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Specific Multiphase Assemblages of Carbonatitic and Al-Rich Silicic Diamond-Forming Fluids/Melts: TEM Observation of Microinclusions in Cuboid Diamonds from the Placers of Northeastern Siberian Craton

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Received: 5 December 2018; Accepted: 10 January 2019; Published: 15 January 2019

Abstract: The microinclusions in cuboid diamonds from Ebelyakh River deposits (northeastern Siberian craton) have been investigated by FIB/TEM techniques. It was found that these microinclusions have multiphase associations, containing silicates, oxides, carbonates, halides, sulfides, graphite, and fluid phases. The bulk chemical composition of the microinclusions indicates two contrasting growth media: Mg-rich carbonatitic and Al-rich silicic. Each media has their own specific set of daughter phases. Carbonatitic microinclusions are characterized by the presence of dolomite, phlogopite, apatite, Mg, Fe-oxide, KCl, rutile, magnetite, Fe-sulfides, and hydrous fluid phases. Silicic microinclusions are composed mainly of free SiO_2 phase (quartz), high-Si mica (phengite), Al-silicate (paragonite), F-apatite, Ca-carbonates enriched with Sr and Ba, Fe-sulfides, and hydrous fluid phases. These associations resulted from the cooling of diamond-forming carbonatitic and silicic fluids/melts preserved in microinclusions in cuboid diamonds during their ascent to the surface. The observed compositional variations indicate different origins and evolutions of these fluids/melts.

Keywords: cuboid diamonds; microinclusions; diamond-forming fluids/melts; mantle

1. Introduction

Syngenetic inclusions of minerals, melts, and fluids in natural diamonds suggest a multicomponent environment in the Earth's deep mantle, where diamonds are formed. The recent progress of investigations into these polyphase inclusions is obvious from the analysis of numerous works concerning diamond growth media. Most of these studies were focused on natural fibrous diamonds containing abundant microinclusions (submicron size inclusions) of the multiphase associations of fluids/melts [1–17]. The microinclusions are believed to provide pristine information on the mantle diamond-producing fluids/melts. These fluids/melts generally show a range of compositions between three end-members: carbonatitic, silicic, and saline. Model experimental studies have revealed that these fluids/melts may be efficient diamond growth media [18–20]. It is important to note the finding of a fluid rim mainly composed by H_4SiO_4 (orthosilicic acid) + $H_6Si_2O_7$ (persilicic fluid), which is a typical feature of diamonds and is found at the interface between mineral inclusions and their diamond hosts [21]. This fluid is easily detectable by micro-Raman spectroscopy and is present for any type of mineral inclusions in lithospheric diamonds, regardless of their being peridotitic or ecloglitic. These silicic fluids were suggested to represent residue after the crystallization of diamond and their inclusions [21,22].

Diamond placer deposits in the northeastern part of the Siberian craton are highly productive, but the primary source of diamonds is not established [23,24]. These placer deposits are characterized by specific diamond populations, including typical octahedral-to-rounded diamonds, yellow-orange or dark grey cuboid diamonds, and rounded dark radial-mosaic diamonds. Available data regarding the composition of mineral inclusions in these diamonds testify to the predominance of minerals of eclogitic paragenesis [25,26]. The microinclusions in cuboid diamonds from these deposits carry two contrasting compositions of diamond-forming fluids/melts: essentially carbonatitic and silicic [11]. Apart from constraints of the bulk chemical composition of these two growth environments, other important information may be obtained from identification of particular phases of microinclusions. Here we report new data on the phases in microinclusions, including their relationships and abundances in alluvial fibrous diamonds from the northeastern Siberian craton. The phases of original primary fluids/melts described here are the first empirical observations of two contrasting types of diamond-forming fluids.

