Effect of Oxygen on Diamond Crystallization in Metal–Carbon Systems

Yuri N. Palyanov,* Yuri M. Borzdov, Igor N. Kupriyanov, Yuliya V. Bataleva, and Denis V. Nechaev

ABSTRACT: In this article, we report the influence of oxygen concentration in the transition-metal solvent-catalyst on the crystallization processes, morphology, and defect-and-impurity content of diamond crystals. In a series of experiments, the concentration of oxygen \((C_O)\) in the growth system was varied by adding \(\text{Fe}_2\text{O}_3\) to the charge, and the other parameters and conditions of the growth were constant: \(\text{Ni}-\text{Fe}_3\) solvent-catalyst, \(P = 6.0\ \text{GPa}, T = 1400\ \text{°C},\) and duration of 40 h. It is found that on increasing \(C_O\) in the growth system from 0 to 10 wt %, the crystallization of diamond proceeds through the following stages: single crystal \(\rightarrow\) block crystal \(\rightarrow\) spontaneous crystals \(\rightarrow\) aggregate of block crystals and twin crystals. At \(C_O \geq 5\ \text{wt} %\), diamond crystallizes jointly with wustite (\(\text{FeO}\)) and metastable graphite. The oxygen solubility in the iron–nickel melt is estimated at about 2 wt %. With increasing oxygen content in the system, the range of nitrogen concentrations in diamonds crystallized in one experiment significantly broadens with the maximum nitrogen concentrations being increased from 200–250 ppm in the experiment without \(O\) additives to 1100–1200 ppm in the experiment with 10 wt % \(O\) added. The established joint growth of diamond and wustite suggests possible crystallization of natural diamonds in the \(\text{Fe}–\text{Ni}–\text{O}–\text{C}\) system over a wide range of oxygen concentrations up to 10 wt %.

INTRODUCTION

Diamond crystallization aided by transition-metal (TM) catalysts at high-pressure, high-temperature (HPHT) conditions has been studied for more than five decades following the pioneering works of the General Electric diamond research team.\(^1\)–\(^5\) At present, the HPHT synthesis with TM catalysts has evolved into a mature technology of industrial production of a variety of diamond materials ranging from abrasive grids to large single-crystal diamonds (SCDs).\(^6\)–\(^10\) In addition, TM catalysts represent a well-elaborated basic system for investigating the effects of various synthesis conditions on the growth and properties of diamond. One of the most important factors determining the boundary conditions of crystallization, morphology, real structure, and properties of diamond is the effect of impurities. Nitrogen, which is an omnipresent impurity in synthetic and natural diamonds, has been shown to drastically influence diamond growth process and lead to significant changes in the real structure and properties of diamond crystals.\(^7\)–\(^9\) It has been shown that the addition of small amounts of \(\text{H}_2\text{O}\) to the metal–carbon systems gives rise to the impurity adsorption effect on diamond growth and leads to the formation of specific antiskeletal crystals.\(^10,11\) An increase in the \(\text{H}_2\text{O}\) content in the growth system leads to a decrease in the nitrogen content in diamonds and the appearance of hydrocarbon inclusions.\(^10\) When \(\text{H}_2\text{O}\) is added in concentrations more than 0.43 wt %, diamond nucleation and growth are completely terminated and only graphite crystallizes in the experiments.\(^10\)

In the majority of experimental studies undertaken in recent years, various chemical compounds were added to metal–carbon systems, making it possible to investigate the joint effect of several additives on diamond crystallization.\(^12\)–\(^14\) Among the individual impurities whose effect on the crystallization of diamond in metal–carbon systems has not been thoroughly studied yet, special attention should be paid to oxygen. First of all, oxygen is a common uncontrolled impurity in the processes of synthesis and growth of diamond, since it is always present in the starting reagents and materials of high-pressure cells as an adsorbed gaseous component. Therefore, it is important to get a clear understanding of how the oxygen content in the growth system can affect diamond crystallization. Another factor determining the interest in studying the effect of oxygen on diamond crystallization from the metal–carbon media is associated with the formation of natural diamond. It is known that oxygen fugacity is an important factor controlling the formation of carbon and carbon-bearing phases (carbides, diamond, graphite, carbonates, hydrocarbons, and \(\text{CO}_2\)) in the Earth’s deep zones.\(^15\)–\(^23\) According to modern concepts, with increasing depth, the

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conditions in the Earth’s mantle become more reduced and, starting from a pressure of about 7.5 GPa, the occurrence of metallic iron is possible.\textsuperscript{24,25} Findings of metal inclusions in natural diamonds suggest that some of them were formed with direct participation of metal–carbon melts.\textsuperscript{26–32} Moreover, inclusions of iron and wustite or magnesiowustite have been found in natural diamonds, indicating the presence of oxygen in the diamond-forming medium based on the metal–carbon system.

