METALLIC INCLUSIONS IN NATURAL DIAMONDS AND THEIR EVOLUTION DURING THE POST-CRYSTALLIZATION PERIOD

© 2024 V. M. Sonin [1],*, A. I. Chepurov [1],, E. I. Zhimulev [1],**
A. A. Chepurov [1], A. M. Logvinova [1], N. P. Pokhilenko [1]
[1] V.S. Sobolev Institute of Geology and Mineralogy, Siberian Branch of the Russian Academy of Sciences,
Koptyug Ave., 3, Novosibirsk, 630090 Russia
**E-mail: sonin@igm.nsc.ru*
***E-mail: chepurov @igm.nsc.ru*

Received May 03, 2024
Revised May 28, 2024
Accepted for publication August 19, 2024

Based on experimental results of diamond growth and the phase diagram of the iron-carbon system at high pressures and temperatures, an analysis of phase formation conditions in metallic inclusions in natural diamonds from kimberlites was conducted. Metallic inclusions are present in both lithospheric and sublithospheric diamonds associated with both peridotite and eclogite associations of mantle minerals. It is argued that the equilibrium phases at the post-crystallization stage of natural diamond genesis are iron carbides and oxides; the presence of native metals in inclusions indicates that equilibrium was not reached. The presence of native iron in inclusions also indicates a high rate of pressure and temperature decrease during the post-crystallization stage of natural diamond genesis. Changes in *PT*-parameters during the transport of diamonds to the Earth's surface likely occurred like an explosion, namely: a sharp drop in pressure while maintaining high temperature for some time.

Keywords: diamond, metallic inclusions, iron carbide, iron oxide, high pressure and temperature
DOI: 10.31857/S00167770250104e9

INTRODUCTION

In scientific literature, considerable attention is paid to the study of inclusions in natural diamonds, as it is believed that the information obtained helps to reconstruct their crystallization environment (for example, see reviews by Shirey et al., 2013; Stachel et al., 2022). This is especially true for diamonds from kimberlites, as they are mainly of practical significance. It has been established that inclusions in diamonds are represented by a wide range of silicate, oxide, sulfide, carbonate minerals, as well as a fluid phase. Nevertheless, there is a specific type of inclusions in natural diamonds that, in our opinion, does not receive due attention. These are the so-called "metallic" inclusions. Often, carbides and oxides of iron subgroup elements are associated with inclusions of native metals.

Articles (Titkov et al., 2003; Smith et al., 2017) directly indicate that metallic inclusions in natural diamonds were often interpreted as inclusions of graphite or sulfides. For example, diamonds from placers in the northeast of the Yakutian diamond-bearing province contain a large number of graphite and fluid phase inclusions (Afanasiev et al., 2000). However, with detailed research, metallic inclusions have only recently been discovered in them (Shatsky et al., 2020). Inclusions of native metals in natural diamonds have been known for quite a long time (Bulanova et al., 1979; Sobolev et al., 1981). This also applies to cohenite, magnetite, wüstite ((Gnevushev, Nikolaeva, 1961; Bulanova et al., 1979; Sharp, 1966). Metal inclusions, oxides, and iron carbides have also been diagnosed in sublithospheric diamonds (Kaminsky, 2012). Some interest in metallic inclusions began to emerge after their discovery in low-nitrogen diamonds of jewelry quality, type CLIPPIR (Cullinan-like, inclusion-poor, relatively pure, irregularly shaped, and resorbed). Therefore, the hypothesis of diamond crystallization in a melt of Fe-Ni-S-C composition in the presence of a reduced fluid has become relevant (Smith et al., 2016; 2017; 2018; Nestola, 2017; Daver et al., 2022).

The specificity of such inclusions lies in the fact that they are represented by so-called transition metals, mainly metals of the Fe group. They are elements with variable valence, therefore their valence state and, accordingly, the type of compound depend on the redox conditions. The second important feature of Fe group metals is the high solubility of carbon, especially in the molten state. Phases that do not dissolve carbon and, accordingly, do not interact with the diamond matrix, can be preserved in diamond crystals as inclusions in an unchanged form for an indefinitely long time. But this does not apply to metallic inclusions. Therefore, the question seems relevant: why have metallic inclusions been preserved in natural diamonds, especially considering the high temperature and pressure during their formation in the Earth's mantle? Currently, significant factual material has been accumulated both from the results of experimental studies and from natural diamonds from kimberlites. To resolve this issue, in the present work, numerous published data on metallic inclusions in natural and synthetic diamonds, their associations and transformation under the influence of experimental processing were analyzed. This article also presents the results of studying the association of metallic inclusions in diamonds using the method of analytical transmission electron microscopy.

RESULTS OF EXPERIMENTAL STUDIES AT HIGH TEMPERATURE AND PRESSURE

Since Fe is the predominant element in the composition of metallic inclusions in natural diamonds, it is reasonable to consider the phase diagram of the Fe-C system at high temperatures and pressures. Fe-based systems are widely used for artificial diamond growth (D'Haenens-Johanson et al., 2022). The phase diagram of the Fe-C system was published in a frequently cited article (Lord et al., 2009). This system is characterized by the presence of carbide phases: Fe_3C and Fe_7C_3 (fig. 1). According to (Lord et al., 2009), the Fe_7C_3 phase is recorded at a pressure of 10 GPa, while at lower pressure only the Fe_3C phase is present. But recently, Fe_7C_3 carbide has also been obtained at lower pressure (Zhimulev et al., 2012; 2016; Walker et al., 2013; Gromilov et al., 2019; Martirosyan et al., 2019). A more probable diagram of the Fe-C system is shown in fig. 2. It should be noted that there is also no established opinion regarding the value of the Fe-Fe_3C eutectic temperature at high pressure. According to (Wood, 1993), at 5 GPa, the eutectic temperature slightly exceeds 1300°C. According to (Fei et al., 2007), it is in the range of 1240-1250°C, and according to (Chabot et al., 2008), it is in the interval of 1200-1250°C. Similarly, there are disagreements about the carbon content in the eutectic: from 3.2 to 4.7 wt%. The version of the diagram shown in fig. 2 is based mainly on data from (Kocherzhinsky et al., 1992; Zhimulev et al., 2016). Ni and Co, when added to the growth system, enter the carbide phases as isomorphic impurities (Zhimulev et al., 2012).

