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Composition of trapped fluids in cuboid fibrous diamonds from the Udachnaya kimberlite: LAM-ICPMS analysis

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Abstract

The bulk major- and trace-element compositions of micro-inclusions in 24 cuboid diamonds from the Udachnaya kimberlite pipe (Siberia, Russia) have been quantitatively analyzed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LAM-ICPMS). Micro-inclusions in the studied diamonds represent a bulk sample of the fluids from which the diamonds crystallized; they define a continuous range between magnesian and calcic carbonate-rich compositions at relatively constant Fe contents (Ca/(Ca+Mg)=0.31–0.68; Mg/(Mg+Fe)=0.66–0.78). In general the major- and trace-element patterns of the trapped fluids in Udachnaya cuboid diamonds are similar to those of kimberlites and carbonatites. However, some important differences are observed: (1) the fluids in diamonds are enriched in K, Na, Fe and depleted in Al relative to the host kimberlite; (2) the REE patterns of the fluids are steeper than those of kimberlites; (3) many of the fluids show strong depletion in Ti, Zr and Y.

The observed geochemical features are consistent with a genetic link between the diamond-forming fluids and ephemeral carbonatitic fluids/melts which may be precursors of the host kimberlite. These fluids/melts may originate either from the metasomatic and influx of carbonatitic agents or from partial melting of previously carbonated eclogites and peridotites. Some elemental variations may be explained by fractional crystallization of such fluid/melts, or mixing between fluids with different compositions.

Keywords: Diamond; Fluid; Carbonatitic melt; Kimberlite; Trace elements; LAM-ICPMS

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1. Introduction

Natural diamonds are the subject of extensive research because they provide information on the geochemistry, mineralogy and P–T–fO$_2$ regimes of the mantle. These studies concern either diamond itself or inclusions trapped during its growth, and provide important information about diamond-forming processes. Previous investigations of crystalline inclusions in diamonds from the subcontinental lithospheric mantle have shown that diamonds grow in a range of peridotitic (P-type) and eclogitic (E-type) host-rocks (Sobolev, 1974; Meyer, 1987; Harris, 1992). Both associations commonly indicate diamond growth at depths between 150 and 200 km and at temperatures of 900–1300 °C.

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Melt inclusions in octahedral diamonds, which are usually the most abundant diamond population, are extremely rare (Bulanova et al., 1988; Novgorodov et al., 1990; Zedgenizov et al., 1998). In octahedral diamonds (both P- and E-types) fluid and melt inclusions do occur in the nucleation zones of diamonds, as a component of the heterogeneous "seeds" on which at least some diamonds appear to have grown (Bulanova et al., 1998). There are also many indications that the genesis of fibrous diamonds is associated with the presence of fluids or volatile-rich melts (e.g. Navon, 1999; Navon et al., 2003).

Cuboid fibrous diamonds (crystals with a cubic overall habit, and a radiating structure) are particularly interesting for study of mantle-derived fluids. Although large inclusions are rare in such diamonds, most of them contain numerous tiny inclusions less than 1 μm in size. FTIR and Raman studies of the micro-inclusion-bearing zones in such diamonds have revealed the presence of water and carbonates along with silicates, apatite and CO_2 (Chrenko et al., 1967; Navon et al., 1988; Zedgenizov et al., 2004). Transmission and analytical electron microscopy (TEM and AEM) has confirmed the presence of apatite, carbonates, halides, mica and quartz (Lang and Walmsley, 1983; Guthrie et al., 1991; Walmsley and Lang, 1992a,b; Klein-BenDavid et al., 2006). "Cloudy" diamonds from the Koffiefontein mine (South Africa) carry mineral phases, identified by EPMA as phlogopite, high-Si mica, an Al–Mg-rich phase and carbonates (Izraeli et al., 2004). In fibrous diamonds from the Jwaneng mine (Botswana) and Brazil the bulk composition of fluids trapped in micro-inclusions varies continuously between two endmembers: carbonatitic and hydrous-silicic (Schrauder and Navon, 1994; Schrauder et al., 1996; Navon et al., 2003; Shiryaev et al., 2005). Carbonatitic fluids are rich in CO_2, CaO, FeO and MgO, while hydrous fluids are rich in H_2O, SiO_2, and Al_2O_3; K_2O contents are high in both endmembers. Micro-inclusions of hydrous brines, rich in chlorine and potassium, have been reported in "cloudy" diamonds from Koffiefontein and Canada (Izraeli et al., 2001; Klein-BenDavid et al., 2004). Micro-inclusions in cuboid diamonds preserve a high residual pressure, 1.5–2.1 Gpa at room-temperature conditions (Navon, 1991; Kagi et al., 2000, 2006); extrapolation to mantle temperatures (1000–1300 °C) yields pressures of 4–7 GPa, within the diamond stability field.

Thus micro-inclusions in fibrous diamonds provide well-preserved samples of the deepest fluids available for research. It is suggested that the multi-phase assemblage of such micro-inclusions represents a mantle-derived fluid or volatile-rich melt, which was trapped in the diamonds as they grew and subsequently crystallized yielding a range of daughter minerals. At the pressures and temperatures of the diamond stability field, many systems that carry silicate melts, carbonatitic melts and hydrous fluids, are beyond a second critical point and are fully miscible (Wyllie and Ryabchikov, 2000; Kessel et al., 2005). It seems likely that the fluids were trapped as uniform, highly concentrated, high-density fluids that are similar to sub-critical melts, but may have higher volatile contents.

The Udachnaya kimberlite pipe, located in the central part of the Yakutian diamond province (Siberia, Russia) is the largest diamond deposit in Russia and one of the largest in the world. It consists of two bodies, East and West, which are both diamondiferous. The diamond population from Udachnaya has a comparatively high proportion of cuboid diamonds with fluid micro-inclusions. Previous FTIR and Raman studies of these diamonds have revealed a complex assemblage of daughter phases in these micro-inclusions: carbonates, olivine, apatite, graphite, and an amorphous silicate phase (Zedgenizov et al., 2004). The micro-inclusions in most cuboid stones from Udachnaya are carbonatitic (carbonate-rich compositions with (water/(water+carbonate) ~ 0.05–0.2) and fall in the lower end of the hydrous-silicic to carbonatitic join observed in Botswanian diamonds (Navon et al., 1988; Schrauder and

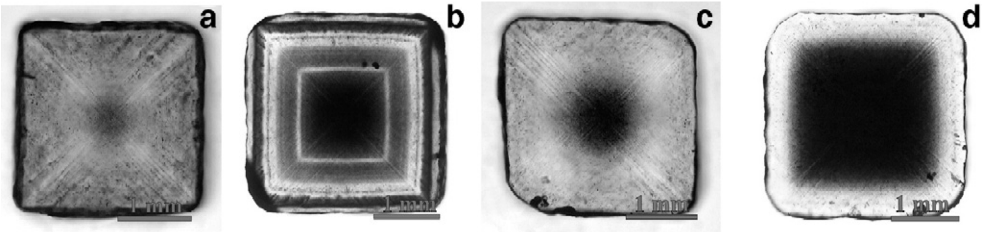

Fig. 1. Micro-inclusions in cuboid diamonds from Udachnaya kimberlite pipe. Transmitted light micrographs of polished slabs of cuboid diamonds showing zonal structure: a — Ud-02-171, b — Ud-02-172, c — Ud-02-308, d — Ud-02-163. Arrays of micro-inclusions trace the fibrous internal structure.

Navon, 1994). In this study the bulk major- and trace-element compositions of the micro-inclusions in 24 cuboid diamonds from Udachnaya have been quantitatively analyzed by Laser Ablation Inductively Coupled Plasma Mass Spectrometry (LAM-ICPMS). These results are used to characterize the diamond-forming fluids and to discuss their origin and evolution within the mantle. We also address the question of whether there is a genetic relationship between the fluid micro-inclusions in cuboid diamonds and their host kimberlite magma.