Given the presence of oxygen in the crystallization environment of synthetic and natural diamonds, as well as the lack of experimental data on its effect on the nucleation and growth of diamond, we conducted a series of experiments in the Fe-Ni-O-C system with different oxygen contents and evaluated the effect of oxygen content on diamond crystallization, its properties, and morphology.

\section*{RESULTS AND DISCUSSION}

To investigate the effect of oxygen concentration on diamond crystallization, we performed a series of experiments using a Ni\textsubscript{7}Fe\textsubscript{3} solvent-catalyst with Fe\textsubscript{2}O\textsubscript{3} additives. The concentrations of the metallic iron and hematite in the starting charge were varied to change the oxygen concentration in the growth system from 0 to 10 wt \% while keeping the solvent-catalyst to the nominal Ni\textsubscript{7}Fe\textsubscript{3} composition. The experimental conditions and results are summarized in Table 1. The oxygen concentrations are given in weight percent relative to the weight of the metal solvent-catalyst. In the control experiment (\textnumero\textsuperscript{659/8}) performed without Fe\textsubscript{2}O\textsubscript{3} additives, three single-crystal diamonds (SCDs) with a total weight of 152.15 mg were grown on the seeds (Figure 1a). No spontaneously nucleated diamonds were found in the run products. The produced crystals had a form of flattened octahedrons with minor {100} faces. From the Fourier transform infrared (FTIR) analysis, it was found that the crystals contained nitrogen impurities predominantly in the form of isolated substitutional atoms (C centers) with a concentration of 200–300 ppm. Note that nitrogen concentrations in the crystals increased, the IR spectra in the one-phonon region changed to demonstrate nitrogen pairs (A centers). The latter was formed through the nitrogen aggregation process, whose rate depends on nitrogen concentration.\textsuperscript{33}

![Diamond crystals grown on the seeds in the Ni\textsubscript{7}Fe\textsubscript{3}-C system with different oxygen concentrations: (a) single crystals from the run without O additives and (b) a block crystal from the run with 0.25 wt \% O.](https://dx.doi.org/10.1021/acsomega.0c02130)

In the experiment with the oxygen concentration of 0.25 wt \% (run 699/6), single-crystal diamonds grew on two seeds and a diamond crystal having a block structure grew on the third seed (Figure 1b). For convenience, diamond crystals of the latter type will be further referred to as the block crystals. Figure 2 shows the infrared absorption spectra recorded for diamond crystals produced in run 699/6. From the calculations, it was found that the single-crystal diamonds contained 350–400 ppm of nitrogen, whereas nitrogen content of the block crystal was in the range 200–250 ppm. Note that as the nitrogen concentrations in the crystals increased, the IR spectra in the one-phonon region changed to demonstrate both isolated substitutional nitrogen (C centers) and nitrogen pairs (A centers). The latter was formed through the nitrogen aggregation process, whose rate depends on nitrogen concentration.\textsuperscript{33}

![IR spectra of diamond crystals produced at C\textsubscript{O} = 0.25 wt \% (run 699/6). The spectra were recorded for (a) a single crystal and (b) a block crystal grown on the seeds. Spectrum (a) is 4 cm\textsuperscript{-1} offset for clarity.](https://dx.doi.org/10.1021/acsomega.0c02130)

At C\textsubscript{O} of 0.5 wt \%, it was found that, in addition to diamond growth on the seeds, diamond formation via spontaneous nucleation also took place. Several relatively large spontaneously grown crystals formed irregular intergrowths with block diamonds grown on the seeds. The morphology of the crystals was determined by the dominant octahedral faces and minor cubic and trapezohedral faces. The crystals were characterized by the skeletal structure of individual {111} faces, blocking, and twinning. The crystals contained inclusions of the metal catalyst. The nitrogen concentration was found to vary in the range of 350–450 ppm for the single-crystal diamonds and 200–250 ppm for the block crystals. An