Previously, the so-called "carbide hypothesis" was used to explain diamond synthesis in metal-carbon systems, meaning that diamond was thought to crystallize during the decomposition of the carbide phase. But attempts to synthesize diamond directly from carbides Fe_3C and Ni_3C proved unsuccessful (Vereshchagin et al., 1970; Strong, Hanneman, 1967; Wentorf, 1974). This fact is explained quite simply. Theoretically, when the temperature exceeds the melting point of the carbide, it is possible to obtain diamond, but upon cooling, the system will return to the state corresponding to the composition of the carbide. Diamond can only be preserved with very rapid cooling of the system, which is unattainable even in experiments. For stable synthesis and growth of diamond, supersaturation of the system with carbon is necessary, meaning the carbon content must exceed its amount in the carbide phase.

The situation is further complicated by the fact that in the Fe-C system during incongruent melting of Fe_3C carbide, Fe_7C_3 carbide crystallizes. Therefore, according to the phase diagram of the Fe-C system, for diamond crystallization it is necessary to overcome the melting temperatures of intermediate carbide phases, meaning the minimum temperature for diamond synthesis is determined not by the melting temperature of the eutectic in this system, but by the melting temperature of Fe_7C_3 carbide as a higher-temperature phase compared to the Fe_3C phase.

During growth, diamond crystals capture the substance of the medium from which they grow. In this case, it is a metal melt with dissolved carbon. In synthetic diamonds, including low-nitrogen crystals of type II according to the physical classification, inclusions of the growth medium mostly have a faceted appearance with a shiny surface (Chepurov et al., 2007; D'Haenens-Johanson et al., 2015; Sonin et al., 2022). As an example, we present microphotographs of such inclusions (Fig. 3). The shiny surface of metallic inclusions of the solvent/catalyst is a consequence of the fact that in experimental works, the cooling of the growth system is carried out by quenching, i.e., a very rapid decrease in temperature at high pressure.

However, let us recall that Fe is characterized by a very high solubility of carbon, which leads to a high probability of alteration of metallic inclusions in diamonds during the post-crystallization period. The paper (Anthony, 1999) lists the causes that induce these changes with decreasing pressure and cooling (or with increasing PT -parameters) of synthetic diamond crystals: (1) differences in thermal expansion coefficients between diamond and inclusion material; (2) phase changes in the inclusion material; (3) formation of cracks or plastic deformation in the diamond matrix; (4) changes in carbon concentration in the inclusion material; (5) graphitization on the walls of inclusions; (6) deposition or formation of new compounds in the inclusion. These processes usually occur together to varying degrees depending on temperature and pressure changes.

For example, in the study (Chepurov et al., 2005), the phenomenon of crack formation around metal inclusions due to differences in thermal expansion coefficients of inclusions and diamond was established. Diamond plates cut from crystals with metal inclusions, which were grown in the Fe-Ni-C system at 5.5 GPa and 1400-1500°C, were subjected to temperatures of 1800-2500°C at pressures of 7.0-7.7 GPa. It was found that when the temperature increases compared to the crystallization temperature of diamonds, a system of cracks forms around metal inclusions trapped by diamonds during growth. When inclusions open, the cracks are filled with inclusion material. At the crack propagation front, as the distance from the main inclusion increases, two-phase metal-fluid microinclusions up to 1-3 μm in size are detected (Fig. 4). It was also found that individual isometric metal-fluid microinclusions develop facets during heat treatment (Fig. 5).

Around metal inclusions in synthetic diamonds, the presence of CH_4 and H_2 was detected by Raman spectroscopy (Smith, Wang, 2016). In reality, the fluid composition in equilibrium with the metal-carbon melt in synthetic diamonds has a very complex composition (Tomilenko et al., 2018; Sonin et al., 2022). Diagnostics were carried out using gas chromatography-mass spectrometry. It has been shown that high-molecular-weight hydrocarbon compounds play a significant role in the diamond growth process, with their total share in the fluid composition potentially exceeding 86 rel. %. The reduced state of the fluid is confirmed by the H/(O+H) ratio (up to 0.95).

Since the solubility of carbon in Fe melt depends on temperature, even minor temperature changes can affect the carbon concentration inside the inclusion, and temperature gradients can lead to differences in carbon concentration. As a result, carbon dissolves on one wall of the inclusion and deposits as a diamond phase on the opposite wall. This process enables the migration of metal inclusions within the host diamond, up to the complete purification of diamond crystals from inclusions during the post-crystallization period (Fedorov et al., 2005; Chepurov et al., 2000; Sonin et al., 2003).

Graphite formation in a metallic inclusion can occur in two cases. First, at constant pressure when temperature increases to values at which diamond becomes a thermodynamically unstable phase. In this case, well-structured graphite appears. The second scenario is related to a decrease in temperature due to the temperature-dependent solubility of carbon in metal, especially during the transition of the inclusion material from liquid to solid state. The structure of graphite depends on the cooling rate. Very rapid cooling results in the crystallization of amorphous carbon (Chepurov et al., 1997). However, if cooling occurs relatively slowly and the system remains at *PT* -parameters of diamond thermodynamic stability, then as solubility decreases, it is possible for the diamond phase to precipitate within the inclusion volume. This phenomenon is likely related to the discovery of tiny diamond crystallites in metallic inclusions in natural diamonds (Garanin et al., 1991).