2. Samples

Twenty-four diamonds of cubic habit with abundant micro-inclusions (Fig. 1) were selected from the diamond collections of the Udachnaya pipe. The selected diamonds are colorless to yellow and greenish-yellow crystals 1–3 mm in size. The samples were polished along the cube plane into plates 100–200 μm thick. The size of individual micro-inclusions observed in the samples is usually less than 1 μm. Many of these samples have a fibrous internal structure that is defined by trains of micro-inclusions (see Fig. 1 a, b, c, d).

FTIR spectroscopy of these samples has been reported by Zedgenizov et al. (2004). All of the studied samples are classified as type IaA. The hydrogen impurity (peaks at 3107 and 1405 cm^{-1} (Woods and Collins, 1983)) is always present in them, and the absorption intensity of the 3107 cm^{-1} peak ranges from 1 to 5 cm^{-1}. The concentration of nitrogen is in the range 400–1100 ppm; the nitrogen abundance is not constant within individual crystals and may vary within the above limits.

3. Methods

Laser Ablation (LAM-) ICPMS is the most promising technique for multi-element analysis of diamonds; it causes relatively little damage to the diamond, drilling a hole 50–200 μm across and 15 μm deep. This hole samples all materials in the given volume, including numerous micro-inclusions. The technique used here has been described in detail by Rege et al. (2005); it is based on a synthetic multi-element doped cellulose pellet as the external standard, and carbon as the internal standard. Ablations with the 266 nm Nd:YAG laser are carried out in He, which is mixed with Ar before entering the ICPMS torch. Analyses are carried out on an Agilent 7500s ICPMS, tuned to optimize sensitivity across the mass range from Li to U. Data reduction is done using the in-house GLITTER software, which displays each run in a way that highlights spikes, inclusions and other heterogeneities, and allows selection of the most stable part of the signal for integration (van Achterbergh et al., 2001). A typical run will include two analyses of the cellulose standard, one analysis of the NIST612 glass, one analysis of a "standard" diamond (JWA115; see below), ten unknown diamonds (2 spots each), and two further analyses of the cellulose standard to correct for any instrumental drift; drift in all cases was minimal and was treated as linear (Rege et al., 2005).

The technique as currently applied for routine use collects data for a "short list" of 38 elements (Na, Mg, Al, K, Ca, Ti, V, Mn, Fe, Co, Ni, Cu, Ga, Rb, Sr, Y, Zr, Nb, Mo, Cs, Ba, La, Ce, Pr, Nd, Sm, Eu, Gd, Dy, Ho, Er, Yb, Lu, Hf, Ta, Pb, Th, U), with detection limits ranging from 1–15 ppm for some light elements to 2–10 ppb for many heavy elements. In many fibrous diamonds 25–38 of these elements are above detection, including the light REE (La, Ce, Pr) and some heavy REE (Yb, Lu). Standard deviations on the individual analytical values (Supplementary Table 1) are calculated from counting statistics (see Rege et al., 2005). A synthetic CVD diamond (pure carbon) has been repeatedly analyzed to identify and quantify artefacts such as molecular interferences (e $^{25}Mg = ^{12}C + ^{13}C$); the "blank values" determined in this way (Rege et al., 2005) have been subtracted from the raw analyses.

4. Results

The absolute elemental concentrations show a wide range, which depends strongly on the density of micro-inclusions and correlates with the abundance of water and carbonate in the diamonds, as determined from the IR extinction coefficients of Navon et al. (1988) (Supplementery Table 1). These correlations demonstrate that most of the analyzed elements in these diamonds reside in micro-inclusions, rather than in specific lattice sites. However, Ni and Co may produce specific defects in the lattice of natural and synthetic diamonds and thus may not completely reside in micro-inclusions (Hayakawa et al., 2000; Lang et al., 2003). The bulk compositions of the micro-inclusions for individual analytical points (center, intermediate, rim) are given in Supplementary Table 1. As the absolute concentrations of elements vary widely depending on the density of micro-inclusions, we have used inter-elemental ratios and spider-diagrams for presentation of the data. Tomlinson et al. (2005) have carried out analyses of fibrous diamonds without an internal standard, and derived concentrations for individual elements by

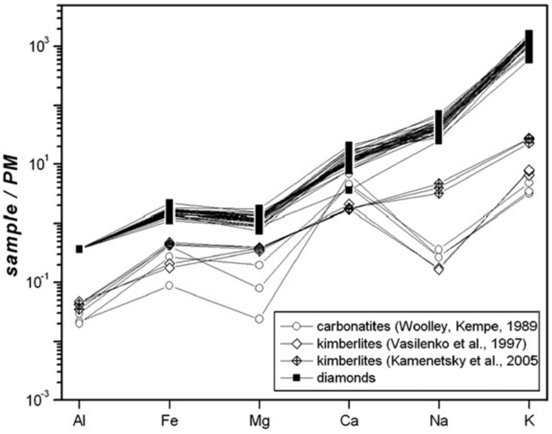

Fig. 2. Major-element abundances of bulk micro-inclusions in Udachnaya diamonds normalized to Primitive Mantle values (McDonough, Sun, 1995). The abundances in the host kimberlite (Vasilenko et al., 1997; Kamenetsky et al., 2004) and average carbonatites (Woolley and Kempe, 1989) are also shown. The concentrations of elements in micro-inclusions are normalized to the chondrite value of Al = 8600 ppm [cf. Tomlinson et al. (2005)].

normalizing their ICPMS data to the chondrite value of Al. To allow comparison of patterns in our data with those of Tomlinson et al. (2005) and to simplify comparison between the diamond-forming fluids, kimberlites and carbonatites, we have applied this normalization in Figs. 2 and 5.

4.1. Major elements

Major-element abundances, normalized to the Primitive Mantle composition (McDonough and Sun, 1995), of micro-inclusions in diamonds from Udachnaya are compared to the average composition of host kimberlite (East and West bodies) (Vasilenko et al., 1997) and extremely fresh group I kimberlite from the East body (Kamenetsky et al., 2004) and an average carbonatite (Woolley and Kempe, 1989) in Fig. 2. The micro-inclusions show a general enrichment in Ca, Na and K compared to Al, Fe and Mg. In comparison with host kimberlite or natural carbonatite rocks the main feature of the micro-inclusions is an enrichment in alkalis (K and Na) relative to other major elements. K/Na in Udachnaya diamonds is from 1.5 to 4.5, similar to that of the host kimberlite (3.5 — Udachnaya East, 4.2 — Udachnaya West). Natural carbonatites have lower K/Na (about 1.2). The high K content is a common feature of diamond-related fluids captured in micro-inclusions (Schrauder and Navon, 1994; Schrauder et al., 1996; Izraeli et al., 2001; Navon et al., 2003; Klein-BenDavid et al., 2004; Shiryaev et al., 2005).

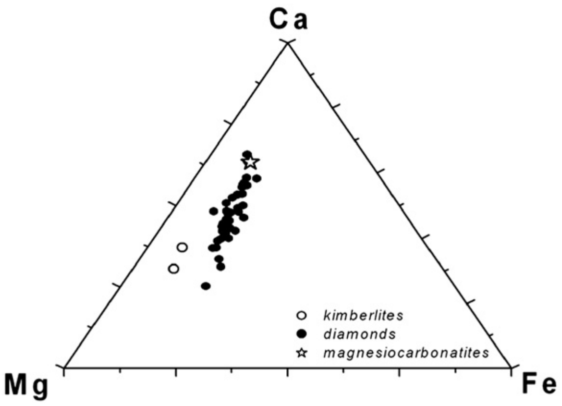

Fig. 3. The composition of the micro-inclusions in 24 diamonds from Udachnaya, projected on a Ca–Mg–Fe ternary diagram, with the compositions of the host kimberlite rocks (averages for East and West bodies) from the Udachnaya pipe (data from Vasilenko et al., 1997).