\begin{table}
\centering
\caption{Experimental Conditions and Results}
\begin{tabular}{|c|c|c|c|c|c|}
\hline
run & additive & C\textsubscript{O} (wt \%) & product\textsuperscript{a} & nitrogen content (ppm) & min & max \\
\hline
659/8 & Fe\textsubscript{2}O\textsubscript{3} & 0.1 & SCD & 200 & 250 \\
1228/7 & Fe\textsubscript{2}O\textsubscript{3} & 0.25 & SCD + BCD & 220 & 400 \\
699/6 & Fe\textsubscript{2}O\textsubscript{3} & 0.5 & BCD + SCD + SpCD & 200 & 450 \\
1224/7 & Fe\textsubscript{2}O\textsubscript{3} & 1 & SpCD + ADC + BCD & 200 & 550 \\
662/8 & Fe\textsubscript{2}O\textsubscript{3} & 2 & ADC + SpCD + BCD & 200 & 650 \\
1225/7 & Fe\textsubscript{2}O\textsubscript{3} & 5 & ADC + GR + Wu & 200 & 800 \\
1227/7 & Fe\textsubscript{2}O\textsubscript{3} & 10 & ADC + Wu + GR & 200 & 1200 \\
\hline
\textsuperscript{a}SCD, single-crystal diamond; BCD, block crystal diamond; SpCD, spontaneously nucleated diamond crystals; ADC, aggregate of diamond crystals; GR, graphite; Wu, wustite.
\end{tabular}
\end{table}
experiment with the oxygen content of 1 wt % yielded a large number of spontaneous diamond crystals, aggregates of spontaneous crystals, and block crystals grown on the seeds. Diamonds formed a polycrystalline aggregate of differently oriented crystals, among which there were numerous polysynthetic and cyclic twins and crystals with a block structure of the {111} faces. The morphology of diamonds was determined by the dominant {111} faces, while the cubic and trapezohedral faces were less developed. Most of the block crystals whose IR spectra were recorded contained around 200–250 ppm of nitrogen. Spontaneous diamond crystals showed a broader range of nitrogen concentrations reaching up to 500–550 ppm. At C_O equal to 2 wt %, diamond crystallized mainly in the form of spontaneous crystals up to 1–2 mm in size, which formed irregular intergrowths. Diamond growth on the seeds was negligible relative to the spontaneous crystallization. The crystals forming the intergrowths were characterized by intense twinning and blocking. From the IR measurements, it was found that the nitrogen concentration in crystallized diamonds varied from about 200 to 600–650 ppm.

In the experiment with the oxygen content of 5 wt %, aggregates of octahedral diamond crystals, wustite crystals, and metastable graphite were established. Figure 3 shows a typical aggregate of diamond crystals, illustrating the joint growth of diamond and graphite (Figure 3b), as well as spherical graphite crystals formed at the quenching stage (Figure 3c,d). In the experiment with C_O of 10 wt %, an aggregate consisting of spontaneous diamond crystals, graphite, and wustite was produced. A sample illustrating an overgrowth of diamond, graphite, and wustite is shown in Figure 4a. The aggregate of diamond crystals consisted of isometric, plate, or prismatic crystals and diamond twins. Many diamond crystals formed intergrowths with wustite crystals, indicating their joint crystallization from the metal catalyst melt saturated with carbon and oxygen (Figure 4b–d). Some of the diamond crystals demonstrated pronounced features characteristic of antiskeletal growth (Figure 5a–c). The joint growth of wustite and graphite led to the formation of specific intergrowths shown in Figure 6a. Separate octahedral wustite crystals were always coated with a thin layer of graphite (Figure 6b). The crystallized diamond, newly formed metastable graphite, and quenched graphite or graphite-like carbon produced in experiments with C_O equal to 5 and 10 wt % were readily discriminated by Raman microspectroscopy (Figure 7).