As previously indicated, in artificial conditions the temperature reduction after the experiment is carried out by quenching, that is, by turning off the electric current to the heating element. The temperature decreases very rapidly, therefore inclusions solidify in the form of a solid solution of carbon in metal. However, as follows from the state diagram of the system (Fig. 1, 2), with a slow temperature decrease, inclusions should consist mainly of carbide phases. This position is proved by research (Bharuth-Ram et al., 1994), in which the composition of metal inclusions in diamonds synthesized in the Fe-Co-C system at high *PT* -parameters was investigated using Mössbauer spectroscopy. It was established that the inclusions consist mainly of Fe-Co alloy, with a small amount of carbide (cogenite). But when annealing crystals at atmospheric pressure (0.1 MPa) at temperatures above 880°C, intensive carbide formation in the solid state was detected in the inclusions.

METALLIC INCLUSIONS IN NATURAL DIAMONDS

Table 1 presents the reports we found in scientific publications about the discovery of metal inclusions, oxide and carbide phases in natural diamonds. Inclusions of this type in diamonds are associated with minerals of both peridotite and eclogite paragenesis (Sobolev et al., 1981; Bulanova et al., 1993; Vinokurov et al., 1998; Gorshkov et al., 2003; Titkov et al., 2006 $_1$et al.). However, they appear to be more characteristic of sublithospheric diamonds (Hayman et al., 2005; Jones et al., 2008; Kaminsky, Wirth, 2011, etc.), including CLIPPIR-type diamonds (Smith et al., 2016, etc. - see Table 1). The vast majority of such inclusions are compounds of Fe group metals. This occurs due to the predominance of the bulk content of Fe in mantle rocks over Ni and Co. The presence of Ni is often detected. Native metals and Fe carbide have also been diagnosed in intergrowths with diamonds and in diamond indicator minerals (for example, Titkov et al., 2001; De et al., 1998; Jacob et al., 2004; Haggerty, 2017; Jacob, Mikhail, 2022)

The carbide phase in inclusions in diamonds is represented mainly by cohenite, but Fe carbide $_7C_3$ (Smith et al., 2018; Shatsky et al., 2020) has also been diagnosed. The presence of carbide phases in inclusions is of great interest. After crystallization of elemental carbon (diamond/graphite), the system under consideration evolves according to the liquidus line during cooling (Fig. 1, 2). As a result of peritectic reactions, Fe_7C_3 and Fe_3C carbides crystallize sequentially, and only after that the melt solidifies as a cohenite-solid solution of carbon in metal eutectic. As a result of this evolution, the Fe content in the melt constantly increases. Thus, native Fe can appear in inclusions only after passing through these stages of evolution, and the diagnosed phases in diamond inclusions confirm this.

Upon solidification of the melt in the eutectic, the evolution of the system does not cease. The interaction between the inclusion material and the diamond matrix should continue under subsolidus conditions. In particular, unlike metal inclusions in synthetic diamonds (Fig. 3), in natural diamonds, large inclusions of native Fe have irregular contours (Hutchison et al., 2012), which indicates this interaction. The specificity of the diamond-inclusion system is that it exists in an infinite saturation of carbon, as the inclusion is surrounded on all sides by the diamond matrix. Therefore, when the temperature decreases to subsolidus values, solid-phase reactions should occur, changing the composition toward the formation of carbides: $Fe \rightarrow Fe_3C \rightarrow Fe_7C_3$. Carbide Fe_7C_3 is a stable phase, at least from a pressure value of 5.5 GPa (Zhimulev et al., 2016; Gromilov et al., 2019); at lower pressure values, carbide Fe_7C_3 is a metastable phase, and in an inclusion in equilibrium with diamond, cementite is more likely. According to experiments (Bharuth-Ram et al., 1994), the rate of these reactions in the range of 800-900°C is quite high: hours, but not millions of years. We emphasize that during the cooling of natural diamonds with metallic inclusions, the stable phase in them should be carbide, as shown in Fig. 6. A specific feature of the depicted inclusion is the presence of nanoscale diamond inside the carbide phase. This leads to the conclusion that if native metals have been preserved in the inclusions, the cooling of diamond crystals under natural conditions occurred very rapidly by geological standards.

In the paper (Shatsky et al., 2020), it has been established that metallic inclusions in natural diamonds have a heterogeneous phase composition: carbide phase, oxide phase, and carbon, which means that another component must be considered - oxygen (Fig. 7). Wüstite typically develops from native Fe at the boundary with the diamond matrix. This fact is highlighted in the works of (Stachel et al., 1998; Shatsky et al., 2020). Magnetite formations also develop from native Fe (Sobolev et al., 1981; Vinokurov et al., 1998; Kaminsky, Wirth, 2011). The simplest explanation for the observed phenomenon is the crystallization of diamonds across a wide range of oxygen fugacity, which, nevertheless, does not explain the position of oxide phases at the boundary with the diamond matrix.

As noted earlier, the specific nature of the "inclusion - host diamond" system is that the inclusion is completely surrounded by diamond. Therefore, if there are no cracks connecting the inclusion to the crystal surface, then the redox conditions and, consequently, the fluid regime in the inclusion are determined by the CCO oxygen buffer. Of course, phase formation in this case is also determined by temperature.

Fig. 8 shows the buffer equilibrium lines of CCO, IW (iron - wüstite), WM (wüstite - magnetite), NNO (nickel - bunsenite) at 0.1 MPa and 5 GPa (Chepurov et al., 1997). At high pressure (5 GPa) under conditions controlled by the CCO buffer, at temperatures above 1250°C, the stable phases are magnetite and Ni oxide, not wüstite, and even less so native Fe and Ni. Magnetite has been diagnosed in inclusions in synthetic type IIa diamonds, that is, in a growth system in which a strong reducing agent Ti was present (Sonin et al., 2022). This proves the stability of magnetite under CCO buffer equilibrium conditions (inside the diamond crystal). Apparently, the kinetics of phase formation in metallic inclusions in natural diamonds was determined not so much by PT-parameters under which diamond crystals grew, but by post-crystallization conditions.