Some of the K in micro-inclusions may reside in K-bearing daughter minerals such as phlogopite, but, a large proportion of the K remains in the low-density fluid within the inclusions (Klein-BenDavid et al., 2006).

The Mg# (Mg/(Mg + Fe)) of the micro-inclusions varies in a narrow range between 0.66 and 0.78. Ca/(Ca + Mg) shows much wider variation, from 0.31 to 0.68. On the ternary plot Ca–Mg–Fe (Fig. 3) micro-inclusions define a

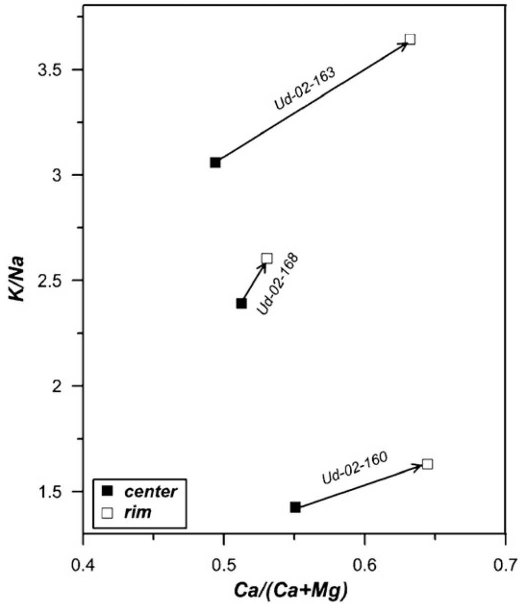

Fig. 4. Center-to-rim variations of the composition of bulk micro-inclusions in three diamonds from the Udachnaya kimberlite pipe.

continuous range of near-dolomitic compositions with a relatively constant Fe content. The compositions of micro-inclusions at the calcic end of this range correspond to the average composition of magnesiocarbonatites (Mg# 0.73 and Ca/(Ca+Mg) 0.7) (Woolley and Kempe, 1989). In contrast, the compositions of the host kimberlites lie near the magnesian end of the range of micro-inclusions and have lower Fe contents (Ca/(Ca+Mg)=0.33–0.4 Mg# 0.87). Thus the micro-inclusions in Udachnaya cuboid diamonds compositionally lie in the range between magnesiocarbonatites and kimberlite. The excess of Mg relative to pure dolomite in some diamonds may be linked with the presence of Mg-silicate phases (e.g. olivine, anamorphous silicate phase (Zedgenizov et al., 2004) or magnesite).

Several of the studied diamonds show radial variations in the bulk composition of micro-inclusions: rimward increases of Ca/Mg and K/Na are the most obvious (Fig. 4). The opposite trend, with a rimward decrease of Ca/Mg and K/Na of fluid micro-inclusions has been described in one diamond from the Diavik mine (Canada), suggesting mixing between an already evolved brine and a freshly introduced carbonatitic melt (Klein-BenDavid et al., 2004). Two Brazilian diamonds show the opposite evolution along the carbonatitic–hydrous-silicic join (Shiryaev et al., 2005). The rimward increases of K/Na and Ca/Mg in the Udachnaya diamonds suggest that the parental fluid evolved from Ca–Mg carbonatitic to more calcic alkali-rich compositions during diamond precipitation, but that the fluids stayed within a relatively narrow range of carbonatitic compositions.

4.2. Minor and trace elements

The concentrations of minor and trace elements in cuboid diamonds are very low and in many cases below the detection limits of the technique (<DL in Supplementary Table 1). The trace-element patterns (Fig. 5) include only data from regions of the diamonds rich in micro-inclusions. The patterns show a general similarity to those of the host kimberlite (Agashev, 2002; Kamenetsky et al., 2004) and natural carbonatites (Woolley and Kempe, 1989).

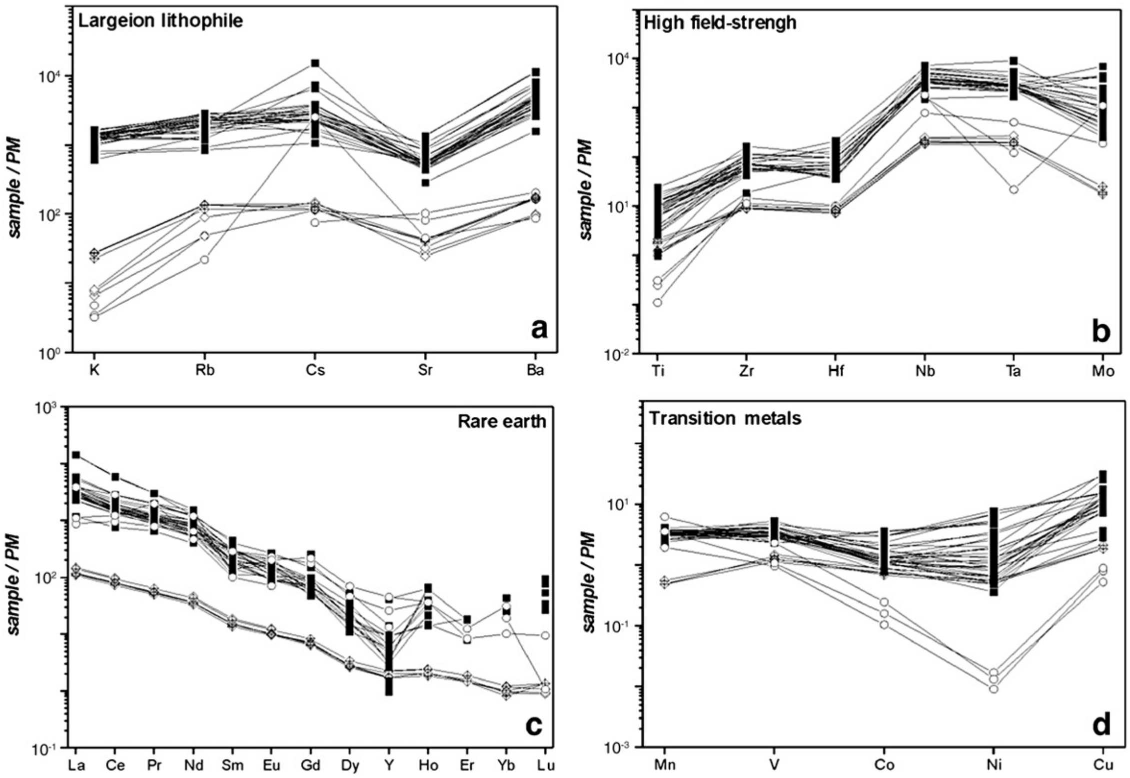

Fig. 5. Trace-element abundances of bulk micro-inclusions in Udachnaya diamonds normalized to Primitive Mantle values (McDonough, Sun, 1995): a — large ion lithophile elements; b — high field-strength elements; c — rare earth elements; d — transition metals. The abundances in the host kimberlite (Agashev, 2002; Kamenetsky et al., 2004) and average carbonatite are also shown (Woolley and Kempe, 1989). The element concentrations in the bulk micro-inclusions are normalized to the chondrite value of Al=8600 ppm (cf. Tomlinson et al., 2005). The legend is as in Fig. 2.

The fluids in the micro-inclusions show smooth patterns for the LILE (large ion lithophile elements) such as K, Rb, Cs, Ba and Sr, when normalized to a Primitive Mantle composition (McDonough and Sun, 1995) (Fig. 5 a). However, the relative abundance of K in the fluids is higher than observed in the host kimberlite and carbonatites. The K/Rb ratio of most Udachnaya diamond fluids (170–350) is higher than that of the host kimberlite (~ 50). Some samples show enrichment in Cs which is similar to that observed in calciocarbonatites. The Rb/Sr of the micro-inclusions (0.03–0.16) is similar to that of host kimberlite (0.05–0.12) and higher than that of carbonatites (~ 0.015).