2. Samples and Methods

Four dark green and brown cuboid crystals have been selected from the collection of diamonds from the placer deposits of the Ebelyakh region, northeastern Siberian craton, Russia. The diamonds were mostly isometric, partly resorbed cuboid crystals. The {100} surfaces show a continuous pattern of small tetragonal pits; the edges are usually replaced by rounded surfaces, which correspond in position to a tetrahedron or rhombic dodecahedron [27]. The diamonds are opaque because of numerous microinclusions. Some of them shows zoning structure (Figure 1). Microinclusions are arranged unevenly in cubic diamonds. This is due to the growth characteristics of each particular crystal. Microinclusions track diamond growth zones (Figure 1a,b). Diamonds containing significant numbers of microinclusions are fully opaque and black (Figure 1c). Some diamonds are characterized by the presence of such an opaque zone only in the central part; nearer to the edge, the amount of microinclusions decreases (Figure 1d). A previous study has revealed the bulk composition of predominantly carbonatitic (HI-105 and HI-111) and Al-rich silicic (HI-91 and HI-95) microinclusions in these diamonds [11].

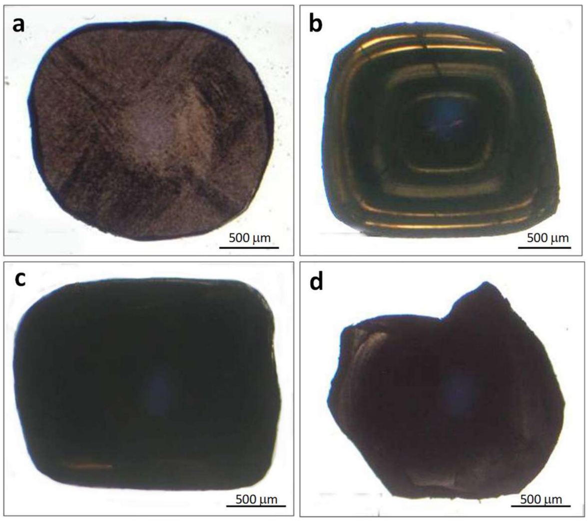

Figure 1. Polished thin sections of cuboid diamonds from placers in the northeastern Siberian craton with predominantly silicic ((**a**) HI-91 and (**b**) HI-95) and predominantly carbonatitic ((**c**) HI-105 and (**d**) HI-111) microinclusions. Transmitted light.

The nitrogen contents of these diamonds varied significantly: 630–740 ppm in sample HI-91; 240–700 ppm in HI-95; 450–470 ppm in HI-105; <80 ppm in HI-111. Relatively low nitrogen content, such as that found in HI-111, is not typical for cuboid diamonds, which normally have a higher nitrogen content (>500 ppm). The nitrogen aggregation in the samples is low and amount of nitrogen in the form of aggregated B1 defects (a group of four nitrogen atoms replacing carbon around the vacancy [28]) do not exceed 25%. Carbon isotope composition of the studied diamonds show no significant variations (δ^{13}C −4.3‰ in HI-95 and HI-111, −5.3‰ in HI-91, and −7.1‰ in HI-105) and fall close to the suggested average mantle values [29].

Phase compositions of microinclusions located in different growth zones of diamonds have been identified using transmission electron microscope (TEM) techniques. For TEM analyses, eight ultra-thin foils size 15 μm × 10 μm and 0.15–0.20 μm thicknesses were prepared using a focused ion beam (FIB) device (FEI FIB 200 instrument) following procedures given by Wirth [30,31]. After milling, the foil was cut free, extracted, and placed on a carbon-coated Cu grid.

TEM imaging and analysis were performed with a FEI Tecnai™G2 F20X-Twin transmission electron microscope (FEI Company, Hillsboro, OR, USA) with a FEG electron source at the GeoForschungsZentrum, Potsdam. The TEM was operated at 200 kV acceleration voltage. A GatanTridiem™ filter allowed energy-filtered imaging applying a 20 eV window to the zero loss peak. Analytical electron microscopy (AEM) was performed with an energy dispersive X-ray analyzer (EDX). Counting time was 60–120 s. Analyses usually were carried out in scanning transmission mode (STEM). Beam size was approximately 1 nm in diameter. Images in the STEM mode were acquired with a high angle annular dark field detector (HAADF). Electron energy-loss spectra (EELS) were recorded in diffraction mode with a dispersion of 0.1 eV/channel. The resolution of the energy filter was 0.9 eV at half width, at full maximum of the zero loss peak. Thirty-four individual microinclusions have been identified in eight foils

3. Results

In this work, 34 microinclusions were studied using TEM in four cuboid diamonds with essentially carbonatitic (HI-105 and HI-111) and essentially Al-rich silicic (HI-91 and HI-95) microinclusions (Figure 2). All microinclusions, ranging between 40 and 800 nm in size, are composed of polyphase assemblages, which include silicates, carbonates, oxides, halides, non-crystalline material, and fluid bubbles.

