

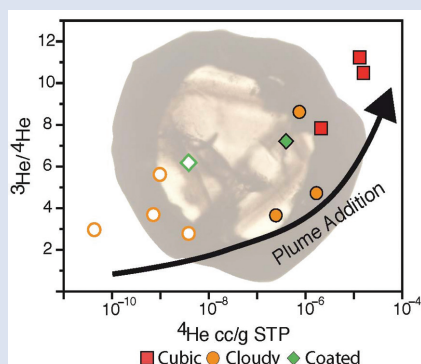
Plume-lithosphere interaction, and the formation of fibrous diamonds

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Abstract



Fluid inclusions in diamond provide otherwise inaccessible information on the origin and nature of carbonaceous fluid(s) in the mantle. Here we evaluate the role of subducted volatiles in diamond formation within the Siberian cratonic lithosphere. Specifically, we focus on the halogen (Cl, Br and I) and noble gas (He, Ne and Ar) geochemistry of fluids trapped within cubic, coated and cloudy fibrous diamonds from the Nyurbinskaya kimberlite, Siberia. Our data show Br/Cl and I/Cl ratios consistent with involvement of altered oceanic crust, suggesting subduction-derived fluids have infiltrated the Siberian lithosphere. $^3\text{He}/^4\text{He}$ ranging from 2 to 11 R_A , indicates the addition of a primordial mantle component to the SCLM. Mantle plumes may therefore act as a trigger to re-mobilise subducted carbon-rich fluids from the sub-continental lithospheric mantle, and we argue this may be an essential process in the formation of fluid-rich diamonds, and kimberlitic magmatism.

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Introduction

Diamond formation events within the sub-cratonic lithospheric mantle (SCLM) are related to metasomatism, often coeval with tectonothermal events, such as subduction and plume emplacement (Haggerty, 1999; Gurney *et al.*, 2010). These fluids can be trapped as microinclusions along the surfaces of diamond fibres and surrounding diamond-hosted mineral inclusions (Navon *et al.*, 1988; Nimis *et al.*, 2016; Skuzovatov *et al.*, 2016). Diamond-hosted fluids therefore represent the only direct samples of mantle fluids, and provide a unique insight into the composition of carbonaceous fluids from the mantle.

Fluids trapped in diamonds are categorised into four major compositional groups, distinguishable on a ternary plot for K + Na (saline), Al + Si (silicic), and Ca + Mg + Fe (high- and low-Mg carbonatitic) (Klein-BenDavid *et al.*, 2009). The four compositional end members are considered to form either *via* immiscible separation of hydrous and carbonatitic fluids within the SCLM (Schrauder and Navon, 1994), or *via* the interaction of a parental saline fluid with the lithosphere, producing silicic and carbonatitic fluids (Weiss *et al.*, 2015). Saline fluids

in diamonds have been shown to have high concentrations of Cl of up to ~40 wt. % (Izraeli *et al.*, 2001; Klein-BenDavid *et al.*, 2007). Diamonds from Canadian kimberlites, previously shown to contain saline inclusions (Tomlinson *et al.*, 2009) have highly elevated Br/Cl and I/Cl values, suggesting parental fluids may have been introduced to the SCLM during ancient subduction-related processes (Johnson *et al.*, 2000).

Halogens and noble gases are concentrated in surface reservoirs, and have distinguishable elemental/isotopic ratios within different reservoirs, making them sensitive tracers of subduction-related metasomatism (Broadley *et al.*, 2016). Here we report halogen abundance (Cl, Br and I) and noble gas isotopic (He, Ne and Ar) data from a suite of cubic, cloudy and coated diamonds from the Nyurbinskaya kimberlite, Nakynsky field, Siberia (Fig. S-1). The Nyurbinskaya kimberlite contains a higher proportion of eclogitic diamonds, relative to other Siberian kimberlites – potentially indicating the diamonds have a subduction-related origin (Spetsius *et al.*, 2008). We combine halogen and noble gases to explore the origin(s) of diamond-hosted fluids within the Siberian SCLM.

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Halogen Geochemistry

The range of Cl (0.5–20.3 ppm), Br (2.7–168.6 ppb) and I (0.1–2.1 ppb) concentrations within the diamonds ($n = 7$; Table S-1) are higher than previously reported measurements of Siberian fibrous diamonds (Burgess *et al.*, 2002). Halogen concentrations are higher in cubic diamonds indicating that halogens are predominantly sited within microinclusions, given the greater proportion of inclusions in the cubic diamonds compared to the coated or cloudy samples.