To clarify the effect of oxygen impurities on diamond crystallization and the specificity of phase formation, cross-section plates were prepared from the quenched metal samples recovered after the experiments, which were then used for SEM/energy-dispersive spectrometry (EDS) investigations of the phase composition and texture. The representative samples are shown in Figure 9. In the experiment without Fe_2O_3 additives, quenched metal melt with the composition close to the starting one and quenched carbon were established (Figure 9a). At C_O of 0.1 wt %, single wustite dendrites were detected in the quenched melt. On increasing the oxygen content in the system to 0.5 wt %, the quantity and sizes of the wustite dendrites increased. A typical structure of a sample consisting of a Ni–Fe alloy and quenched carbon is shown in Figure 9b. At C_O equal to 0.5 wt %, quenched wustite dendrites surrounded with quenched carbon were abundant in the
sample (Figure 9b,c) and their amount further increased on increasing $C_O$ to 2 wt %. In the experiment with 5 wt % oxygen content in the system, relatively large wustite crystals were formed from the melt (Figure 9d,e). At $C_O$ equal to 10 wt %, the amount and sizes of the wustite crystals further increased (Figure 9f). It should also be noted that with increasing oxygen content in the growth system, the width of the reaction zone between the metal melt and the MgO insulating sleeve increased. This reaction zone consisted of magnesiowustite containing up to 8.5 wt % Mg in the systems with an oxygen content of 10 wt %. The appearance of wustite macrocrystals at $C_O \geq 5$ wt % indicates that the metal melt was saturated with oxygen. On increasing the concentration of Fe$_2$O$_3$ additive and the oxygen content in the system, partial oxidation of iron in the melt took place. As a result, the composition of the melt changed relative to the starting experiment with 29.4 wt % Fe towards substantially less ferrous compositions containing 8.2 wt % Fe at $C_O = 10$ wt %. Elemental EDS analysis showed that the oxygen content in the sample recovered from the control run without Fe$_2$O$_3$ additives was below the detection limit, that is, less than approximately 0.3 wt %. For the sample recovered from the experiment with 2 wt % O, the concentration of oxygen in the quenched melt was determined as approximately 2 wt %. Samples produced in the experiments with 5 and 10 wt % O showed a highly inhomogeneous distribution of quenched wustite microdendrites that complicated the precise determination of the bulk oxygen content in the quenched catalyst melt. In this case, we applied an areal EDS analysis confining to those parts of the samples that did not contain wustite macrocrystals. Form these measurements, we found that for both samples the concentration of oxygen in the quenched metal melt was nearly 2 wt %. Consequently, we can infer that the solubility of oxygen in the molten Fe−Ni alloy at 6.0 GPa and 1400 °C is approximately 2 wt %.

The results obtained in this study on the effect of oxygen additives on diamond crystallization show that in the region of low oxygen contents, the growth of single-crystal diamonds on the seeds is affected. At $C_O \geq 0.25$ wt %, the growth of high-quality diamond single crystals is replaced by the growth of block crystals. At $C_O \geq 0.5$ wt %, spontaneous diamond crystals appear in the run products, which at higher oxygen concentrations dominate over the diamond growth on the seeds. The established regularity is of importance for growing high-quality diamond single crystals. It is possible that oxygen,
which is always present in the starting reagents and represents a poorly controlled factor, may be one of the reasons for the unsuccessful experiments on the growth of high-quality diamond single crystals. In iron-bearing growth systems, the occurrence of quenched wustite can be an indicator of the increased concentration of oxygen in the system.

It is of interest to compare the effect of oxygen, nitrogen, and water additives on diamond crystallization from the Ni\textsubscript{7}Fe\textsubscript{3} catalyst at similar $P$--$T$ conditions. An increase in nitrogen and oxygen contents in the growth system leads to the following change in the growth stages: single crystal $\rightarrow$ block crystal $\rightarrow$ aggregate of block crystals and twins.\textsuperscript{7} The effect of H\textsubscript{2}O is different. It is established that the addition of H\textsubscript{2}O gives rise to the phenomenon of the impurity adsorption effect and leads to the formation of a series of morphologically diverse crystals with the antiskeletal structure of the faces.\textsuperscript{10,11} The principal distinction of water and nitrogen additives from oxygen additives is that the addition of water in concentrations above 0.43 wt % and nitrogen in concentrations above 0.4 atomic % completely blocks the nucleation and growth of diamond and leads to crystallization of exclusively metastable graphite.\textsuperscript{10,11} Oxygen, when added even in relatively high concentrations, does not completely block synthesis and growth of diamond. Only at $C_{O} = 5$ wt %, metastable graphite starts to crystallize, and even at 10 wt % O, diamond continues to crystallize, although together with metastable graphite.

An increase in the oxygen content in the growth system also leads to changes in the defect-and-impurity content of crystallized diamonds. Figure 10 shows how the minimum and maximum nitrogen concentrations in crystallized diamonds change with increasing oxygen content. Two trends are clearly visible: (i) an increase in the maximum concentration of nitrogen in the crystals from about 200 to 1100--1200 ppm and (ii) an increase in the interval of nitrogen concentrations found for the crystals produced in one experiment. We suggest that the observed variations in the nitrogen content of the synthesized diamonds can be explained as follows. We found that on increasing Fe\textsubscript{2}O\textsubscript{3} concentration in the starting composition, the amount of magnesiowustite formed at the interface between the metal melt and the MgO insulating sleeve increases. In addition, at high oxygen contents (5 and 10 wt %), macrocrystalline wustite crystallizes in the system. Because of the formation of magnesiowustite and wustite, the overall amount of the melt progressively decreases and the melt composition becomes substantially depleted in iron. Therefore, one may expect that the concentration of nitrogen dissolved in the catalyst melt increases. Since diamond crystallization took place over the entire period of a synthesis run, then, it follows that diamond crystals formed at different stages were crystallized from catalyst melts with different compositions. Existing experimental data indicate that a decrease in the iron content in iron--nickel melts leads to the formation of diamonds with higher nitrogen concentrations.\textsuperscript{14} Thus, both the enrichment of the catalyst melt composition with nitrogen and depletion of iron favors crystallization of diamonds with higher nitrogen content.
proposed model can explain both the observed increase in the maximum concentration of nitrogen in synthesized diamonds with increasing oxygen content in the system and the increase in the range of nitrogen concentrations found for the crystals produced in one experiment.