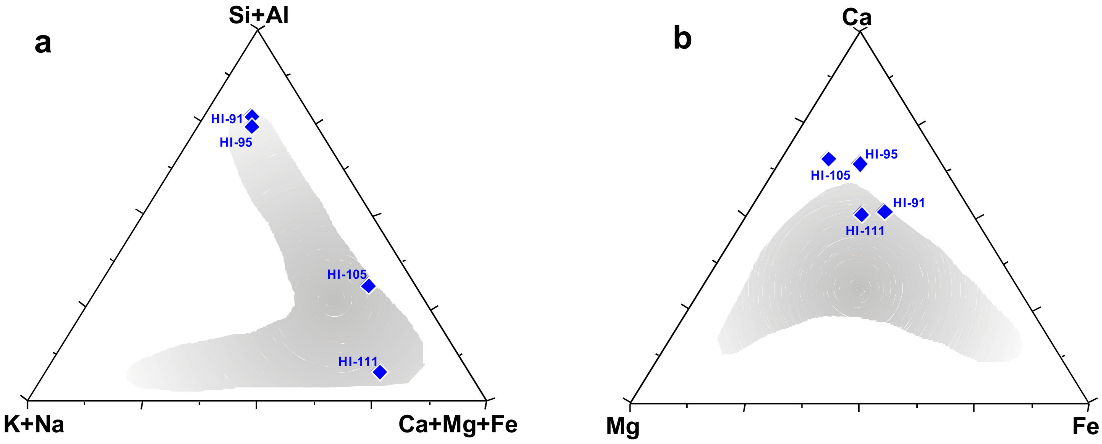

Figure 2. Compositional variations (EDS, mol %) of microinclusion in diamonds from placers in the northeastern Siberian craton, as compared with microinclusions in the diamonds from other worldwide localities (shaded areas). (**a**) (K + Na) − (Si + Al) − (Ca + Mg + Fe) triangle plot; (**b**) Mg − Ca − Fe triangle plot.

3.1. Al-Rich Silicic Microinclusions (Group 1)

The diamonds HI-91 and HI-95 have microinclusions predominantly of silicic Al-rich composition. Another specific feature of these microinclusions is low MgO content. The FTIR spectra of the diamonds in this study contain absorption bands related to different phases in the microinclusions. The spectra show clearly the bands related to water (3420 and 1650 cm^{-1}), carbonates (1430 and 880 cm^{-1}), silicates (950–1150 cm^{-1}), and other phases (Figure 3). The strong absorption band at 1100 cm^{-1} and two weaker sharp peaks at ~785 and 812 cm^{-1} of quartz are specific only for microinclusions of group 1. Both carbonate bands testify to the presence of minor amounts of calcite.