The Br/Cl and I/Cl ratios for the fluids progress from mantle-like signatures towards elevated Br/Cl values (Fig. 1). Similar Br/Cl signatures have been previously measured in fibrous diamonds from Canada (Johnson *et al.*, 2000; Burgess *et al.*, 2009). The above mantle Br/Cl and I/Cl values in Canadian diamond-fluids were attributed to either the subduction of volatiles into the SCLM or fractionation of halogens during the separation of immiscible fluids (Burgess *et al.*, 2009). The latter process was considered most feasible given the lack of a known subduction component with similar Br/Cl and I/Cl values (Burgess *et al.*, 2009).

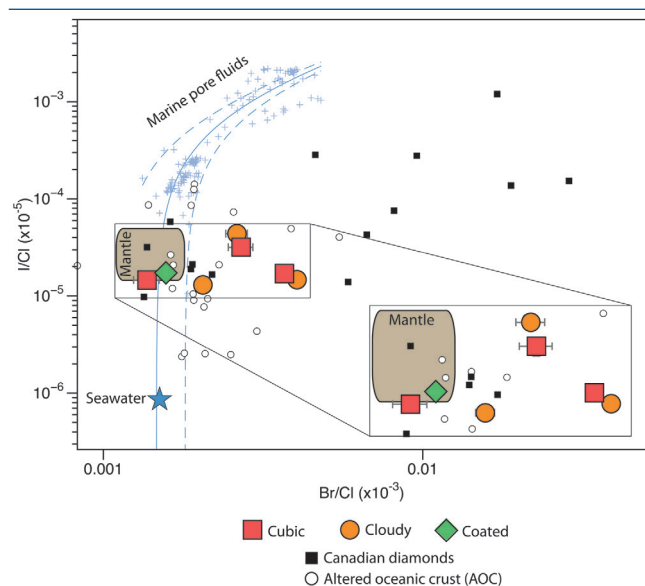


Figure 1 Log-log plot of I/Cl vs. Br/Cl (mol/mol) for the Nyurbinskaya diamonds. Seawater, average mantle, marine pore fluids, altered oceanic crust fluids (AOC) and Canadian diamonds are shown for reference (Johnson *et al.*, 2000; Muramatsu *et al.*, 2007 and references therein; Kendrick *et al.*, 2012; Chavrit *et al.*, 2016). Nyurbinskaya diamonds range from mantle values towards enriched Br/Cl, similar to AOC and Canadian diamonds suggesting there has been an input of Br-rich fluids to the Siberian lithosphere. Uncertainties are 1σ when shown and are often smaller than symbol size.

However, the separation of immiscible fluids during diamond formation would likely lead to combined fractionation of both Br/Cl and I/Cl ratios. The I/Cl ratio is expected to be fractionated to a greater degree given that halogen fractionation is most likely controlled by differences in solubility in the aqueous fluid, which increases from NaCl < NaBr < NaI, leading to the heavier halogens being concentrated in the brine fraction, relative to the lighter halogens (Bureau *et al.*, 2000). Fractionation should therefore result in a steeper profile of Br/Cl and I/Cl than that measured in the Nyurbinskaya and Canadian diamonds (Johnson *et al.*, 2000). The I/Cl of Nyurbinskaya diamonds are also consistently mantle-like, suggesting fractionation during diamond formation is not the main mechanism controlling the increase in Br/Cl. To explain the relative enrichment in Br without an associated enrichment

of I, is therefore more consistent with mixing between two distinct components (mantle-like + high Br/Cl component; Fig. 1).

A potential high Br/Cl source is the fluid fraction trapped within altered oceanic crust (AOC) (Chavrit *et al.*, 2016). High Br/Cl in AOC fluids is attributed to phase separation of saline fluids during seawater-basalt interaction, and/or the sequestering of Cl into alteration minerals (Chavrit *et al.*, 2016). This process fractionates Br/Cl, whereas I/Cl ratios remain mostly intermediate between mantle and seawater values. This suggests that interaction between seawater and the oceanic crust with a mantle composition predominantly controls I/Cl, without affecting Br/Cl, given that seawater and mantle have indistinguishable Br/Cl values. Higher than mantle I/Cl in AOC may indicate a limited degree of fractionation or the presence of an I-rich sedimentary component (Fig. 1; Chavrit *et al.*, 2016). Whilst Nyurbinskaya and Canadian diamonds generally range from mantle values towards higher Br/Cl and I/Cl, some diamonds have I/Cl lower than the mantle, which could not be formed from the same fractionation process responsible for the elevated Br/Cl and I/Cl and may therefore signify a subducted AOC component in the parental fluids (Fig. 1).