The results obtained in this study are also of interest in reconstructing the conditions of the formation of a part of natural diamonds, whose crystallization is associated with metallic media. Such diamonds contain inclusions of iron, carbides, wustite, and magnesiowustite.\(^{26−32,35−40}\) Our experiments showed that oxygen, as opposed to nitrogen and water, does not have a pronounced inhibitory effect on diamond crystallization. Diamond nucleation and growth are possible over a wide range of compositions in the Fe–Ni–O–C system at oxygen contents up to 10 wt %. At the \(P−T\) conditions of natural diamond formation, diamond crystallization occurs in metal–carbon melts saturated with oxygen. At higher oxygen contents in the system, diamond crystallizes jointly with wustite, making it possible for wustite inclusions to be entrapped by the growing diamond.

Finally, we want to note that after this work had been carried out and submitted for consideration of publication in ACS Omega, we became aware of a recently published article\(^{41}\) reporting the effect of Fe\(_3\)O\(_4\) additive on the synthesis and characteristics of diamond from a Fe–Ni catalyst. Despite the fact that the present study and the study reported by Fang et al.\(^{41}\) were performed using different catalyst compositions, oxygen additives, and the range of oxygen concentrations, the obtained results show some similar trends in oxygen effects on diamond growth and nitrogen impurity content of synthesized diamonds.

**CONCLUSIONS**

The results obtained in this study allow us to draw the following main conclusions.

1. For the first time, the effect of oxygen impurity on diamond crystallization in metallic (Fe, Ni) melt has been studied. It is found that as the oxygen content in the growth system increases from 0 to 10 wt %, the crystallization of diamond proceeds through the following stages: single crystal → block crystal → spontaneous crystals → aggregate of block crystals and twin crystals. Our results show that even small concentrations of oxygen in the growth system lead to a marked deterioration in crystal quality and an increase in the intensity of spontaneous nucleation. Therefore, it is important to control the oxygen content in experiments on the growth of large high-quality single crystals of diamond.

2. At 6 GPa, 1400 °C, and high oxygen contents in the system, comprising 5 and 10 wt %, diamond crystallizes jointly with wustite (FeO) and metastable graphite. The oxygen solubility in the iron–nickel melt can be estimated at about 2 wt %.

3. It is found that with increasing oxygen content in the system, the range of nitrogen concentrations in diamonds crystallized in one experiment significantly broadens with the maximum nitrogen concentrations being increased from 200−250 ppm in the experiment without O additives to 1100−1200 ppm in the experiment with 10 wt % O added. It is suggested that the observed variations in the nitrogen content of diamonds are associated with a change in the composition of the solvent-catalyst caused by the crystallization of magnesiowustite and wustite.

4. Joint growth of diamond and wustite is established, suggesting possible crystallization of natural diamonds in the Fe–Ni–O–C system over a wide range of oxygen concentrations up to 10 wt % and explaining possible conditions for the formation of wustite or wustite–metal inclusions in some natural diamonds.

**EXPERIMENTAL SECTION**

Experiments on diamond crystallization via the temperature gradient method were carried out using a split-sphere high-pressure apparatus.\(^{7}\) A Fe–Ni alloy was used as a solvent-catalyst. Fe\(_2\)O\(_3\) (hematite) was used as an oxygen-containing additive. The powders of iron, nickel, and hematite were thoroughly mixed and pressed. The concentrations of starting reagents in the charge were calculated so that the Ni–Fe–O system contained Ni and Fe in a constant ratio corresponding to the Ni\(_3\)Fe\(_7\) composition. Graphite (99.99%) was used as a carbon source. In each experiment, three 0.5 mm synthetic diamond seeds were used, which were oriented along the (111) plane. In a series of experiments, an identical sample assembly, a pressure of 6 GPa, a temperature of 1400 °C, and a duration of 40 h were applied. The only variable parameter was the oxygen content in the system, which was varied from 0 to 10 wt %. After experiments, a fragment of the quenched metal catalyst was sawed out, from which a polished section was prepared for the analysis of the structure and composition of the quenched catalyst melt. The remaining samples were dissolved in a heated mixture of HCl and HNO\(_3\) acids to recover diamonds.