The pattern of high field-strength elements (HFSE) (Fig. 5 b) in the micro-inclusions shows an order of magnitude depletion in Zr and Hf and two orders of depletion in Ti, relative to Ta, Nb and Mo. This pattern is very similar to that of host kimberlite. Carbonatites are even more depleted in Ti and with the exception of magnesiocarbonatites have negative Ta anomalies, which are also not observed in the studied micro-inclusions. The Zr/Hf ratio of the micro-inclusions varies in a wide range from 28 to 67, covering the range in the host kimberlites (40–43) and magnesiocarbonatites (52). The Nb/Ta ratio of the micro-inclusions spans a narrow range (19–27) and is intermediate between those of the host kimberlites (16–18) and magnesiocarbonatites (27).

The normalized REE (rare earth elements) pattern for Udachnaya diamonds reveals low abundances of the heavy REE and high light REE concentrations (Fig. 5 c). The Sm/Nd of the micro-inclusions (0.5–0.14) is similar to that of carbonatites (0.7–0.14) and slightly lower than in the host kimberlite (~ 0.14). The La/Dy ratio of micro-inclusions varies widely (13–273) and correlates with the Ca/(Ca+Mg+Fe) ratio, gradually decreasing from calcic to magnesian compositions (Fig. 6). The REE compositions of the former are generally similar to those of the calciocarbonatites (La/Dy ~ 18). The REE pattern for most micro-inclusion-bearing diamonds from Udachnaya is steeper than that of the host kimberlites (La/Dy ~ 38), reflecting the overall enrichment of LREE in the fluids. Many samples from Udachnaya have a negative anomaly in Y (Y/Ho 0.8–18), that also distinguishes them from the host kimberlites (Y/Ho 23–29) and carbonatites (Y/Ho 20–34).

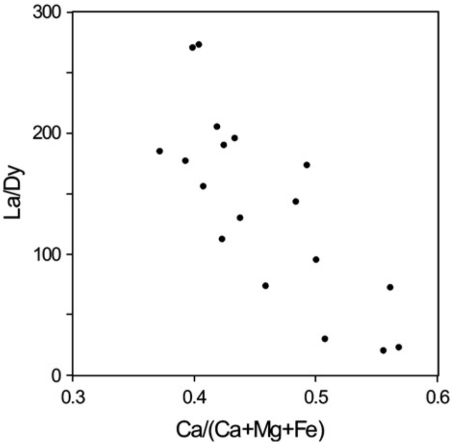

Fig. 6. Covariation of La/Dy vs. Ca/(Ca+Mg+Fe) in the fluids trapped as micro-inclusions in diamonds from Udachnaya.

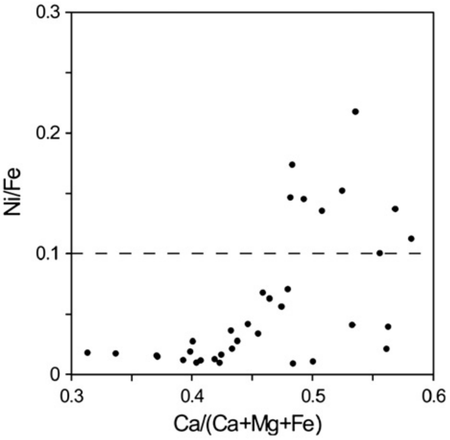

Fig. 7. Covariation of Ni/Fe ratio vs. Ca/(Ca+Mg+Fe) in the fluids trapped as micro-inclusions in diamonds from Udachnaya.

The micro-inclusions have low contents of transition metals relative to other trace-elements patterns (Fig. 5 d). Some micro-inclusions are enriched in Ni and Co relative to carbonatite compositions. The relative abundances of Ni and Co in micro-inclusions from Udachnaya cuboid diamonds are in general similar to that in host kimberlites and clearly inter-correlated. High Ni/Fe and Co/Fe ratios may indicate the presence of a sulfide component in micro-inclusions (cf. Tomlinson et al., 2005). However, there is no correlation between concentrations of Fe, Ni and Co. Some of the analyses of the diamonds have Ni/Fe higher than 0.1 and thus may contain sulfide components (Fig. 7). The samples which may contain sulfides also have Ca/(Ca+Mg+Fe) higher than 0.45.

5. Discussion

5.1. Diamond growth medium

It has been suggested that the cuboid habit of diamonds is a primary feature, reflecting rapid growth under high degrees of carbon supersaturation which operates as the driving force for diamond growth (Sunagawa, 1990). The rapid growth promotes the capture of numerous micro-inclusions of the parental medium (fluid), while during the slow growth of octahedral diamonds potential fluid inclusions tend to be pushed away from the surface.

The presence of hydrous species (in the form of molecular water and the hydroxyl group) and carbonates in micro-inclusions has been demonstrated by FTIR and EMPA, and provides evidence of their nucleation and crystallization from fluids. The multi-phase assemblage of daughter minerals in micro-inclusions in fibrous diamonds suggests that the parental fluids were either high-density super-critical fluids or volatile-rich melts (e.g. Navon et al., 1988; Navon, 1999; Navon et al., 2003).

A series of successful experiments on diamond growth from carbonate and carbonate–silicate melts support the possibility of natural diamond formation from carbonatitic melts (e.g. Akaishi et al., 1990; Pal'yanov et al., 1999; Litvin and Zharikov, 2000). The addition of water and up to 10% SiO_2 was shown to enhance the efficiency of diamond growth from such melts (Shatsky et al., 2002; Pal'yanov et al., 2005). The nucleation and growth of diamonds proceeded either via precipitation of free carbon dissolved in a carbonatitic melt or through carbonate–silicate interaction. The carbon-isotope composition of cuboid diamonds from Udachnaya varies within a very narrow range of $\delta^{13}C$ from −3 to −6‰ (Reutsky and Zedgenizov, 2007). This uniformity suggests that this diamond population formed from a fluid/melt that originated from a common source having carbon isotopic characteristics close to the mantle average (Galimov, 1991).

5.2. Comparison with previously reported fluid compositions in diamonds

While the micro-inclusions within individual diamonds typically are relatively uniform in composition, an inter-diamond comparison reveals a wide range of compositions between three endmembers: (a) a silicic endmember rich in water, Si, Al, and K; (b) a carbonatitic endmember rich in carbonate, Mg, Ca, Fe and K and (c) a saline endmember rich in water, Cl and K. Compositions intermediate between the carbonatitic and silicic components have been found in fibrous diamonds from Zaire, Botswana and Brazil (Navon et al., 1988; Schrauder and Navon, 1994; Shiryaev et al., 2005). Saline inclusions with minor carbonates were found in a fibrous Canadian diamond and in cloudy diamonds from South Africa (Klein-BenDavid et al., 2007; Izraeli et al., 2001). No intermediate compositions between the saline component and the silicic component have been detected.