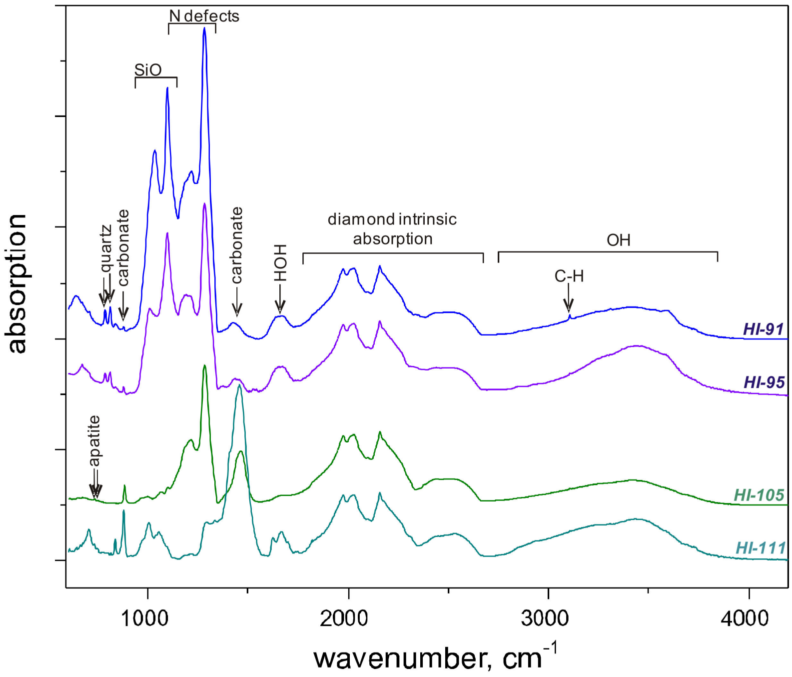

Figure 3. FTIR spectra of diamonds from placers in the northeastern Siberian craton with carbonate-dominated (HI-105 and HI-111) and silicate-dominated (HI-91 and HI-95) microinclusions.

Seven individual microinclusions ranging in size from 50 to 300 nm have been studied in HI-91, and nine microinclusions in HI-95. All microinclusions are represented by polyphase associations. The phases are identified by chemical composition, and some of them by diffraction data. Representative TEM images of microinclusions and energy dispersive spectroscopy (EDS) spectra of common phases in Al-rich silicic microinclusions are shown in Figure 4. As carbonates are not stable under an electron beam, the information on carbonates was obtained using electron energy loss spectroscopy (EELS) and EDS with nanometer resolution.

The major phases of Al-rich silicic microinclusions are SiO_2 (quartz), Ti-phengite, F-apatite, Fe-sulfide, and Sr- and Ba-bearing calcium carbonate. Undetermined Al-rich silicates also presented in this association. The main phases in this group of microinclusions are quartz and Al-rich Ti-bearing mica (phengite). Phengite has elongated tabular forms (Figure 4a–c). As seen from the lattice fringe image, the phengite is predominantly a highly ordered homogeneous phase, almost free of stacking disorder (Figure 4i). Phengite is observed to be intergrown with an Al-rich silicate phase (Figure 4f). Based on chemical composition and published data, we assume that it is paragonite [32]. The carbonate phase is represented by Sr- and Ba-bearing calcium carbonates (Figure 4b,e), usually forming fine aggregates with potassium chloride and a fluid phase. Minor amounts of KCl have also been detected in several microinclusions (Figure 4b). Fluid phases (bubbles, pores) are encountered in all inclusions (Figure 4a–c). Pores are formed as a result of opening the fluid phases during the cutting of the foil, resulting in the volatile components being removed. Each these phases are found in all

16 microinclusions. At the moment, these associations represent a set of daughter phases crystallized with decreasing temperature from high-density fluid or volatile-rich melt originally trapped during the formation of the host diamonds.