But the paradoxical features of metallic inclusions in natural diamonds do not end there. Sublithospheric diamonds contain inclusions of magnesioferrite, ferripericlase with tiny inclusions of native Fe and Ni (Hayman et al., 2005; Wirth et al., 2014; Anzolini et al., 2020). The CCO buffer at "normal" total pressure (0.1 MPa) is a strong reducer (Fig. 8), capable of reducing not only Ni but also Fe from oxide and silicate minerals. The composition of metallic inclusions in natural diamonds was likely influenced not only by temperature but also by pressure. Phase formation in metallic inclusions occurred mainly during the stage of diamond transport from the Earth's mantle, and the presence of native metals directly indicates that this stage is the result of some explosive process, in which relatively high temperature was maintained after a rapid decrease in pressure.

ASSOCIATED PHASES IN METALLIC INCLUSIONS IN NATURAL DIAMONDS

In metallic inclusions in natural diamonds, sulfide phases are often present together with native metals, carbides, and oxides. Sulfides are considered the most common type of inclusions in diamonds. They are represented by an association of pyrrhotite + pentlandite + chalcopyrite ± pyrite (Efimova et al., 1983; Bulanova et al., 1990). In most cases, they consist of fine-grained exsolution structures of monosulfide solid solution (Mss). This process is strongly dependent on temperature and cooling rate: even at relatively low temperatures (200–300°C), it occurs within minutes (Taylor, Lee, 2009). Considering the size of sulfide phases in diamond inclusions, it can be assumed that the crystallization of sulfides in them also occurred rather quickly. Due to the difference in thermal expansion coefficients between diamond and Mss inclusions, cracks form around them during cooling. The volume increase causes the decomposition of Mss (Taylor, Lee, 2009).

In the study (Chepurov et al., 2008), natural diamond crystals with sulfide inclusions of Fe-Ni-Cu-Co-S composition were subjected to temperature exposure at 5 GPa. Before the experiments, the sulfide inclusions were surrounded by a system of small cracks filled with dark matter - a characteristic feature of sulfide inclusions (Sobolev et al., 2001). It was established that in experiments conducted at temperatures below the melting point of sulfides, no changes in the inclusions were observed. When the melting temperature was reached, the cracks around the inclusions became lighter. This is probably due to the consolidation of the inclusion material and the cleaning of cracks from it. At temperatures corresponding to the thermodynamic stability of graphite (1600°C), the cracks became dark again due to graphitization. Thus, changes occurred only in the crack system, but the inclusions themselves did not change either in shape or location - this is due to the absence of carbon solubility in melts with M/S ~1 (Zhang et al., 2015). Accordingly, there was no interaction between the inclusion material and diamond. The conducted study (Chepurov et al., 2008) confirms the opinion expressed in works (Efimova et al., 1983; Harris, 1972) about the formation of "rosettes" of cracks around sulfide inclusions at the post-crystallization stage of diamond transport to the Earth's surface as a result of pressure reduction while maintaining high temperature.

In metal-sulfide melts, carbon solubility depends on sulfur content. Thus, the sulfur content in metal-sulfide inclusions in CLIPPIR-type diamonds reaches 6-7 wt.% (Smith et al., 2016; 2017). Such melts at high pressure have a very high carbon solubility - up to 5.5 wt.% according to (Zhang et al., 2018). The possibility of diamond synthesis in metal-sulfide melts with "pre-eutectic" compositions has been experimentally tested (Chepurov, 1988; Chepurov et al., 1994). But it should be emphasized that in this system, sulfur is not part of carbide phases, and, accordingly, carbon is not part of sulfides (Zhimulev et al., 2012; 2016).

CONCLUSIONS

- Metallic inclusions (native Fe, Fe oxides and carbides) have been diagnosed in both lithospheric and sublithospheric diamonds.
- Metallic inclusions have been diagnosed in diamonds of both peridotite and eclogite paragenesis.
- When diamonds cool down, native Fe should interact with the diamond matrix to form a carbide phase; the presence of native Fe indicates that this reaction did not complete, meaning the temperature reduction of diamonds during the post-crystallization stage occurred rather quickly.
- Metallic inclusions in natural diamonds were under redox conditions controlled by the CCO oxygen buffer, in which oxide phases are stable under high pressure conditions; the presence of native Fe in association with oxide phases also indicates a high rate of temperature decrease.
- The equilibrium phases during the post-crystallization stage of natural diamond genesis are Fe carbides and oxides; the presence of native metals in inclusions indicates that equilibrium was not achieved.
- The appearance of small Fe precipitates in inclusions at the contact between (Mg,Fe)O grains and the diamond matrix indicates changes in *PT* -parameters during diamond transport to the Earth's surface, similar to an explosion, specifically: a sharp pressure drop while maintaining high temperature for some time.

ACKNOWLEDGMENTS

The authors express deep gratitude to Dr. Richard Wirth for research conducted using transmission electron microscopy at the Helmholtz Centre Potsdam - GFZ German Research Centre for Geosciences (Germany). The authors are also grateful to the reviewers for reading the manuscript and providing valuable comments.

FUNDING

This work was carried out under the state assignment of the IGM SB RAS (Project State Registration No. 122041400157-9).