The continuous arrays connecting the carbonatitic component with the saline and the hydrous-silicic endmembers suggest that the three fluids are genetically related. Navon et al. (2003) suggested that it is possible to derive all three endmembers from a single parental fluid and the most straightforward evolution is from a carbonatitic melt to each of the other fluids (or to all three, by immiscibility). Experiments in the boundary joins of the system have demonstrated that both the carbonate–silicate and chloride–carbonate melts are homogeneous; while high-temperature (above 1800 °C) liquid immiscibility is assumed for the chloride–silicate join of the above system (Perchuk et al., 2002). Addition of a silicate component to the chloride–carbonate melts and a chloride component to the carbonate–silicate

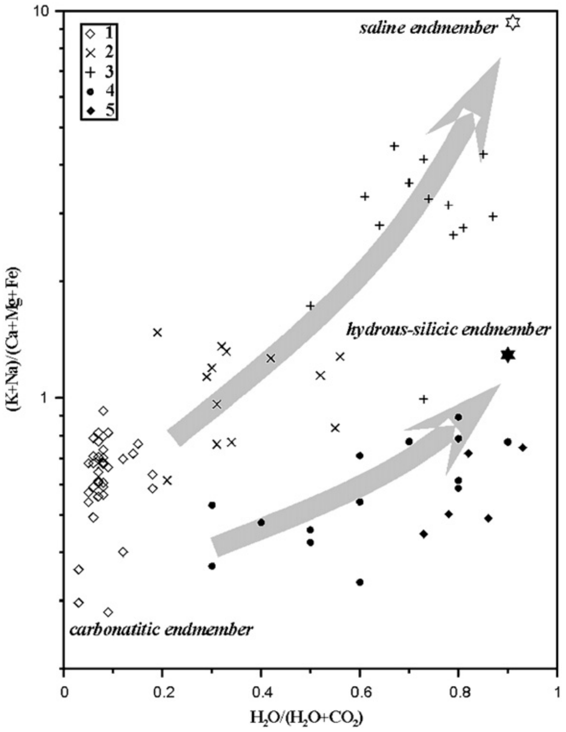

Fig. 8. $H_2O/(H_2O+CO_2)$ molar ratio vs. (K + Na)/(Ca + Mg + Fe) in the fluids trapped as micro-inclusions in diamonds: (1) Udachnaya; (2) Snap Lake, Canada (authors' unpublished data); (3) Diavik, Canada (data from Klein-BenDavid et al., 2007); (4) Jwaneng, Botswana (data from Schrauder and Navon, 1994); (5) Brazil (data from Shiryaev et al., 2005). Saline endmember is from Klein-BenDavid et al. (2007) and hydrous-silicic endmember is from Schrauder and Navon (1994). The carbonatitic endmember is deduced from our Udachnaya data.

melts results in splitting of the homogeneous liquids into the immiscible chloride–carbonate brine and carbonate–silicate melt (Safonov et al., 2007). The carbonate–silicate and chloride–carbonate branches of the miscibility gap converge within the carbonate-rich region of the system.

The micro-inclusions in cuboid diamonds from Udachnaya are of extreme carbonatitic composition. On the plot (K+Na)/(Ca+Mg+Fe) vs. water/(water+carbonate) (Fig. 8) they lie at the start of the carbonatitic-to-saline and carbonatitic-to-hydrous-silicic arrays of compositions of micro-inclusions previously reported for diamonds from Jwaneng, Botswana, Brazil and Diavik, Canada (Schrauder and Navon, 1994; Shiryaev et al., 2005; Klein-BenDavid et al., 2007) and for diamonds from Snap Lake, Canada (authors' unpublished data; Fig. 8). These observations suggest that the fluids in the micro-inclusions of cuboid diamonds from Udachnaya represent carbonatitic fluids/melts that were not significantly evolved toward saline and hydrous-silicic compositions.

The high CO_2 concentration ensures that most Mg, Fe, and Ca in the micro-inclusions are bonded in stable carbonates during cooling (Klein-BenDavid et al., 2006). Two types of carbonates were recognized by AEM (analytical electron microscopy) in Zairean diamonds, a high-Ca variety (dolomite-like) and low-Ca variety (magnesite-like) (Guthrie et al., 1991). TEM–EDAX (Energy Dispersive X-ray spectrometry) observation of micro-inclusions in diamonds from several localities has shown that most carbonates have molar compositions indicative of ferroan dolomite (50% Ca; 30% Mg and 20% Fe) (Klein-BenDavid et al., 2006). The micro-inclusions in Udachnaya diamonds similarly have a continuous range of near-dolomitic compositions with a relatively constant Fe content.

Tomlinson et al. (2005) have reported qualitative LAM-ICPMS data on the trace-element composition of micro-inclusions in five coated diamonds from Zaire. They found that the coat fluids have incompatible element ratios similar to those of natural carbonatites. Carbonatitic fluids in micro-inclusions from Udachnaya diamonds show enrichment in incompatible elements (K, Ba, Nb, LREE). Schrauder et al. (1996) have also demonstrated that the concentrations of most incompatible elements determined by Neutron Activation Analysis (NAA) of micro-inclusion-bearing diamonds from Jwaneng (Botswana) are generally higher in carbonate-rich samples. The LREE abundance of the micro-inclusions in diamonds from Udachnaya correlates with the Ca/(Ca+Mg+Fe) ratio, gradually decreasing from calcic to magnesian compositions. Hence the total compositional range of micro-inclusions found in Udachnaya diamonds reflects the evolution of parental carbonatitic fluids/melts in the mantle.

5.3. The origins of the carbonatitic fluids

The origin of upper mantle fluids or melts with geochemical features similar to those observed in the micro-inclusions of cuboid diamonds from Udachnaya may be attributed either to (i) mantle metasomatism with influx of carbonatitic and hydrous agents or (ii) partial melting of carbonated eclogites and peridotites (Schrauder et al., 1996; Tomlinson et al., 2005). The present study reveals compositional variations of fluids in Udachnaya cuboid diamonds from magnesian to calcic carbonatitic endmembers, which generally fall in the geochemical range between magnesiocarbonatites and kimberlites; these variations may be explained by different sources and origin of fluids by processes including fractional crystallization, liquid immiscibility or the mixing of such fluids.

5.3.1. Mantle metasomatism and fractional crystallization

Mantle metasomatism may be responsible for the influx of carbonate into a silicate substrate and could cause diamond crystallization. In this case, the trapped material in the micro-inclusions may represent either the infiltrating fluid itself, or a product of reaction between the mantle minerals and the infiltrating carbonatitic metasomatic agent (Navon et al., 2003). A major source of carbonate-rich melts in the convecting mantle may be subducted carbonates (e.g. Shatsky et al., 1995; Barker, 1996; Hoernle et al., 2002). However no signs of a "crustal connection" (i.e. light carbon-isotope composition or Eu anomalies) have been observed in micro-inclusions from Udachnaya cuboid diamonds.

Experiments have revealed a regular evolution of carbonate–silicate melts with decreasing temperature, toward an alkali-rich carbonatitic liquid (Safonov et al., 2007). This effect is governed by the precipitation of silicate phases even from silica-bearing carbonate melts. These trends are similar to the evolution of the fluid micro-inclusions in some diamonds from Botswana, Brazil and Canada indicating their growth during cooling. Crystallization of Mg-silicate minerals from a volatile-rich silicate magma can produce a carbonatitic fluid with strong enrichment in alkali and incompatible elements (Schrauder and Navon, 1994). The residual carbonatitic fluid will be similar to that observed in Udachnaya diamonds and may than evolve from magnesian compositions to calcic-alkali ones. Reaction of carbonatitic melts with peridotite wall-rock at depths shallower than 70 km may produce calciocarbonatite magmas (Dalton and Wood, 1993). However, diamond formation occurs at depths greater than 150 km and this scenario cannot explain the variations of fluid compositions observed in the Udachnaya cuboid diamonds.

Schrauder and Navon (1994) suggested fractional crystallization as an explanation for the range of carbonatitic to hydrous compositions of fluid micro-inclusions in Botswanian diamonds: the precipitation of Ca–Mg carbonate, apatite, titanates and K-bearing phases from this fluid will drive the residual fluid composition towards more H_2O-rich compositions. The compositions of fluids in micro-inclusions from Udachnaya diamonds may be the result of such fractional crystallization. The range of Ca/Mg between 0.3 and 0.6 suggests the primary crystallization of dolomite and/or some Mg-silicates (e.g. olivine). High contents of K and some HFSE (Nb, Ta) in micro-inclusions require the involvement of other phases (e.g. mica or chloride). Such fractional crystallization could cause the differentiation of fluids from magnesian to calcic-alkali compositions as found in the micro-inclusions from Udachnaya. The more evolved fluids would have high (K+Na)/(Ca+Mg+Fe) and H_2O-contents, similar to those observed in micro-inclusions in diamonds from Diavik and Snap Lake (see Fig. 8). Some saline components of micro-inclusions in diamonds may also represent an evolved form of carbonatitic fluid formed by crystallization of mantle phases (Navon et al., 2003; Klein-BenDavid et al., 2007).