Mantle xenoliths from Nyurbinskaya show $\delta^{18}\text{O}$ values up to +9.65 ‰, higher than typical mantle samples (+5.5 ‰; Matthey *et al.*, 1994). Elevated $\delta^{18}\text{O}$ is interpreted as evidence for subduction of oceanic crust, which has undergone low temperature alteration (Gregory and Taylor, 1981). Notably, Br/Cl of AOC fluids decreases with depth in the oceanic crust (Chavrit *et al.*, 2016), suggesting the release of fluids from the upper oceanic crust, where low temperature alteration occurs, may be the potential source of the halogen-rich fluids within the Siberian SCLM. The subduction of AOC fluids can therefore provide a Br/Cl enriched source necessary to explain the signature of the Nyurbinskaya diamonds.

An AOC Br/Cl and I/Cl origin could also account for some of the values measured within other fibrous diamonds (Fig. 1). The extreme Br/Cl and I/Cl measured in some Canadian diamonds cannot be accounted for by the simple addition of AOC-like fluids to the SCLM, suggesting that another process may be responsible for enriching diamond-forming fluids in Br and I relative to Cl. This process may be related to an unknown fractionation process during subduction or within the SCLM, however the processes driving further enrichment of Br and I remain unknown.

Noble Gas Geochemistry

The $^3\text{He}/^4\text{He}$ of the diamonds released during crushing and laser heating are similar and range from 2.8–11.2 R_A . However, the concentrations of He released during laser heating are 2–4 orders of magnitude lower than that released during crushing (Fig. 2), suggesting the noble gases are primarily hosted within microinclusions and are efficiently released by crushing. The upper range of $^3\text{He}/^4\text{He}$ in the diamonds is similar to values obtained from Siberian Flood Basalts (<12.7; Basu *et al.*, 1995) indicating that the diamonds contain at least two noble gas components; a low $^3\text{He}/^4\text{He}$ SCLM component and a high $^3\text{He}/^4\text{He}$ primitive mantle component, potentially related to the Siberian plume. The $^3\text{He}/^4\text{He}$ signatures of the diamonds differ according to type, with the cubic diamonds having $^3\text{He}/^4\text{He}$ extending above the MORB range ($8 \pm 1 R_A$; Graham, 2002), whilst the coated and cloudy diamonds range from MORB-like to lower values. The cubic diamonds therefore appear to be dominated by volatiles associated with the plume-like signature, whilst coated and cloudy diamonds retain more of the original lithospheric signature (4–6 R_A ; Gautheron

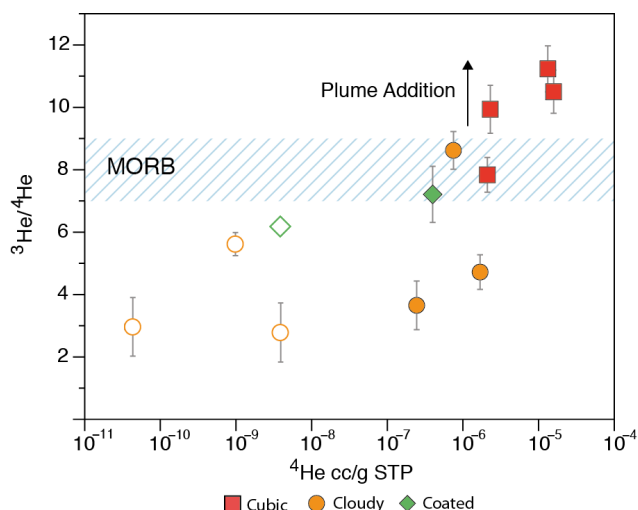


Figure 2 $^3\text{He}/^4\text{He}$ vs. ^4He concentrations from crushing and laser heating (open symbols) of Nyurbinskaya diamonds. $^3\text{He}/^4\text{He}$ from the cubic diamonds are higher than the cloudy and coated diamonds and plot above MORB values suggesting the diamond-hosted inclusions contain a mixture of lithospheric and deep mantle volatiles. Uncertainties shown are 1σ and for ^4He concentrations are smaller than symbol size.