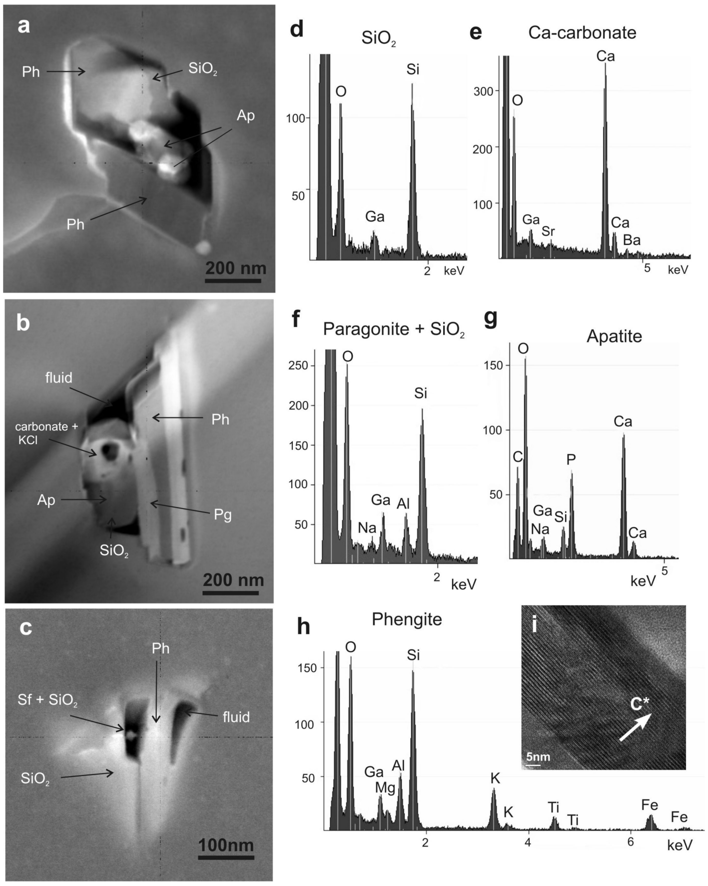

Figure 4. (**a**–**c**) TEM bright field image of the nanometer-sized polyphase inclusions: diamond HI-91, foil #2793, inclusion 5 (**a**) and inclusion 2 (**c**); diamond HI-95, foil #2800, inclusion 2 (**b**). The main phases are indicated: Ph (phengite), Ap (apatite), Pg (paragonite), Sf (sulfide). (**d**–**h**) EDX spectra from mineral phases composed the nanometer-sized inclusion: quartz (**d**), Ba- and Sr-bearing Ca-carbonate (**e**), paragonite (combined with spectrum of quartz) (**f**), apatite (**g**), phengite (**h**). Ga intensity in the spectra is due to implanted Ga during FIB sample preparation. (**i**) High-resolution image of phengite super structure.

3.2. *Carbonatitic Mg-Rich Microinclusions (Group 2)*

Carbonatitic Mg-rich fluids/melts were described in diamonds HI-105 and HI-111. The bulk chemical composition of microinclusions show high amounts of MgO, CaO, FeO, and KCl. FTIR spectra reveal strong absorption caused by carbonates at 880 and 1440 cm^{-1}. The positions of these bands correspond to dolomite. The absorption in the 950–1150 cm^{-1} region is due to phlogopite and apatite. Apatite’s main band is at ~1060 cm^{-1}, with additional weaker peaks at 1095, 575, and 605 cm^{-1}, while phlogopite’s main band is situated at ~1000 cm^{-1} [17].

Crystalline phases in microinclusions are suggested to appear from initially homogeneous fluids/melts due to cooling during or after the host diamonds were transported to the surface. Eighteen individual microinclusions have been studied in these diamonds. Figure 5a–c displays the typical individual microinclusions of former carbonatitic Mg-rich fluids/melts. These microinclusions consist of dolomite, phlogopite, rutile, F-apatite, Fe-sulfide, and KCl. The main phases containing MgO are phlogopite, dolomite, and magnesium iron oxide (Figure 5k). Each of these phases contains a small amount of FeO. Phlogopite presented as tabular euhedral grains (Figure 5a–c). It was identified by chemical composition and diffraction pattern (Figures 5h and 6). Dolomite is the only carbonate phase detected in these microinclusions (Figure 5a,c,j). The magnesium iron oxide corresponds to ferropericlase by stoichiometry ($(Mg_{0.8}Fe_{0.2})O$). The presence of KCl, rutile, Fe-sulfide, and magnetite (Figure 5d,e,i,g) testify to another important components of parental fluids/melts, such as potassium, titanium, and ferrous iron. Magnetite contains minor amounts of Cr, Nb, and Ti (Figure 5g). Apatite is characterized by the presence of F (Figure 5f). KCl is clearly observed in the spongy porous areas. Such porous areas are formed as a result of opening the volatile (fluid) phases during cutting the foil (Figure 5a). Fluid phases preserved as bubbles are also typical of this assemblage.