5.3.2. Partial melting and liquid immiscibility

Carbonate-rich magmas may be generated at depths >70 km by very small degrees of partial melting of carbonated peridotite and eclogite (Dalton and Presnall, 1998; Moore and Wood, 1998; Hammouda, 2003; Yaxley and Brey, 2004). Carbonate melts derived from peridotites are dolomitic with Ca/(Ca+Mg) between 0.7 and 0.5 from 2 GPa to at least 7 GPa and contain 5–7 wt.% total alkalis. Both the total alkali contents and the Na/K of the melts are strongly dependent on the composition of the peridotite (Thibault et al., 1992; Sweeney, 1994). Carbonatites produced by melting of eclogites (Ca/(Ca+Fe+Mg)=ca 0.80) are more calcium-rich, than those produced by melting of carbonated peridotite (Ca/(Ca+Fe+Mg)=ca 0.50) (Hammouda, 2003). The range of carbonatitic compositions of micro-inclusions in Udachnaya cuboid diamonds may also have resulted from the partial melting of chemically different substrates, such as peridotite and eclogite. The Nb/Ta of the micro-inclusions varies between 14 and 32, with an average near 25, which is similar to the modeled values for 1% carbonatitic melt, derived from a Primitive Mantle composition (Green, 1995). Dalton and Presnall (1998) have demonstrated systematic variation of melt compositions with temperature from carbonatitic (Mg/Ca ~ 1; 5 wt.% SiO2) at the solidus (1380 °C) through intermediary compositions to kimberlitic (Mg/Ca ratios >2; >25 wt.% SiO_2) 70–100 °C above the solidus. For melting of model lherzolite with a CO_2 content of 0.15 wt.% this continuous change in melt composition from carbonatitic to kimberlitic takes place in the melting range 0–1%. The observed carbonatite–kimberlite continuum in melt compositions supports petrogenetic links between carbonatites and kimberlites. The geochemical features of micro-inclusions in Udachnaya cuboid diamonds showing some general variations between magnesiocarbonatites and kimberlites suggest that the fluids/melts parental to diamond growth may have a similar origin.

Blundy and Dalton (2000) demonstrated that partition coefficients for Zr, Ti, Y, Al and the HREE are higher in the silicate system than in the carbonate system. Thus, during partial melting these elements will be preferentially retained in the residual silicate minerals, whereas incompatible trace elements (e.g. K, Ba, Nb, LREE) will be concentrated in the carbonate melt. Using these coefficients, it is possible to reproduce the multi-element patterns observed in natural carbonatites through low-degree batch melting of carbonated garnet lherzolite and carbonated eclogite (Blundy and Dalton, 2000). Carbonatitic fluids in the micro-inclusions from Udachnaya diamonds show similar enrichment in K, Ba, Nb, and LREE, suggesting that they originated through low-degree partial melting of mantle peridotites and eclogites. Some of the studied samples with Ti and Zr depletions require the presence of phases such as rutile and zircon, which are common in eclogite but not in peridotite.

Carbonatite melts may be also generated through immiscibility of a carbonated silicate melt. Some hydrous carbonated silicate melts may bypass the high-temperature miscibility gap and reach the silicate–carbonate field boundary. Immiscible carbonate-rich liquids in model systems simulating magmatic conditions tend to be concentrated near calciocarbonatite compositions (<80% $CaCO_3$) (Lee and Wyllie, 1998). This suggests that dolomitic carbonatites such as those found in micro-inclusions in Udachnaya cuboid diamonds are not produced as immiscible liquids from silicate parental melts.

5.4. Relationship with the host kimberlite

Carbon and nitrogen isotopic values recorded for cuboid diamonds from many localities are quite uniform and fall in a tight range: −4 to −8‰ for $\delta^{13}C$ and −2 to −9‰ for $\delta^{15}N$ (Boyd et al., 1987, 1994; Cartigny et al., 2003). The majority of cuboids and fibrous coats on diamonds have also uniform nitrogen aggregation of type IaA (N pairs), suggestive of a relatively short mantle residence time (Evans, 1992). The short mantle residence time of cuboid diamonds has been used as an argument in favour of their growth being closely related in time to kimberlite magmatism. Boyd et al. (1987) suggested that these diamonds may precipitate during the accumulation and emplacement of the kimberlite melt.

Akagi and Masuda (1988) have demonstrated that the chondrite-normalized elemental abundance patterns of the cubic diamonds from Mbuji Mayi roughly resemble that of kimberlite and the $^{87}Sr/^{86}Sr$ ratios are similar to that of the kimberlite. The broad similarity of the trace-element patterns of cuboid diamonds from many localities to those of kimberlites and especially carbonatites has also been noted in a series of publications (Schrauder et al., 1996; Rege et al., 2003, 2005; Tomlinson et al., 2005). This observation suggests that fluid inclusions in fibrous diamonds were trapped as the diamond grew, either in the kimberlite melt, or in the mantle source for the kimberlite.

Tomlinson et al. (2005) proposed that the host kimberlite should lie along an extension of the compositional trend of the diamond micro-inclusions if the trapped fluid and kimberlite are genetically related. In the Ca–Mg–Fe ternary plot (Fig. 3) the average compositions of Udachnaya kimberlite (East and West bodies) lie in the area of the magnesian endmembers of the diamond micro-inclusions expanding to magnesiocarbonatites. This may indicate that the carbonatitic fluids in diamond micro-inclusions are products of an intermediate degree of melting between those characteristics of carbonatitic and kimberlitic magmas. However, other elemental ratios show large differences, and this suggests that the relationship between diamond growth and kimberlite petrogenesis is more complex. In comparison with the host kimberlite, micro-inclusions in the Udachnaya samples are enriched in K, Na, Fe and LREE and depleted in Al, Ti, Zr and Y.

Carbonatites associated with kimberlites may have crystallized from liquids residual after the crystallization of kimberlitic magma (Dalton and Presnall, 1998). The composition of the fluid/melt in micro-inclusions may also have evolved by the crystallization of aluminum silicates, titanates and zircon. In this scenario the cuboid diamonds may have grown during the ascent of the kimberlite, at depths within the diamond stability region. The phenocrystic growth of fibrous diamond in an evolving kimberlite magmatic system may also be responsible for the compositional variations of the trapped fluids.

6. Conclusions

Micro-inclusions in cuboid diamonds from Udachnaya kimberlite pipe define a continuous range from magnesian to calcic compositions (Ca/(Ca+Mg) 0.31–0.68) with a relatively constant Fe content (Mg/(Mg+Fe) 0.66–0.78). The excess of Mg relative to pure dolomite in some diamonds may be linked with the presence of Mg-silicate phases. In general the major- and trace-element patterns of fluid micro-inclusions in Udachnaya cuboid diamonds are closely similar to that of the host kimberlite as well as carbonatites, and compositionally lie in the range between them. However, some important differences have been found: (1) In comparison with the host kimberlite micro-inclusions are enriched in K, Na, Fe and depleted in Al; (2) the REE patterns of the fluid micro-inclusions in diamonds are steeper than those of kimberlites; (3) in many diamonds the fluid micro-inclusions show strong depletion in Ti, Zr and Y.

The geochemical features of fluids trapped as micro-inclusions in cuboid diamonds from Udachnaya are consistent with a genetic link to ephemeral carbonatitic fluids/melts (Green and Wallace, 1988), which may be precursors to the host kimberlite. These fluids/melts may originate either from mantle metasomatism involving the influx of carbonatitic and hydrous agents, or through partial melting of previously carbonated eclogites and peridotites. Some elemental variations may be explained by fractional crystallization of such fluid/melts or mixing of fluids with different compositions. These fluids seem to be important for volatile and trace-element transport between mantle reservoirs and may also affect the stability of many mantle phases and facilitate melting. These processes may generate kimberlitic magmas and diamond growth.