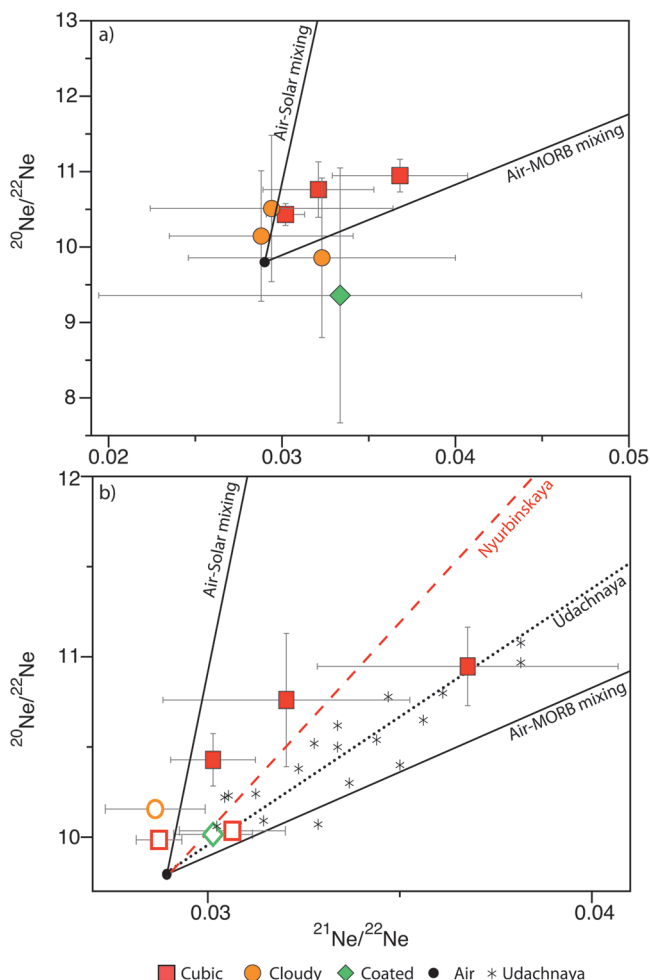


Figure 3 (a) Neon three-isotope plot for crushing of Nyurbinskaya diamonds. (b) Zoomed in section showing data from laser extraction (open symbols) plus the crushing data from the cubic diamonds. Diamonds show excess in $^{20}\text{Ne}/^{22}\text{Ne}$ and $^{21}\text{Ne}/^{22}\text{Ne}$ relative to air and plot intermediate between the MORB-Air mixing line and the Solar-Air mixing line. Dashed red line is a regression line fitted through all the Nyurbinskaya

diamond data and forced through the atmospheric values. Dashed black line is the trend for Udachnaya olivine xenocrysts (Sumino *et al.*, 2006). Uncertainties are 1σ .

et al., 2005). Some of the coated and cloudy diamonds have lower than SCLM $^3\text{He}/^4\text{He}$ suggesting the additional input of radiogenic ^4He to the SCLM from a subducted component (Barry *et al.*, 2015).

Neon isotopic ratios from the Nyurbinskaya diamonds further indicate the involvement of a mantle plume in the Siberian SCLM. Diamonds with Ne isotopic ratios distinct from atmosphere (Fig. 3) are intermediate between the Air-MORB mixing line and the Air-Solar mixing line on the $^{20}\text{Ne}/^{22}\text{Ne}$ - $^{21}\text{Ne}/^{22}\text{Ne}$ isotope diagram. The neon isotope composition of Nyurbinskaya diamonds is similar to those from Udachnaya (Sumino *et al.*, 2006), suggesting that the formation of kimberlites and fibrous diamonds in the Siberian Craton around 360 Ma may be linked to the injection of plume material. The He and Ne isotopic composition of Nyurbinskaya diamonds indicates that they contain a mixture of air and a mantle end member, the latter having high $^3\text{He}/^4\text{He}$ and mantle-like $^{20}\text{Ne}/^{22}\text{Ne}$ compositions similar to the Siberian Flood Basalts, with an additional contribution from the low $^3\text{He}/^4\text{He}$ SCLM (Fig. S-5).

Diamond Formation during Plume-Lithosphere Interaction

The nitrogen aggregation state in diamonds provides a qualitative method to investigate the mantle residence time and temperature of diamonds (Supplementary Information). Nitrogen aggregation states of fibrous diamonds indicate they have short mantle residence times, and ^{40}Ar - ^{39}Ar ages of fibrous coats suggests their growth is related to kimberlite magmatism (Taylor *et al.*, 1996; Burgess *et al.*, 2002). Low nitrogen aggregation states determined for Nyurbinskaya cubic and cloudy diamonds (Fig. 4) confirm that they formed not long before emplacement. The core of the coated diamonds however, show nitrogen aggregation states more consistent with a mantle residence age of between 1 Ma and 200 Ma based on a residence temperature of 1200-1300 °C, as estimated from mantle xenoliths in the nearby Udachnaya kimberlite (Boyd *et al.*, 1997). Individual FTIR measurements on the coats of the fibrous samples show low degrees of N aggregation, indicating fibrous coats formed around the same time and resided at similar mantle temperatures, as the cubic diamonds.