The produced diamond crystals as well as phase and chemical compositions of samples were studied by scanning electron microscopy (SEM) and energy-dispersive spectroscopy (EDS) using a Tescan MIRA3 LMU scanning electron microscope. Analyses of final phases were acquired at an accelerating voltage of 20 kV, a probe current of 20 nA, a counting time of 20 s on each analytical line, and an electron beam probe diameter of 2−4 μm. In the case of quenched melts, we reduced the accelerating voltage to 15 kV, the probe current to 10 nA, the counting time to 10 s, and used a defocused beam (20−100 μm in diameter). The estimation of oxygen content in the quenched melt was performed by SEM and EDS analyses (measurement accuracy of ~0.3 wt %), including areal analysis. For each sample, at least 20 analyses of the bulk melt composition were made and averaged. However, due to an uneven distribution of quenched wustite in the melt, the areal abundance of quenched wustite was calculated and converted into the bulk oxygen content. These analytical studies were carried out at the Analytical Center for Multi-Element and Isotope Analysis of the Siberian Branch of the Russian Academy of Sciences.

Carbon phases (diamond/graphite) produced in the experiments were identified using Raman microspectroscopy. Raman spectra were recorded using a Horiba J.Y. LabRAM HR800 spectrometer coupled with an Olympus BX41 microscope. A diode-pumped solid-state laser emitting at 532 nm (Torus, Laser Quantum) was used as the excitation source. An Olympus ×100 (NA = 0.90) objective was used to focus the laser beam onto the sample and to collect the Raman signal.
The produced diamond crystals were studied using infrared (IR) absorption microspectroscopy. IR spectra were measured using a Bruker Vertex 70 Fourier transform infrared (FTIR) spectrometer fitted with a Hyperion 2000 microscope. The recorded spectra were converted to the absorption coefficient units by fitting to the standard infrared spectrum of type IIa diamond to obtain the best fit of the intrinsic two-phonon absorption bands (2700–1700 cm\(^{-1}\)). The concentrations of nitrogen in the form of C and A centers were determined by decomposing the IR spectra, in the one-phonon region (1350–900 cm\(^{-1}\)), into the corresponding components and using conversion factors of 25 atomic ppm cm\(^{-1}\) of absorption at 1130 cm\(^{-1}\) for the C centers\(^{(42)}\) and 16.5 atomic ppm cm\(^{-1}\) of absorption at 1280 cm\(^{-1}\) for the A centers.\(^{(43)}\) The spectra were processed using a Bruker OPUS software package. The total nitrogen concentrations were calculated by summing up the concentrations of C and A centers.