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Appendix A. Supplementary data

Supplementary data associated with this article can be found, in the online version, at doi:10.1016/j.chemgeo.2007.02.003.

References

Agashev, A.M., 2002. Rb–Sr and Sm–Nd isotope systematics and geochemistry of Siberian kimberlites and garnet-pyroxenite xenoliths: an insight into lithospheric mantle evolution and kimberlite origin. PhD thesis, Hokkaido University, Sapporo, Japan, 154 pp.

Akagi, T., Masuda, A., 1988. Isotopic and elemental evidence for a relationship between kimberlite and Zaire cubic diamonds. Nature 336, 665–667.

Akaishi, M., Kanda, H., Yamaoka, S., 1990. Synthesis of diamond from graphite–carbonate system under very high temperature and pressure. J. Cryst. Growth 104, 578–581.

Barker, D.S., 1996. Carbonatite volcanism. In: Mitchell, R.H. (Ed.), Undersaturated Alkaline Rocks: Mineralogy, Petrogenesis, and Economic Potential. Short Course, vol. 24. Mineralogical Association of Canada, pp. 45–61.

Blundy, J., Dalton, J., 2000. Experimental comparison of trace element partitioning between clinopyroxene and melt in silicate and carbonate systems, and implications for mantle metasomatism. Contrib. Mineral. Petrol. 139, 356–371.

Boyd, S.R., Mattey, D.P., Pillinger, C.T., Milledge, H.J., Mendelssohn, M., Seal, M., 1987. Multiple growth events during diamond genesis: an integrated study of carbon and nitrogen isotopes and nitrogen aggregation state in coated stones. Earth Planet. Sci. Lett. 86, 341–353.

Boyd, S.R., Pineau, F., Javoy, M., 1994. Modeling the growth of natural diamonds. Chem. Geol. 116, 29–42.

Bulanova, G.P., Novgorodov, P.G., Pavlova, L.A., 1988. First finding of melt inclusion in diamond of the “Mir” pipe. Geochem. Int. 756–765.

Bulanova, G.P., Griffin, W.L., Ryan, C.G., 1998. Nucleation environment of diamonds from Yakutian kimberlites. Mineral. Mag. 62, 409–419.

Cartigny, P., Harris, J.W., Taylor, A., Davies, R., Javoy, M., 2003. On the possibility of a kinetic fractionation of nitrogen stable isotopes during natural diamond growth. Geochim. Cosmochim. Acta 67, 1571–1576.

Chrenko, R.M., McDonald, R.S., Darrow, K.A., 1967. Infra-red spectrum of diamond coat. Nature 214, 474–476.

Dalton, J.A., Presnall, D.C., 1998. The continuum of primary carbonatitic–kimberlitic melt compositions in equilibrium with lherzolite: data from the system $CaO–MgO–Al_2O_3–SiO_2–CO_2$ at 6 GPa. J. Petrol. 39, 1953–1964.

Dalton, J.A., Wood, B.J., 1993. The compositions of primary carbonate melts and their evolution through wallrock reaction in the mantle. Earth Planet. Sci. Lett. 119, 511–525.

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

Galimov, E.M., 1991. Isotope fractionation related to kimberlite magmatism and diamond formation. Geochim. Cosmochim. Acta 55, 1697–1708.

Green, D.H., Wallace, M.F., 1988. Mantle metasomatism by ephemeral carbonatite melts. Nature 356, 459–462.

Green, T.H., 1995. Significance of Nb/Ta as an indicator of geochemical processes in the crust–mantle system. Chem. Geol. 120, 347–359.

Guthrie, G.D., Veblen, D.R., Navon, O., Rossman, G.R., 1991. Submicrometer fluid inclusions in turbid-diamond coats. Earth Planet. Sci. Lett. 105, 1–12.

Hammouda, T., 2003. High-pressure melting of carbonated eclogite and experimental constraints on carbon recycling and storage in the mantle. Earth Planet. Sci. Lett. 214, 357–368.

Harris, J.W., 1992. Diamond geology. In: Field, J.E. (Ed.), The Properties of Natural and Synthetic Diamond. Academic Press, London, pp. 345–349.

Hayakawa, S., Jia, X.P., Wakatsuki, M., Gohshi, Y., Hirokawa, T., 2000. Analysis of trace Co in synthetic diamonds using synchrotron radiation excited X-ray fluorescence analysis. J. Cryst. Growth 210, 388–394.

Hoernle, K., Tilton, G., Le Bas, M.J., Duggen, S., Garbe-Schonberg, D., 2002. Geochemistry of oceanic carbonatites compared with continental carbonatites: mantle recycling of oceanic crustal carbonate. Contrib. Mineral. Petrol. 142, 520–542.

Izraeli, E.S., Harris, J.W., Navon, O., 2001. Brine inclusions in diamonds: a new upper mantle fluid. Earth Planet. Sci. Lett. 187, 323–332.

Izraeli, E.S., Harris, J.W., Navon, O., 2004. Fluid and mineral inclusions in cloudy diamonds from Koffiefontein, South Africa. Geochim. Cosmochim. Acta 68, 2561–2575.

Kamenetsky, M.B., Sobolev, A.V., Kamenetsky, V.S., Maas, R., Danyushevsky, L.V., Thomas, R., Pokhilenko, N.P., Sobolev, N.V., 2004. Kimberlite melts rich in alkali chlorides and carbonates: a potent metasomatic agent in the mantle. Geology 32, 845–848.

Kagi, H., Lu, R., Davidson, P., Goncharov, A.F., Mao, H.K., Hemley, R.J., 2000. Evidence for ice VI as an inclusion in cuboid diamonds from high *P–T* near infrared spectroscopy. Mineral. Mag. 64, 1089–1097.

Kagi, H., Kiyasu, A., Akagi, T., Nara, M., Sawaki, T., 2006. Near infrared spectroscopy determines salinity and internal pressure of fluid inclusions in minerals. Appl. Spectrosc. 60, 430–436.

Kessel, R., Ulmer, P., Pettke, T., Schmidt, M.W., Thompson, A.B., 2005. The water–basalt system at 4 to 6 GPa: phase relations and second critical endpoint in a K-free eclogite at 700 to 1400 °C. Earth Planet. Sci. Lett. 237, 873–892.

Klein-BenDavid, O., Izraeli, E.S., Hauri, E., Navon, O., 2004. Mantle fluid evolution — a tale of one diamond. Lithos 77, 243–253.

Klein-BenDavid, O., Wirth, R., Navon, O., 2006. TEM imaging and analysis of microinclusions in diamonds: a close look at diamond-growing fluids. Am. Mineral. 91, 353–365.

Klein-BenDavid, O., Izraeli, E.S., Hauri, E., Navon, O., 2007. Fluid inclusions in diamonds from the Diavik mine, Canada and the evolution of diamond-forming fluids. Geochim. Cosmochim. Acta. 71, 723–724.

Lang, A.R., Walmsley, J.C., 1983. Apatite inclusions in natural diamond coat. Phys. Chem. Mineral. 9, 6–8.

Lang, A.R., Yelisseyev, A.P., Pokhilenko, N.P., Steeds, J.W., Wotherspoon, A., 2003. Is dispersed nickel in natural diamonds associated with cuboid growth sectors in diamonds that exhibit a history of mixed-habit growth? J. Cryst. Growth. 263, 575–589.

Lee, W.-J., Wyllie, P.J., 1998. Processes of crustal carbonatite formation by liquid immiscibility and differentiation, elucidated by model systems. J. Petrol. 39, 2005–2013.

Litvin, Yu.A., Zharikov, V.A., 2000. Experimental modeling of diamond genesis: diamond crystallization in multicomponent carbonate–silicate melts at 5–7 GPa and 1200–1570 °C. Dokl. Earth Sci. 372, 808–811.

McDonough, W.F., Sun, S.-s., 1995. The composition of the earth. Chem. Geol. 120, 223–253.