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Table 1. Metallic inclusions in natural diamonds from kimberlites

Inclusions	Location	Reference
Magnetite	Yakutia, Russia	Gnevushev, Nikolaeva, 1961
Cohenite	South Africa	Sharp, 1966
Magnetite	West Africa	Harris, 1968
Magnetite	West Africa, Zaire (DRC)	Prinz et al., 1975
Magnetite	Various sources	Meyer, Tsai, 1976
Native Fe, taenite, wüstite, magnetite, cohenite	Yakutia, Russia	Bulanova et al., 1979; 1993
Native Fe, magnetite	Yakutia, Russia	Sobolev et al., 1981
Native Fe	Colorado, USA	Meyer, McCallum, 1986
Native Fe, magnetite	South Africa	Gurney, 1986
Native Fe, wüstite	Yakutia, Russia	Garanin, Kudryavtseva, 1990; Garanin et al., 1991
Native Fe, native Ni, Fe,Ni-alloy, Fe and Ni oxides	Mato Grosso, Brazil	Wilding et al., 1991
Native Fe, native Ni, wüstite, magnetite	Liaoning, China	Vinokurov et al., 1998
Native Fe, taenite, native Ni, wüstite, cohenite	Yakutia, Russia	Bulanova et al., 1998
Native Fe, wüstite, magnetite	Mwadui, Tanzania	Stachel et al., 1998
Ni,Fe,Cr-alloy, wüstite	Wellington, Australia	Davies et al., 1999
Native Ni	Mato Grosso, Brazil	Kaminsky et al., 2001; Kaminsky, 2012
Native Fe	Myanmar	Win et al., 2001
Native Fe, magnetite	North China	Gorshkov et al., 2002
Native Fe	Argyle lamproite pipe, Australia	Gorshkov et al., 2003
Native Fe, magnetite	Yakutia, Russia	Titkov et al., 2003
Native Fe, magnetite	Mato Grosso, Brazil	Hayman et al., 2005
Fe,Cr-alloy, native Fe	Yakutia, Russia	Titkov et al., 2006 $_1$
Native Fe, magnetite	Yakutia, Russia	Titkov et al., 2006 $_2$
Native Fe, cohenite, Fe-oxides	South Africa	Jones et al., 2008
Native Fe	Zaire	Shiryaev et al., 2010
Native Fe, wüstite, magnetite	Mato Grosso, Brazil	Bulanova et al., 2010
Native Fe, iron carbides (Fe_3C, Fe_2C), magnetite	Mato Grosso, Brazil	Kaminsky, Wirth, 2011
Fe,Ni-alloy	Mato Grosso, Brazil	Hutchison et al., 2012
Fe carbide	South Africa	Mikhail et al., 2014
Native Fe	Mato Grosso, Brazil	Thomson et al., 2014
Fe,Ni-alloy, magnetite	Mato Grosso, Brazil	Wirth et al., 2014

Native Fe	Mato Grosso, Brazil	Zedgenizov et al., 2014
Fe,Ni-alloy, cohenite $(Fe,Ni)_3C$, Fe oxide (presumably wüstite)	CLIPPIR-type diamonds from various sources	Smith et al., 2016; 2017; Nestola, 2017
Awaruite (Ni_2Fe-Ni_3Fe)	Botswana	Motsamai et al., 2018
Wüstite, Fe carbide $_7C_3$	Type IIb diamonds	Smith et al., 2018
Fe,Ni-alloy, magnetite	Mato Grosso, Brazil	Anzolini et al., 2020
Native Fe, iron carbides (Fe_3C, Fe_7C_3), wustite, magnetite	Yakutia, Russia	Shatsky et al., 2020
Fe,Ni-alloy, Fe,Ni-oxide	Type IIb diamonds, South Africa	Daver et al., 2022

Figure captions

Fig. 1. Phase diagram of the Fe–C system at 5 and 10 GPa (Lord et al., 2009).

Fig. 2. Phase diagram of the Fe–C system at 5.5 GPa according to data from (Kocherzhinsky et al., 1992; Zhimulev et al., 2016).

Fig. 3. Inclusion of metal-solvent in synthetic diamond crystals of type IIa (a) and IIb (b). Optical image (MBI-15) with side illumination.

Fig. 4. Evolution of metal-solvent inclusions in synthetic diamonds during heat treatment at high pressure (7.0–7.7 GPa): (a, b) – rosettes of cracks around metal inclusions, c – crack with numerous two-phase microinclusions, d – two-phase microinclusions at the crack propagation front. Optical image in transmitted light (Chepurov et al., 2005).

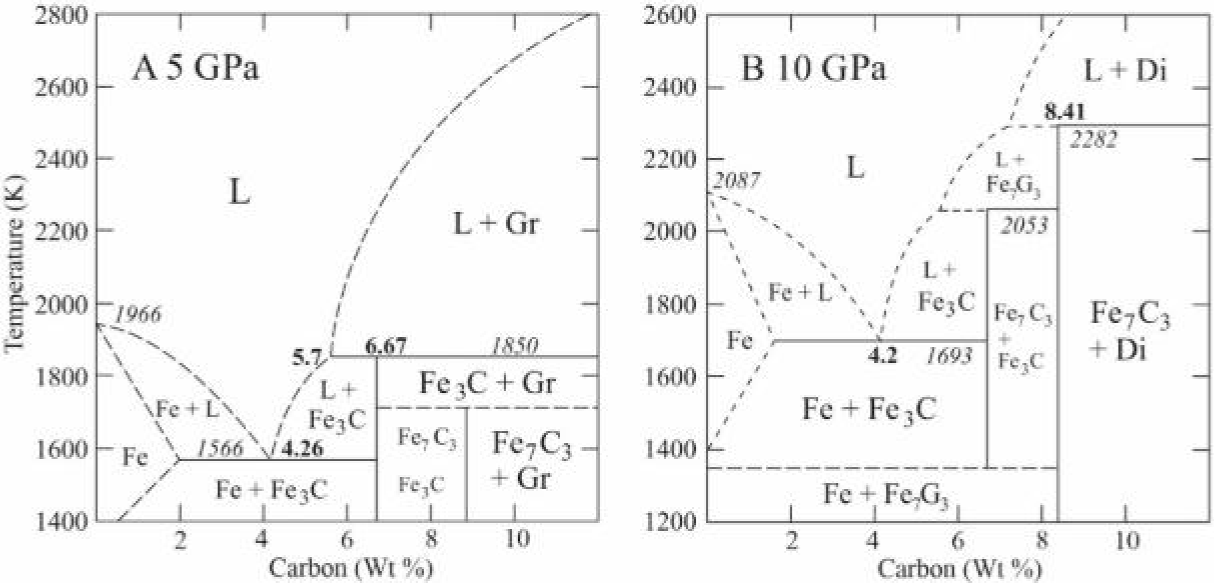
Fig. 5. Faceted metal-fluid inclusion in synthetic diamond after heat treatment at high pressure. Optical image in transmitted light.