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**REFERENCES**

1. Bundy, F. P.; Hall, H. T.; Strong, H. M.; Wentorf, R. H., Jr. Man-made diamonds. Nature 1955, 176, 51–54.
2. Strong, H. M.; Hanneman, R. E. Crystallization of diamond and graphite. J. Phys. Chem. A 1967, 46, 3668–3676.
3. Wentorf, R. H. Some studies of diamond growth rates. J. Phys. Chem. B 1971, 75, 1833–1837.
4. Wedlake, R. J. Technology of Diamond Growth. In The Properties of Diamond, Field, J. E., Ed.; Academic Press: London, UK, 1979; pp 501–535.
5. Palyanov, Y.; Kupriyanov, I.; Khokhryakov, A.; Raichenko, V. Crystal Growth of Diamond. In Handbook of Crystal Growth, Nishinaga, T.; Rudolph, P., Eds.; Elsevier: 2015; Vol. II, pp. 671–713. (Chapter 17).
6. D’Haenens-Johannsson, U. F. S.; Katrusha, A.; Moe, K. S.; Johnson, P.; Wang, W. Large colorless HPHT-grown synthetic gem diamonds from New Diamond Technology, Russia. Gems Genom. 2015, 51, 260–279.
7. Palyanov, Y. N.; Borzdov, Y. M.; Khokhryakov, A. F.; Kupriyanov, I. N.; Sokol, A. G. Effect of nitrogen impurity on diamond crystal growth processes. Cryst. Growth Des. 2010, 10, 3169–3175.
8. Zhang, Y.; Zang, C.; Ma, H.; Liang, Z.; Zhou, L.; Li, S.; Jia, X. HPHT synthesis of large single crystal diamond doped with high nitrogen concentration. Diamond Relat. Mater. 2008, 17, 209–211.
9. Liu, X.; Jia, X.; Zhang, Z.; Li, Y.; Hu, M.; Zhou, Z.; Ma, H. A. Crystal growth and characterization of diamond from carbonyl iron catalyst under high pressure and high temperature conditions. Cryst. Growth Des. 2011, 11, 3844–3849.
10. Palyanov, Y. N.; Borzdov, Y. M.; Kupriyanov, I. N.; Khokhryakov, A. F. Effect of H2O on diamond crystal growth in metal-carbon systems. Cryst. Growth Des. 2012, 12, 5571–5578.
11. Palyanov, Y. N.; Khokhryakov, A. F.; Borzdov, Y. M.; Kupriyanov, I. N. Diamond growth and morphology under the influence of impurity adsorption. Cryst. Growth Des. 2013, 13, 5411–5419.
12. Fang, C.; Zhang, Y.; Shen, W.; Sun, S.; Zhang, Z.; Xue, L.; Jia, X. Synthesis and characterization of HPHT large single-crystal diamonds under the simultaneous influence of oxygen and hydrogen. CrystEngComm 2017, 19, 5727–5734.
13. Huang, G.; Zheng, Y.; Peng, L.; Li, Z.; Jia, X.; Ma, H. Crystallization of HPHT diamond crystals in a floatage system under the influence of nitrogen and hydrogen simultaneously. CrystEngComm. 2015, 17, 6504–6511.
14. Sun, S.; Jia, X.; Yan, B.; Wang, F.; Li, Y.; Chen, N.; Ma, H. A. Synergistic effect of nitrogen and hydrogen on diamond crystal growth at high pressure and high temperature. Diamond Relat. Mater. 2014, 42, 21–27.
15. Luth, R. W. Carbon and Carbonsates in the Mantle. In Mantle Petrology, Fei, Y.; Bertka, C. M.; Mysen, B. O., Eds.; Geochemical Society: St. Louis, 1999; pp 297–316.
16. Shirey, S. B.; Cartigny, P.; Frost, D. J.; Nestola, F.; Nimis, P.; Pearson, D. G.; Sobolev, N. V.; Walter, M. J. Diamonds and the geology of mantle carbon. Rev. Mineral. Geochem. 2013, 75, 355–421.
17. Shirey, S.; Smnit, K.; Pearson, D. G.; Walter, M.; Aulbach, S.; Brenker, F.; Burea, H.; Burnham, A.; Cartigny, P.; Chacko, T.; Frost, D.; Hauri, E.; Jacob, D.; Jacobson, S.; Kohn, S.; Luth, R.; Mikhail, S.; Navon, O.; Nestola, F.; Nimis, P.; Palot, M.; Smith, E.; Stachel, T.; Stagno, V.; Steele, A.; Stern, R.; Thomsassot, E.; Thomson, A.; Weiss, Y. Diamonds and the Mantle Geodynamics of Carbon. In Deep Carbon: Past to Present, Orcutt, B.; Daniel, I.; Dasgupta, R., Eds.; Cambridge University Press: Cambridge, 2019; pp 89–128.
18. Woodland, A. B.; Koch, M. Variation in oxygen fugacity with depth in the upper mantle beneath the Kaapvaal Craton, Southern Africa. Earth Planet. Sci. Lett. 2003, 214, 295–310.
19. McCammon, C.; Kopylova, M. G. A Redox profile of the slae mantle and oxygen fugacity control in the cratonic mantle. Contrib. Mineral. Petrrol. 2004, 148, 55–68.
20. Stagno, V.; Owang, D. O.; McCammon, C. A.; Frost, D. J. The oxidation state of the mantle and the extraction of carbon from Earth’s interior. Nature 2013, 493, 84–88.
21. Yadley, G. M.; Berry, A. J.; Kamenetsky, V. S.; Woodland, A. B.; Golovin, A. V. An oxygen fugacity profile through the Siberian craton: Fe-K-edge XANES determinations of Fe3+/Fe2+ Fe in garnets in
peridotite xenoliths from the Udachnaya East Kimberlite. Lithos 2012, 140–141, 142–151.

(22) Stagno, V. Carbon, carobides, carbonates and carbonatitic melts in the Earth’s interior. J. Geol. Soc. 2019, 176, 375–387.