Meyer, H.O.A., 1987. Inclusions in diamond. Mantle Xenoliths. John Wiley and Sons, New York, pp. 501–522.

Moore, K.R., Wood, B.J., 1998. The transition from carbonate to silicate melts in the CaO–MgO–SiO_2–CO_2 system. J. Petrol. 39, 1943–1951.

Navon, O., 1991. Infrared determination of high internal pressures in diamond fluid inclusions. Nature 353, 746–748.

Navon, O., 1999. Diamond formation in the Earth's mantle. Proc 7 Inter Kimberlite Conf., vol.2 (Nixon vol. P.H.), Red Roof Design, Cape Town, pp. 757–763.

Navon, O., Hutcheon, I.D., Rossman, G.R., Wasserburg, G.J., 1988. Mantle-derived fluids in diamond micro-inclusions. Nature 335, 784–789.

Navon, O., Izraeli, E.S., Klein-BenDavid, O., 2003. Fluid inclusions in diamonds — the carbonatitic connection. 8th International Kimberlite Conference, Extended Abstracts, FLA_0107.

Novgorodov, P.G., Bulanova, G.P., Pavlova, L.A., Mikhailov, V.N., Ugarov, V.V., Shebanin, A.P., Argunov, K.P., 1990. Inclusions of potassic phases, coesite and omphacite in the coated diamond crystal from the "Mir" pipe. Dokl. Akad. Nauk SSSR, Earth Sci. 310, 439–443.

Pal'yanov, Yu.N., Sokol, A.G., Borzdov, Yu.M., Khokhryakov, A.F., Sobolev, N.V., 1999. Diamond formation from mantle carbonate fluids. Nature 400, 417–418.

Pal'yanov, Y.N., Sokol, A.G., Tomilenko, A.A., Sobolev, N.V., 2005. Conditions of diamond formation through carbonate–silicate interaction. Eur. J. Mineral. 17, 207–214.

Perchuk, L.L., Safonov, O.G., Yapaskurt, V.O., Barton, J.M., 2002. Crystal-melt equilibria involving potassium-bearing clinopyroxene as indicator of mantle-derived ultrahigh-potassic liquids: an analytical review. Lithos 60, 89–111.

Rege, S., Davies, R.M., Griffin, W.L., Jackson, S., O'Reilly, S.Y., 2003. Trace element analysis of diamond by LAM ICPMS: preliminary results. Proceedings of the 8th International Kimberlite Conference, FLA_0087.

Rege, S., Jackson, S., Griffin, W.L., Davies, R.M., Pearson, N.J., O'Reilly, S.Y., 2005. Quantitative trace-element analysis of diamond by laser ablation inductively coupled plasma mass spectrometry. J. Anal. At. Spectrom. 20, 601–611.

Reutsky, V.N., Zedgenizov, D.A., 2007. The features of carbon isotope composition and impurities in diamonds of octahedral and cubic habit from Udachnaya kimberlite pipe (Yakutia). Russ. Geol. Geophys 48, 380–392.

Safonov, O.G., Perchuk, L.L., Litvin, Y.A., 2007. Melting relations in the chloride–carbonate–silicate systems at high-pressure and the model for formation of alkalic diamond-forming liquids in the upper mantle. Earth Planet. Sci. Lett. 253, 112–128.

Schrauder, M., Koeberl, C., Navon, O., 1996. Trace element analyses of fluid-bearing diamonds from Jwaneng, Botswana. Geochim. Cosmochim. Acta 52, 761–771.

Schrauder, M., Navon, O., 1994. Hydrous and carbonatitic mantle fluids in fibrous diamonds from Jwaneng, Botswana. Geochim. Cosmochim. Acta 52, 761–771.

Shatsky, V.S., Sobolev, N.V., Vavilov, M.A., 1995. Diamond-bearing metamorphic rocks from the Kokchetav massif (Northern Kazakhstan). In: Coleman, R.G., Wang, X. (Eds.), Ultrahigh Pressure Metamorphism. Cambridge University Press, pp. 427–455.

Shatsky, A.F., Borzdov, Y.M., Sokol, A.G., Pal'yanov, Y.N., 2002. Phase formation and diamond crystallization in carbon-bearing ultrapotassic carbonate–silicate systems. Russ. Geol. Geophys. 43, 940–950.

Shiryaev, A.A., Izraeli, E.S., Hauri, E., Zakharchenko, O.D., Navon, O., 2005. Chemical, optical, and isotopic investigations of fibrous diamonds from Brazil. Russ. Geol. Geophys. 46, 1207–1222.

Sobolev N.V. 1974. Deep-seated inclusions in kimberlites and the problem of the composition of the upper mantle. Novosibirsk, Nauka, 246 p. (in Russian), English translation. 1977. Boyd F.R. eds, AGU, Washington D.C., 279 pp.

Sunagawa, I., 1990. Growth and morphology of diamond crystals under stable and metastable conditions. J. Cryst. Growth 99, 1156–1161.

Sweeney, R.J., 1994. Carbonatite melt compositions in the Earth's mantle. Earth Planet. Sci. Lett. 128, 259–270.

Thibault, Y., Edgar, A.D., Lloyd, F.E., 1992. Experimental investigation of melts from a carbonated phlogopite lherzolite: implications for metasomatism in the continental lithospheric mantle. Am. Mineral. 77, 784–794.

Tomlinson, E., De Schrijver, I., De Corte, K., Jones, A.P., Moens, L., Vanhaecke, F., 2005. Trace element composition of submicroscopic inclusions in coated diamond: a tool for understanding diamond petrogenesis. Geochim. Cosmochim. Acta 69, 4719–4732.

van Achterbergh, E., Ryan, C., Jackson, S., Griffin, W., 2001. Appendix 3 data reduction software for LA-ICP-MS. In: Sylvester, P. (Ed.), Laser-Ablation-ICPMS in the Earth Sciences. Short Course, vol. 29. Mineralogical Association of Canada, pp. 239–243.

Vasilenko, V.B., Zinchuk, N.N., Kuznetsova, L.G., 1997. Petrochemical Models of Diamond Deposits of Yakutia. Nauka, Siberian Enterprise RAS, Novosibirsk. 574 pp.

Walmsley, J.C., Lang, A.R., 1992a. On sub-micrometre inclusions in diamond coat: crystallography and composition of ankerites and related rhombohedral carbonates. Mineral. Mag. 56, 533–543.

Walmsley, J.C., Lang, A.R., 1992b. Oriented biotite inclusions in diamond coat. Mineral. Mag. 56, 108–111.

Wyllie, P.J., Ryabchikov, I.D., 2000. Volatile components, magmas, and critical fluids in upwelling mantle. J. Petrol. 41 (7), 1195–1206.

Woods, G.S., Collins, A.T., 1983. Infrared absorption spectra of hydrogen complexes in type I diamonds. J. Phys. Chem. Solids 44, 471–475.

Woolley, A.R., Kempe, D.R.C., 1989. Carbonatites: nomenclature, average chemical compositions and element distribution. In: Bell, K. (Ed.), Carbonatites — Genesis and Evolution. Unwin Hyman, pp. 1–14.

Yaxley, G.M., Brey, G.P., 2004. Phase relations of carbonate-bearing eclogite assemblages from 2.5 to 5.5 GPa: implications for petrogenesis of carbonatites. Contrib. Mineral. Petrol. 146, 606–619.

Zedgenizov, D.A., Logvinova, A.M., Shatsky, V.S., Sobolev, N.V., 1998. Inclusions in microdiamonds from some kimberlite diatremes of Yakutia. Dokl. Earth Sci. 359, 204–208.

Zedgenizov, D.A., Kagi, H.K., Shatsky, V.S., Sobolev, N.V., 2004. Carbonatitic melts in cuboid diamonds from Udachnaya kimberlite pipe (Yakutia): evidence from vibrational spectroscopy. Mineral. Mag. 68, 61–73.