the XH₂O-ΔQMF relation of 1673 K and 6 GPa with those of 1273 K, 4 GPa and 2073 K, 8 GPa. Although the maximum H₂O condition depends on both

![Figure 6. Isobaric-isothermal phase diagram for the C-O-H system at 1673 K, 6 GPa calculated using the G-Fluid program (Zhang and Duan 2009). The white arrow indicates crystallization of diamond from carbon-oversaturated fluid. Arrows 1–3 indicate the mechanisms of carbon-oversaturation of C-O-H fluid; oxidation of fluid more reduced than H₂O (arrow 1), reduction of fluid more oxidized than H₂O (arrow 2), and mixing of reduced and oxidized fluids (arrow 3).]
temperature and pressure, it varies only within a narrow range of $\Delta QMF$ value from $-2$ to $-4$ under $P-T$ conditions ranging from 1173–2073 K and 4–9 GPa. Zhang and Duan (2009) already showed that the maximum $H_2O$ condition in cratonic upper mantle geotherm is around ca. 2.5–3.5 log units below the QMF buffer in the depth range of 50–250 km. The $f_{O_2}$ condition is consistent with those revealed by mantle xenoliths derived from depths ranging from 120–200 km in cratonic lithosphere (e.g., Woodland and Koch 2003). This suggests that the maximum $H_2O$ condition is the prevailing condition in cratonic lithosphere, and therefore, we think that cratonic upper mantle may be one of the possible locations of carbonado formation. This is consistent with the similarity of IR spectra between hydrous fluid inclusion-bearing cratonic diamond and carbonado, as described previously. In addition, this is also consistent with a temperature constraint from IR spectra (Kagi and Fukura 2008); these authors revealed that a temperature higher than 1173 K was required to form a nitrogen aggregation state in carbonado diamond with duration on the order of 1 Gyr. Temperature in cratonic mantle is generally higher than 1173 K at diamond-stable pressure (Pollock and Chapman 1977). Although the surface of a subducting slab is where $^{13}$C-depleted metamorphic diamond and, in fact, diamonds with $^{13}$C/$^{12}$C isotope ratios lower than carbonado have been reported in subduction-related eclogite (e.g., De Stefano et al. 2000), the temperature is lower than 1173 K even at 9 GPa (Syracuse et al. 2010).

If carbonado was crystallized in the cratonic upper mantle, $^{13}$C-depleted nature of carbonado indicates that its parental C/O-H fluid was derived from any $^{13}$C-depleted carbon reservoir, which is other than the representative mantle carbon reservoir, in deep mantle. Recently, Cartigny (2010) reported diamond single crystals from the Dachine komatiite, French Guiana, with C- and N-isotope compositions identical to those of carbonado and proposed that the diamond single crystals were genetically related to carbonado. The single diamonds in komatiite indicate that a $^{13}$C-depleted reservoir existed in deep mantle. One possible $^{13}$C-depleted carbon reservoir is an accumulated organic carbon recycled into Earth’s interior by subduction. Alternatively, a possible reservoir proposed by Cartigny (2010) is that the mantle transition zone contained a $^{13}$C-depleted carbon reservoir distinct from recycled organic carbon. We cannot identify the carbon source of carbonado from the present results. However, carbonado may contain information on the carbon reservoir in the mantle. Further analyses of carbonado are expected to clarify its carbon source, which may provide fundamental insights into the deep carbon cycle.

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**FIGURE 7.** Composition of diamond-saturated C-O-H fluid system calculated using the G-Fluid program (Zhang and Duan 2009). Thick solid, thin broken, and gray solid curve, respectively, indicates the relation between mole fraction and $\Delta QMF$ (the difference of log $f_{O_2}$ from that of the quartz-magnetite-fayalite buffer) for $H_2O$, CO$_2$, and CH$_4$ under the condition of 1673 K and 6 GPa. The thick broken and dotted curve indicates the relation of $H_2O$ under conditions of 2073 K, 8 GPa and 1273 K, 4 GPa, respectively.
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