Fig. 6. Polyphase inclusion in alluvial diamond An-17 (northeast of the Siberian craton), consisting of iron carbide (Fe_3C), native Fe, troilite (Tro) and nanoscale diamond (Di2) (a); (b, c) – lattice fragment and electron diffraction pattern of iron carbide Fe_3C; (d, e) – energy dispersive spectrum (d) and electron diffraction pattern (e) of troilite. Graphite was detected at the contact between silicon carbide and diamond Di2.

All phases were identified by chemical composition and structural parameters using transmission electron microscopy on a Philips CM200 microscope (LaB_6) at an accelerating voltage of 200 kV. The unit cell parameters of each mineral phase were determined using a diffractometric attachment (HREM). The chemical composition of the phases was determined by analytical electron spectroscopy (AEM) on an energy dispersive spectrometer (EDAX) with an ultra-thin window of 3.8 nm, a sample tilt angle of 20° and an exposure time of 200 s.

Fig. 7. Metallic inclusion consisting of Fe oxide and carbide in diamond from placers of the northeastern Yakutian diamond-bearing province. Image in backscattered electrons on a scanning electron microscope (Shatsky et al., 2020).

Fig. 8. Oxygen fugacity of buffer equilibria at 0.1 MPa (a) and 5 GPa (b) (Chepurov et al., 1997).


A 5 GPa
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1966
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6.67
1850
L + Fe3C
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Fe7C3 Fe3C
Fe7C3 + Gr
Fe + Fe3C
Temperature (K)
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2000
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1600
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Carbon (Wt %)
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4
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B 10 GPa
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L + Di
8.41
2282
L + Fe7G3
2087
2053
L + Fe3C
Fe + L
Fe
4.2
1693
Fe7C3 + Fe3C
Fe7C3 + Di
Fe + Fe3C
Fe + Fe7G3
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Carbon (Wt %)
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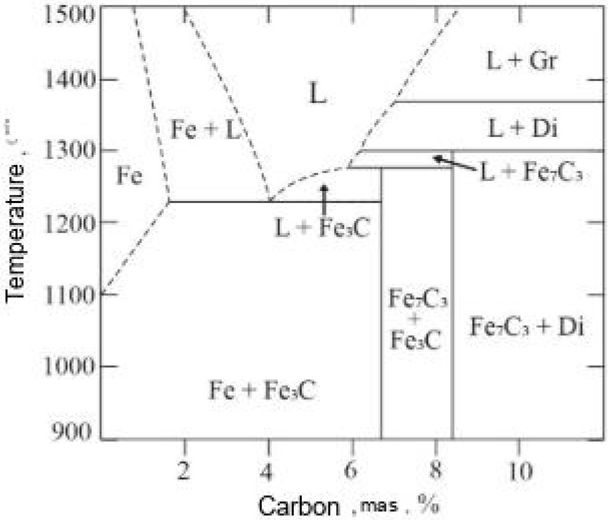
Fig. 1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Carbon , mas , %
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Fig. 2