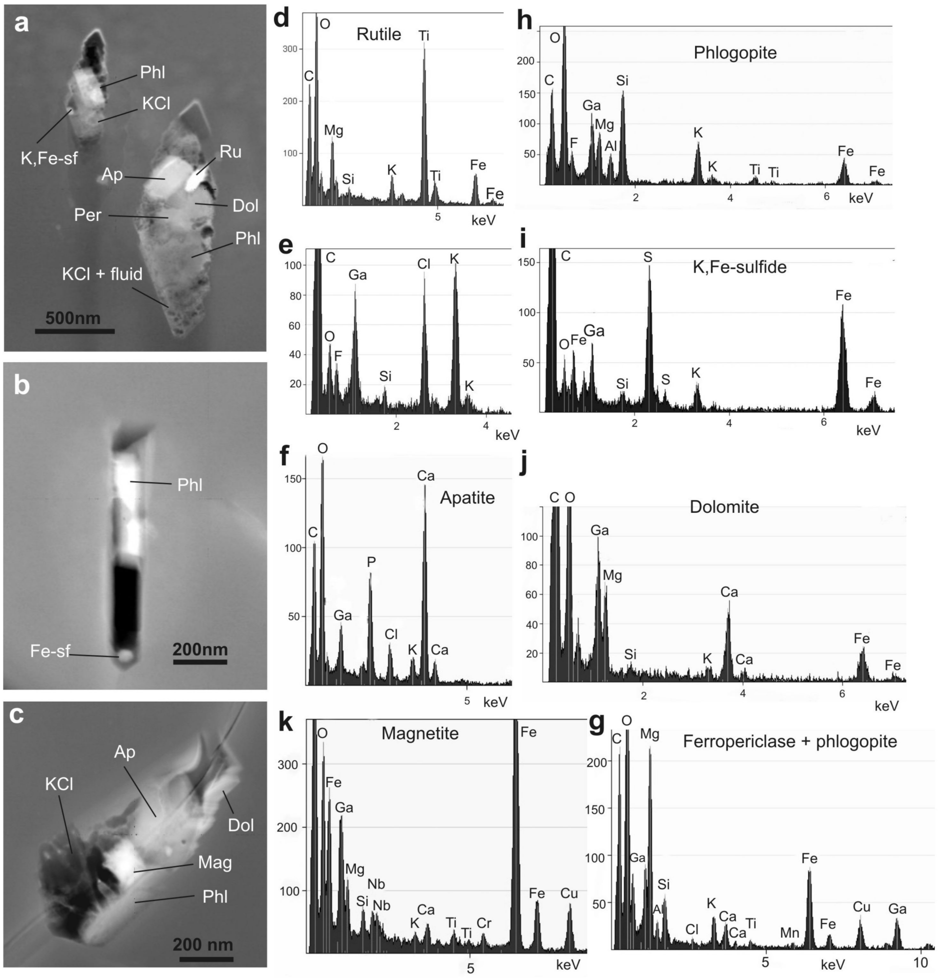

Figure 5. (**a**–**c**) TEM bright field image of the nanometer-sized polyphase inclusions: diamond HI-111, foil #2798, inclusions 2, 3 (**a**); diamond HI-105, foil #2802, inclusion 1 (**b**) and 2 (**c**). The main phases are indicated: Ru (rutile), Phl (phlogopite), Ap (apatite), Dol (dolomite), Mag (magnetite), Per (ferropericlase), Sf (sulfide). (**d**–**k**) EDX spectra from mineral phases composed the nanometer-sized inclusion: rutile (**d**), KCl (**e**), apatite (**f**), magnetite (**g**), phlogopite (**h**), sulfide (**i**), dolomite (**j**), Mg, Fe-oxide (ferropericlase) (**k**). Ga intensity in the spectra is due to implanted Ga during FIB sample preparation and Cu intensity comes from the copper grid.

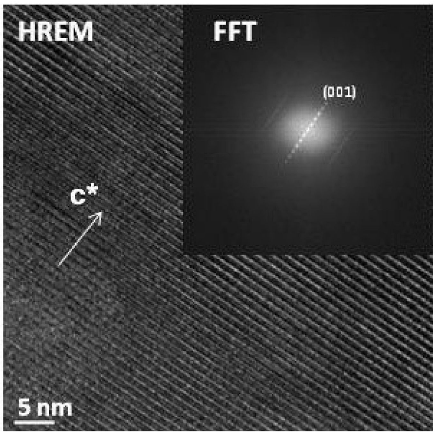

Figure 6. Energy filtered TEM lattice fringe image of phlogopite phase in multiphase inclusion 2 (diamond HI-105, #2802). Diffraction pattern from Fast Fourier Transform (FFT).