Cubic diamonds, which are most abundant in microinclusions and have very short mantle residence times, have the most plume-like noble gas signature suggesting that the fluids may be related to the influx of deep mantle volatiles triggering diamond growth. In contrast, the optically clearer diamond cores of the coated stones have a consistently larger percentage of nitrogen B centres suggesting a longer residence time as well as potentially acting as seeds for the growth of fibrous coats. It should be noted that given the temperature range estimated for the Siberian SCLM at the time of Nyurbinskaya kimberlite formation, all except some of the cloudy diamonds could have mantle residence as low as 5 Ma and therefore may be related to the same metasomatic event(s). Three cubic diamonds that have similar nitrogen contents and aggregation states as the coated diamonds may indicate that even the cubic diamonds retain older diamond cores (*i.e.* seeds), or that the higher temperatures associated with plume accelerated the nitrogen aggregation state over short time scales (Fig. 4).

Therefore, the Siberian lithosphere experienced at least two episodes of diamond growth. The formation of fibrous diamonds in particular requires the precipitation of carbon



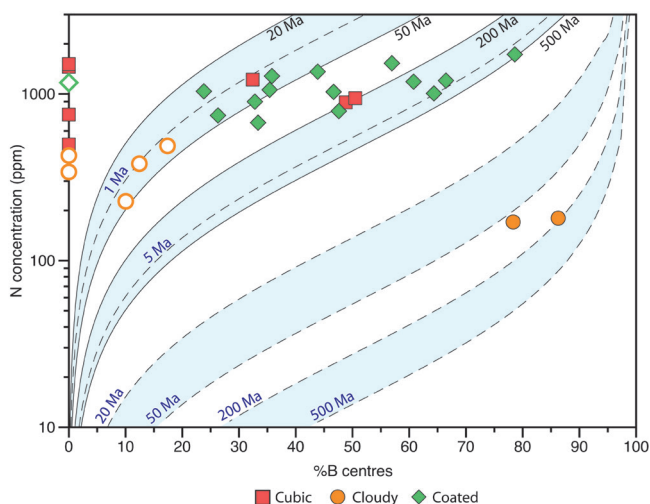


Figure 4 Total nitrogen concentrations vs. the percentage of nitrogen in the B aggregated state. Each point is from the analysis of a single diamond, full symbols are from the bulk measurement, whilst open symbols are from the fibrous coat or cloudy interior of the coated and cloudy diamonds respectively. Isotherms are calculated assuming a temperature range between 1200 °C (solid lines) and 1300 °C (dashed lines) as reported for Udachnaya xenolith (Boyd *et al.*, 1997) and assumed residence times between 1 Ma and 200 Ma. All diamonds indicate a residence time of less than 200 Ma at the temperature estimated for the Siberian SCLM at 360 Ma (eruption age of Nyurbinskaya and Udachnaya kimberlites).

from supersaturated fluids (Sunagawa, 1984), either during the progressive cooling of the C-O-H metasomatic fluids or from a change in the oxidation state where upon dissolved carbon can be precipitated as diamond (Klein-BenDavid *et al.*, 2010). Cooling of C-O-H fluids as they interact with the surrounding lithosphere causes a decrease in the solubility of carbon leading to the supersaturation of the fluid and precipitation of diamond (Stachel and Luth, 2015).

Carbon isotopes in the cores of fibrous diamonds from the Sytykanskaya kimberlite in Yukutia extend from mantle-like to light $\delta^{13}\text{C}$ values (-3.8 to -19.7 ‰) indicating that the Siberian craton contains a subducted carbon component (Skuzovatov *et al.*, 2012). Fibrous diamonds often appear to be genetically linked to the last episode of metasomatism within the SCLM, possibly associated with kimberlite magmatism (Burgess *et al.*, 2002), although there is evidence for the formation of fibrous diamond in older metasomatic events (Zedgenizov *et al.*, 2006). The input of plume mantle material to the Siberian SCLM (Sumino *et al.*, 2006) may therefore have re-mobilised subducted halogen (this study) and carbon-rich material (Jacob *et al.*, 2000) already present within the lithosphere, leading to the precipitation of fibrous diamonds, and fibrous coats around a previous generation of diamonds within the Siberian SCLM.

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Additional Information

Supplementary Information accompanies this letter at <http://www.geochemicalperspectivesletters.org/article1825>.



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