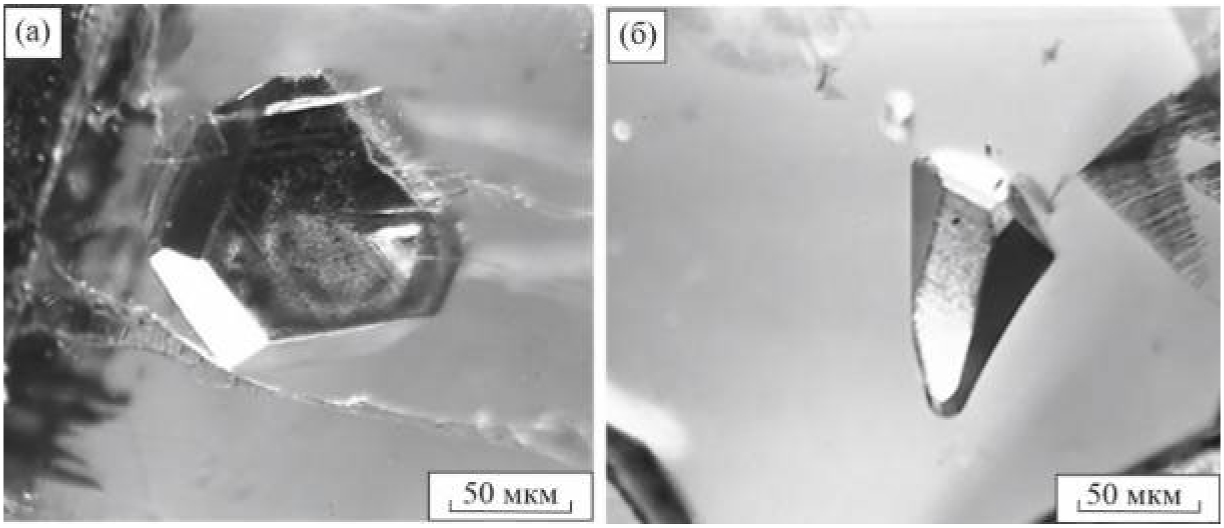

Fig. 3

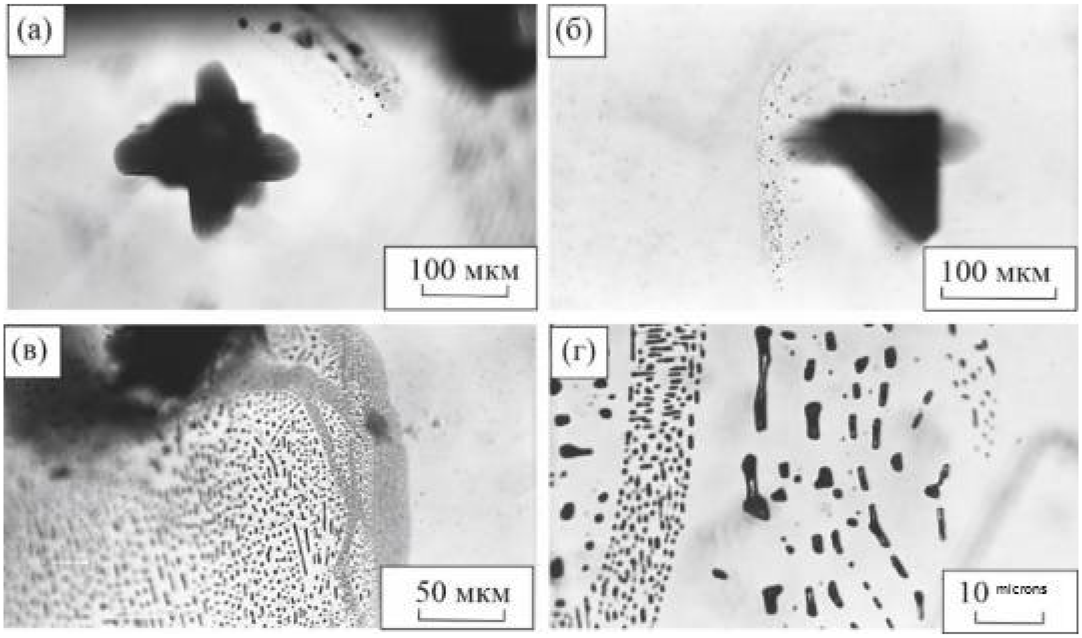

Fig. 4

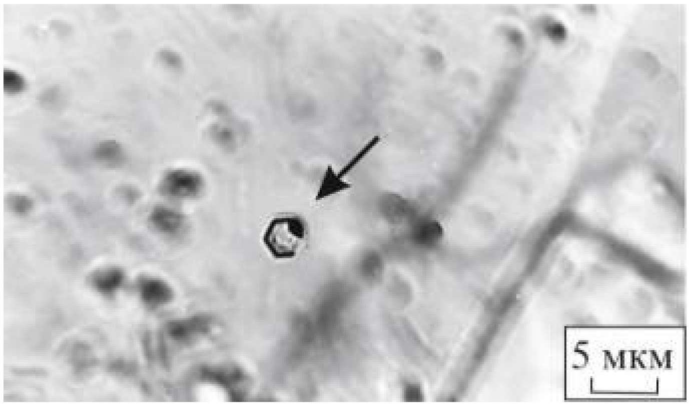
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Fig. 5

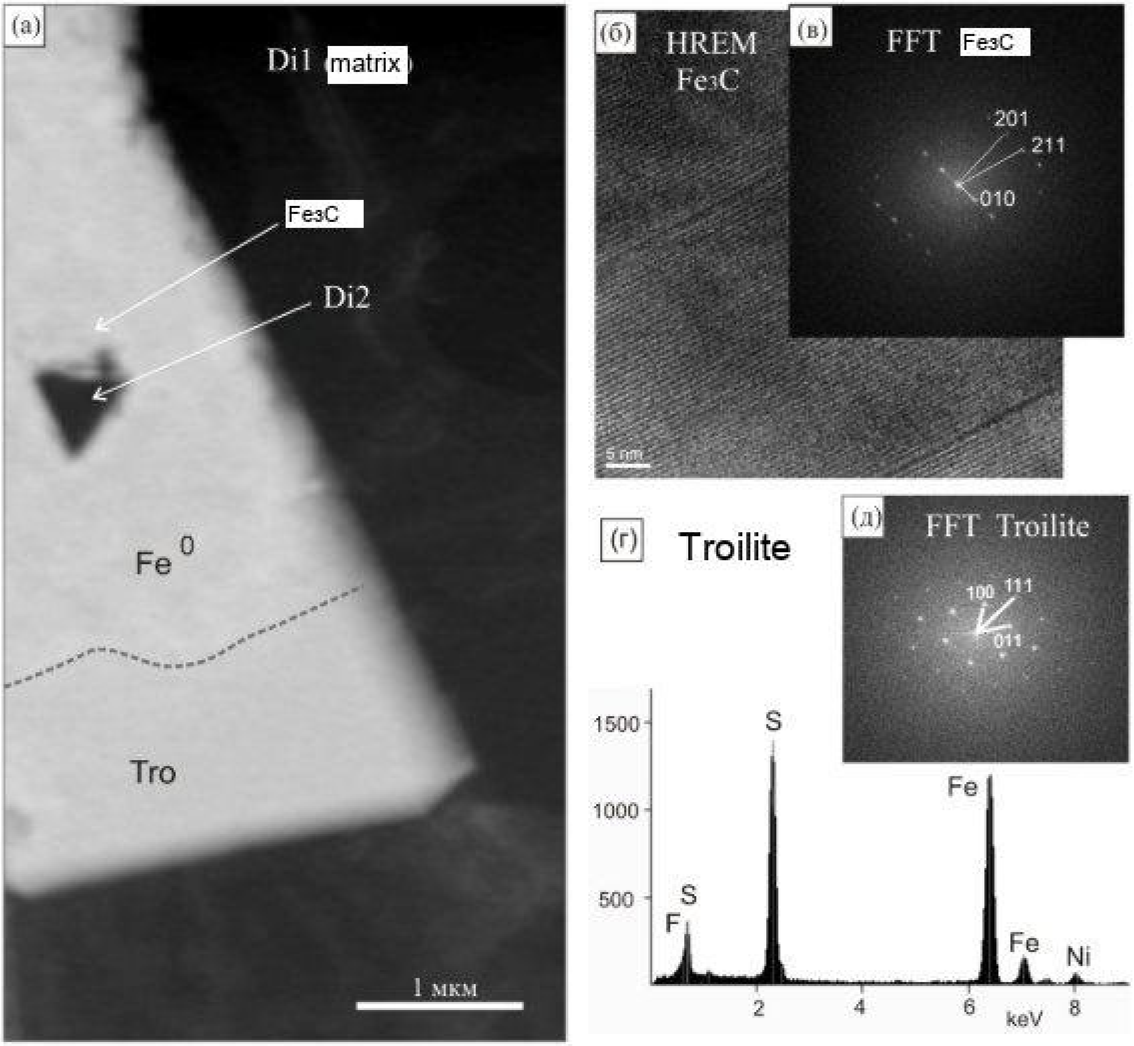
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Fig. 6