4. Discussion

Microinclusions in natural diamonds represent direct samples of mantle-derived fluids or melts from which they crystallized and are a key to constraining the composition of diamond-forming media [1]. The microinclusions of studied diamonds from the placer deposits of the Ebelyakh region, northeastern Siberian craton, are representative of two contrasting growth media: Al-rich silicic and high-Mg carbonatitic. Previous studies of microinclusions in diamonds from different worldwide localities have shown that high- and low-Mg carbonatitic melts and silicic high-density fluids are both important diamond-forming media [1,6–8,10,13–16,33–35]. High-Mg carbonatitic compositions have first been described in Siberian diamonds [8]. FTIR spectroscopy can be used as a semi-quantitative method to determine carbonatitic to silicic compositions of microinclusions in natural diamonds. A combination of EPMA and FTIR data constrain the major components of fluids/melts of different compositions [17]. The high-Mg carbonatitic end-member compositions carry (by weight) 78% carbonates, 9% silicates, 6% water, 5% apatite, and 2% halides. The silicic end-member compositions are (by weight): 69% SiO_2, 14% Al_2O_3, 10% KCl, 4% carbonates, 4% water, and less than 1% FeO, TiO_2, MgO, and P_2O_5. In addition, saline compositions with very high contents of chlorides and water may be involved in the processes of diamond formation [4,12,36,37]. A strong connection has been suggested between high-Mg carbonatitic high-density fluids (HDFs) and a carbonated peridotite source, while silicic and low-Mg carbonatitic melts may be related to hydrous eclogites [16]. The origin of saline fluids/melts is obscure, and its source in the mantle has remained uncertain [38].

It has been shown that the microinclusions in cuboid diamonds from the placers of northeastern Siberian craton possess high-Mg carbonatitic (SiO_2 + Al_2O_3 8 wt %–32 wt %) and Al-rich silicic (SiO_2 + Al_2O_3 55 wt %–75 wt %) compositions [11]. The TEM study of microinclusions has revealed that each group is characterised by their specific set of daughter phases. The microinclusions of high-Mg carbonatitic composition generally consist of dolomite and phlogopite. The overall presence of rutile, ferropericlase, magnetite, sulfide, KCl, apatite, and fluids is observed in this assemblage. The chemistry of these daughter phases suggests diamond-forming media enriched with Ca, Mg, Fe, K, and Ti. Ferropericlase is a common mineral of superdeep (lower mantle) paragenesis [39]. The presence of ferropericlase may be caused by low silica activity in the parental media in the upper mantle. Such conditions can be realized in magnesite bearing dunite where ferropericlase may form by reduction of magnesite during diamond growth [40]. A vastly expanded field of crystallization of ferropericlase in the upper mantle has been suggested for carbonated low-silica melts with decreasing pressure [41]. This model assumes the existence of a carbonatite melt, which can easily move and produce mantle lithologies with very low Si/Mg ratios. Such melts carry some amount of P, S, Cl, and F. Apatite is known as the most abundant phosphate phase in intrusive and extrusive carbonatites [42].

Apatite has been observed in microinclusions of both groups and described in many other diamonds from different localities [10,13,17,43].

The microinclusions of silicic composition are enriched with Si, Al, and K. The dominant phases of these microinclusions are quartz, phengite, and paragonite(?). Phengite phases are occasionally observed to be intergrown with paragonite grains. Phengite commonly occurs in metamorphic rocks, but paragonite is rare compared to phengite. Coexisting paragonite and phengite have been described in eclogite from Cazadero (California) [32]. A specific feature of phengite in microinclusions is a high Ti content, which can be a significant constituent of phengites equilibrated at high temperature and high pressure [44]. Some minor amount of apatite and calcium carbonate with high amounts of Sr and Ba is observed in most microinclusions of silicic composition. Ba-carbonates have previously been identified in multiphase associations of microinclusions in cloudy diamonds from the Internatsionanaya kimberlite pipe [13]. Specific radial-mosaic diamonds (diamond variety V according to Reference [27]) from alluvial deposits of the northeastern Siberian craton contain microinclusions of low-Mg carbonatitic to silicic fluids/melts, rich in Ba and Sr [45]. Microinclusions in these diamonds consist of Ba,Sr,Ca-carbonates, Ca,Fe-carbonates, K,Ba-phosphates, Ti-silicates, KCl, graphite, fluid bubbles, and interstitial silica [14]. The high content of Ba and Sr in some phases is a strong manifestation for processes of deep metasomatism [44,46].