(23) Palyanov, Y. N.; Bataleva, Y. V.; Sokol, A. G.; Borzov, Y. M.; Kupriyanov, I. N.; Reutsky, N. V.; Sobolev, N. V. Mantle–slab interaction and redox mechanism of diamond formation. Proc. Natl. Acad. Sci. U.S.A. 2013, 110, 20408–20413.

(24) Rohrbach, A.; Ballhaus, C.; Golla–Schindler, U.; Ulmer, P.; Kamenetsky, V. S.; Kuzmin, D. V. Metal saturation in the upper mantle. Nature 2007, 449, 456–458.

(25) Rohrbach, A.; Schmidt, M. W. Redox freezing and melting in the Earth’s deep mantle resulting from carbon-iron redox coupling. Nature 2011, 472, 209–212.

(26) Meyer, H. O. A.; Svicero, D. P. Mineral inclusions in Brazilian diamonds. Phys. Chem. Earth 1975, 9, 785–795.

(27) Sobolev, N. V.; Efimova, E. S.; Pospelova, L. N. Native iron in Yakutian diamonds and its paragenesis. Soviet Geol. Geophys. 1981, 22, 18–21.

(28) Bulanova, G. P. The formation of diamond. J. Geochem. Explor. 1995, 53, 1–23.

(29) Stachel, T.; Harris, J. W.; Brey, G. P. Rare and unusual mineral inclusions in diamonds from Mwadui, Tanzania. Contrib. Mineral. Petrol. 1998, 132, 34–47.

(30) Smith, E. M.; Kopylova, M. G. Implications of metallic iron for diamonds and nitrogen in the sublithospheric mantle. Canad. J. Earth Sci. 2014, 51, 510–516.

(31) Smith, E. M.; Shirey, S. B.; Nestola, F.; Bullock, E. S.; Wang, J.; Richardson, S. H.; Wang, W. Large gem diamonds from metallic liquid in Earth’s deep mantle. Science 2016, 354, 1403–1405.

(32) Shatsky, V. S.; Ragozin, A. L.; Logvinova, A. M.; Wirth, R.; Sobolev, N. V.; et al. Diamond-rich placer deposits from iron-saturated mantle beneath the northeastern margin of the Siberian Craton. Lithos 2020, 364–365, No. 105514.

(33) Evans, T. Aggregation of nitrogen in diamond. In The Properties of Natural and Synthetic Diamond, Field, J. E., Ed.; Academic Press: London, 1992; pp 259–290.

(34) Burns, R. C.; Hansen, J. O.; Spits, R. A.; Sibanda, M.; Wellbourn, C. M.; Welch, D. L. Growth of high purity large synthetic diamond crystals. Diamond Relat. Mater. 1999, 8, 1433–1437.

(35) Wirth, R.; Kaminsky, F.; Matsyuk, S.; Schreiber, A. Unusual micro- and nano-inclusions in diamonds from the Juina Area, Brazil. Earth Planet. Sci. Lett. 2009, 286, 292–303.

(36) Kaminsky, F. V.; Wirth, R. Iron carbide inclusions in lower-mantle diamond from Juina, Brazil. Can. Mineral. 2011, 49, 555–572.

(37) Kaminsky, F. Mineralogy of the lower mantle: A review of ‘super-deep’ mineral inclusions in diamond. Earth Sci. Rev. 2012, 110, 147–177.

(38) McCammon, C. Deep diamond mysteries. Science 2001, 293, 813–814.

(39) McCammon, C. A.; Stachel, T.; Harris, J. W. Iron oxidation state in lower mantle mineral assemblages: II. Inclusions in diamonds from Kankan, Guinea. Earth Planet. Sci. Lett. 2004, 222, 423–434.

(40) Harte, B. Diamond formation in the deep mantle: the record of mineral inclusions and their distribution in relation to mantle dehydration zones. Mineral. Mag. 2010, 74, 189–215.

(41) Fang, S.; Ma, H.; Cai, Z.; Wang, C.; Fang, C.; Lu, Z.; Wang, Y.; Chen, L.; Jia, X. Study on the characteristics of Ib diamond crystals synthesized with Fe3O4 doped in an Fe-Ni-C system. CrystEngComm 2020, 22, 3854–3862.

(42) Kiflawi, I.; Mayer, A. E.; Spear, P. M.; van Wyk, J. A.; Woods, G. S. Infrared absorption by the single nitrogen and A defect centres in diamond. Philos. Mag. B 1994, 69, 1141–1147.

(43) Boyd, S. R.; Kiflawi, I.; Woods, G. S. The relationship between infrared absorption and the A defect concentration in diamond. Philos. Mag. B 1994, 69, 1149–1153.