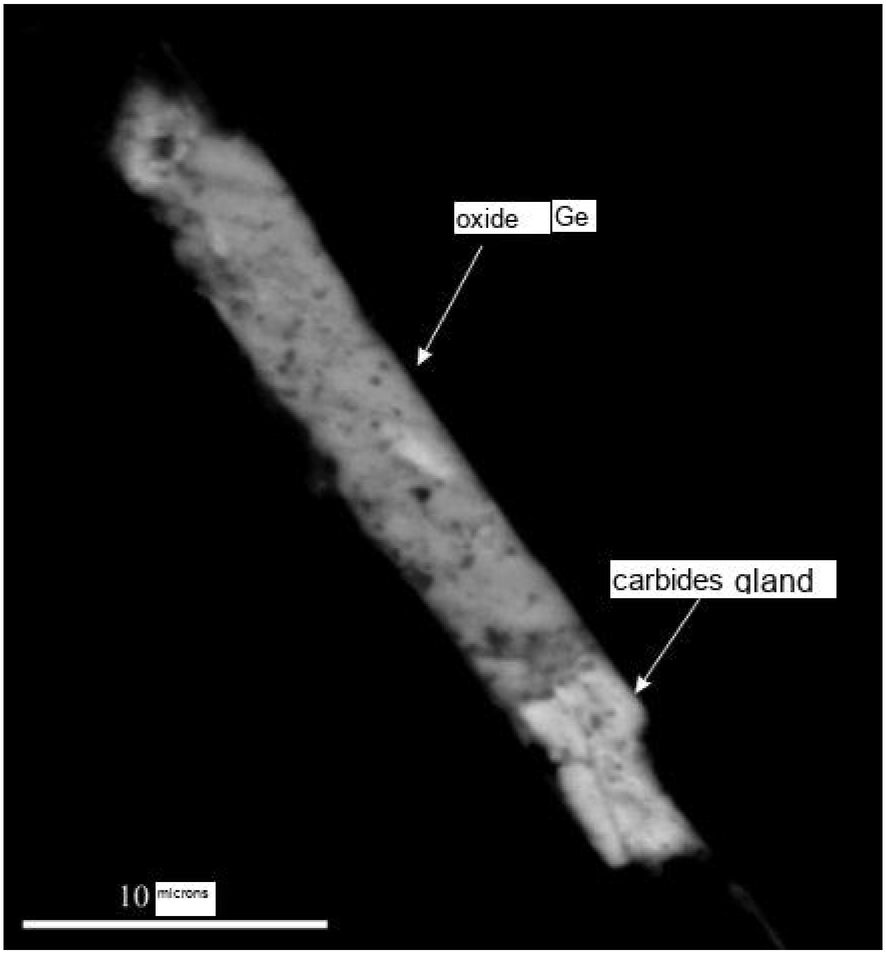
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Fig. 7

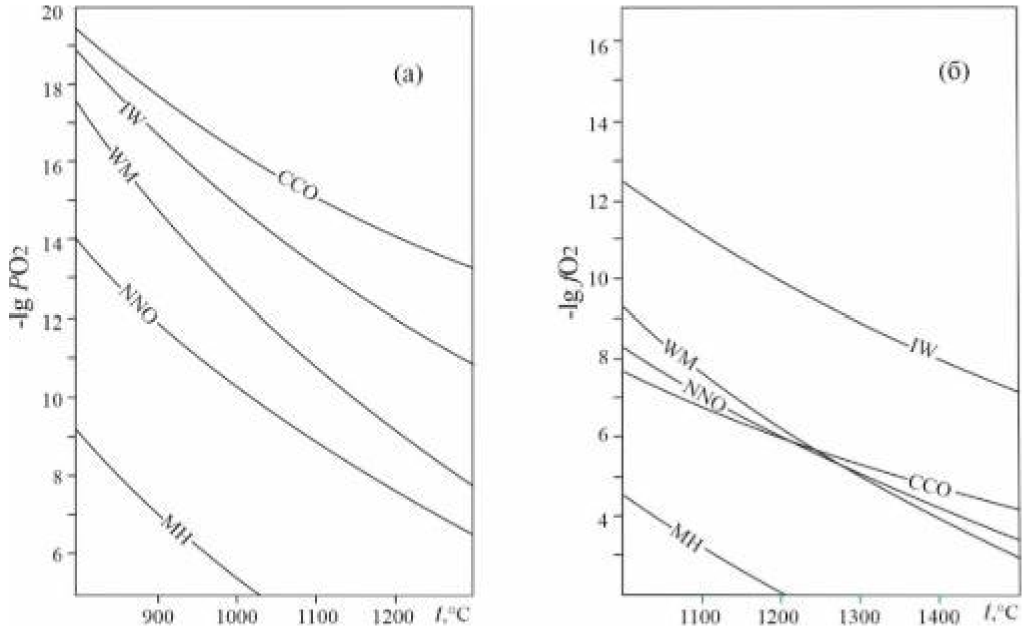
(a)
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Fig. 8