Diamond-forming environments, the relics of which were found as microinclusions in diamonds, probably formed during the partial melting of peridotites and eclogites, due to the influence of external fluids. Dalton and Presnall [47] have demonstrated that during melting of carbonated peridotites, there are systematic variations in the composition of melts from carbonatitic near solidus to silicic with an increase in temperature of 70–100 °C above the solidus. Other experimental studies have established that the melting of carbonated peridotites preferentially leads to the formation of high-Mg carbonatitic melts, while essentially silicic melts can be formed only by melting of Si-rich (i.e. coesite-bearing) eclogites [48,49]. Consequently, essentially carbonatitic and essentially silicic compositions of microinclusions in fibrous diamonds from alluvial placers of the northeast Siberian craton can reflect the formation of the corresponding fluids/melts during the melting of chemically heterogenous substrates, peridotites, and eclogites. Microinclusions in diamonds from placers of the northeastern Siberian craton are characterized by general enrichment with many incompatible elements [11], which probably also confirms their formation during low-grade partial melting of carbonated mantle peridotites and eclogites.

The observed variations in the composition of microinclusions in diamonds within the carbonate-silicate trend can be due to the fractionation of fluids or melts in the process of crystallization, or by mixing of parental fluids/melts of different composition [2]. The interaction of slab-derived chloride-carbonatite fluids/melts with ancient peridotites and eclogites can also lead to the transition to silicic compositions [38]. Schrauder and Navon [33] have first proposed fractional crystallization to explain these variations within carbonatitic to silicic compositional trends of microinclusions in diamonds from Jwaneng (Botswana). Crystallization of Ca-Mg carbonates, apatite, titanates, and K-containing phases from primary carbonatitic melt were suggested to lead to a change in the composition toward a hydrous-silicic end-member. Alternatively, fractional crystallization of Mg-silicates from a carbonate-bearing silicate melt and the evolution of residual liquid toward carbonatitic compositions were also considered [50]. Euhedral crystals of mica in most studied microinclusions (phlogopite in carbonatitic, and phengite+paragonite in silicic) may support this model.

5. Conclusions

The bulk chemical composition of microinclusions in cuboid diamonds from Ebelyakh River deposits (northeastern Siberian craton) indicates two contrasting growth media: Mg-rich carbonatitic and Al-rich silicic. The observed compositional variations indicate different origins and evolutions of these fluids/melts. FTIR spectroscopy can be used to verify the dominant major components of these media. These assemblages of daughter phases of microinclusions of different compositions are first studied by TEM (AEM). It is shown that each media are characterized by their own specific set of phases. Mg-rich carbonatitic microinclusions show the presence of dolomite, phlogopite, apatite, Mg, Fe-oxide, KCl, rutile, magnetite, Fe-sulfides, and hydrous fluid phases. Al-rich silicic microinclusions are composed mainly of free SiO_2 phase (quartz), high-Si mica (phengite), Al-silicate (paragonite?), F-apatite, Ca-carbonates enriched with Sr and Ba, Fe-sulfides, and hydrous fluid phases. These assemblages resulted from the cooling of diamond-forming carbonatitic and silicic fluids/melts preserved in microinclusions in cuboid diamonds during their ascent to the surface.

Author Contributions: A.L. studied samples by TEM; D.Z. studied samples by optical microscopy, polished the plates, and analyzed them via FTIR and EDS; R.W. contributed analysis tools; D.Z. contributed samples; A.L. and D.Z. discussed the results and wrote the paper.

Funding: This study has been supported by Russian Science Foundation (16-17-10067). A.L. appreciates the support of Russian Foundation for Basic Research (18-05-70014).

Conflicts of Interest: The authors declare no conflicts of interest.

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