Polycrystalline diamonds and their mantle-derived mineral and fluid intergrowths

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Polycrystalline diamond aggregates (framesites, boart, diamondite) are an understudied variety of mantle diamond, but can make up 20% of the production in some Group I kimberlites. Their polycrystalline nature indicates rapid precipitation from carbon-oversaturated fluids and individual PDAs often contain a chemically heterogeneous suite of websteritic and pyroxenitic inclusions and minerals intimately intergrown with the diamond crystals. Geochemical and microstructural evidence suggests that fluid-driven redox reactions with lithospheric material occurring episodically over millions of years play a major role in freezing carbon in the subcratonic lithosphere (Jacob et al., 2000; 2016; Mikhail et al., 2014).

A suite of 39 samples from the Venetia kimberlite pipe in South Africa allows a more detailed look at the diamond-forming fluids. $\delta^{13}\text{C}$ values in the diamonds measured by secondary ion mass spectrometry range from +2 to -28‰ and cover the entire range for PDA from the literature. Nitrogen concentrations are mostly very low (less than 100 at ppm), but reach up to 2660 at ppm in individual samples. These high nitrogen concentrations in concert with mostly positive $\delta^{15}\text{N}$ values of up to +17‰ and some very negative $\delta^{13}\text{C}$ values suggest crustal material as the source of the nitrogen and the carbon.

However, detailed analysis of the sample provides evidence for a more complex growth history followed by alteration. Individual diamond crystals show complex growth zonations by cathodoluminescence imaging that can be related with the carbon and nitrogen isotopic compositions and points to growth incorporating several pulses of carbon-nitrogen fluid with distinct isotopic compositions. Most of these growth events show decoupled carbon and nitrogen systematics. In addition, EBSD identifies deformation and recrystallization and nitrogen aggregation states range from pure IaA to pure IaB, supporting a heterogeneous and episodic growth history.

Episodic eclogitic diamond genesis at Jwaneng diamond mine, Botswana

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The diamondiferous Jwaneng kimberlite cluster (~240 Ma) is located on the NW rim of the Archaean Kaapvaal Craton in central Botswana. Previous studies report eclogitic diamond formation in the late Archean (2.9 Ga) and in the Middle Proterozoic (1.5 Ga) involving different mantle and sedimentary components [1;2;3]. Here we report newly acquired Sm-Nd ages of individual eclogitic pyrope-almandine and omphacite inclusions along with their major element data and nitrogen data from the diamond hosts to re-examine Jwaneng’s diamond formation ages.

The Sm-Nd isotope analyses were performed via TIMS using 10¹³Ω resistors [4]. An initial suite of three pyrope-almandine and 14 omphacite inclusions yield ¹⁴³Nd/¹⁴⁴Nd from 0.51102±7 to 0.5155±5. ¹⁴⁷Sm/¹⁴⁴Nd vary from 0.024 to 0.469. Major element data defines two inclusion populations: (1) seven omphacites with high Mg#, high Cr# and one pyrope-almandine with low-Ca define an isochron age of 1.93±0.16 Ga with ɛNdi = +3.5; (2) seven omphacites with low Mg#, low Cr# and two pyrope-almandines with low-Ca define an isochron age of 0.82±0.06 Ga with ɛNdi = +3.7. Nitrogen contents of corresponding diamond host growth zones in Group (1) are ≤50 at.ppm whereas Group (2) range between 50 to 700 at.ppm with N-aggregation > 70 %.B.

Additional data used to define “co-genetic” inclusion suites include Sr-isotopes and trace elements of the inclusions and carbon isotopes of the diamond hosts. Re-Os data of coexisting sulphide inclusions from the same silicate-bearing diamonds further validates the ages and indicates more periods of diamond formation at Jwaneng than previously assumed. The integrated data indicate the possibility of an extensive Paleoproterozoic diamond-forming event in southern Africa.

Oxidation state of the mantle through inclusions in diamonds

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The oxidation state and oxygen fugacity (fO2) of Earth’s mantle exert important influences on the compositions of primary melts the speciation and mobility of carbon and sulphur, diamond formation, and the modification of subducted lithosphere [1, 2]. It is generally observed that the oxygen fugacity of both cratonic and asthenospheric mantle is close to FMQ in the spinel field and that fO2 in the cratons generally decreases with depth. According to experimental studies combined with thermodynamic modelling, at depths below 180-200 km the decreasing oxygen fugacity should destabilise carbonate with all carbon at greater depths being stored as diamond [1, 3]. These pressure effects also tend to stabilise metal in the transition zone following the disproportionation of divalent iron (FeO) into Fe (metal) and Fe3+ (accommodated in garnet) [4].

To date, inclusions in diamond are the only available samples from the mantle transition zone and the lower mantle and these provide the opportunity for study of redox relationships in the deep mantle. In this study we used synchrotron Mössbauer Spectroscopy to measure Fe3+/ (Fe2+ + Fe3+) ratios of majoritic inclusions in diamonds from the lowermost upper mantle and the mantle transition zone for comparison with garnets from the shallow mantle.

We find that there is a systematic increase with depth of the oxidation state of iron in garnets included in diamonds, with the deepest samples (~550 km depth) having Fe3+/ (Fe2+ + Fe3+) of up to 0.30, which is more than twice as great as in non-majoritic upper mantle garnets (< 200 km depth) [5]. When converted to oxygen fugacity these measurements imply conditions just above the stability field of metallic iron (above IW).

Diamondiferous Proterozoic mantle roots beneath Arctic Canada

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The mantle roots directly beneath Archean cratons have been relatively well studied because of their economic importance, yet much less is known about the genesis, age, composition and thickness of the mantle lithosphere beneath the regions surrounding these cratons. However, it is critically important to establish the nature of the relationship between this circum-cratonic mantle and that beneath the cratons, including the diamond potential of circum-cratonic regions. Here we present mineral and bulk elemental and isotopic compositions for kimberlite-borne mantle xenoliths from the Parry Peninsula (PP) and Central Victoria Island (CVI), Arctic Canada. These xenoliths provide key windows into the lithospheric mantle underpinning regions to the North and Northwest of the Slave craton, where the presence of cratonic mantle has been proposed. The mineral and whole rock chemistry of peridotites from both localities is indistinguishable from that of typical cratonic mantle lithosphere. The cool mantle geotherms defined by mineral thermobarometry reveal that the lithospheric mantle beneath the PP and CVI terranes extended well into the diamond stability field at the time of kimberlite eruption, consistent with the recovery of diamonds from both kimberlite fields. Bulk Se, Te, and highly siderophile element abundance systematics, plus Re-Os isotope age data suggest that the mantle beneath these parts of Arctic Canada formed at ~2 Ga, rather than in the Archean. The presence of a diamondiferous Paleoproterozoic mantle root is part of the growing body of evidence for peridotitic diamond generation in mantle roots that stabilized well after the Archean. In the context of regional tectonics, the highly depleted mantle compositions beneath both regions developed during mantle melting associated with hydrous metasomatism in the major Paleoproterozoic Wopmay- Great Bear-Hottah arc systems. These terranes were subsequently accreted along the margin of the Slave craton to form a craton-like thick lithosphere with significant diamond potential.
Boron-Bearing, Type IIb Diamonds from Superdeep Subduction

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Type IIb diamonds, such as the Hope diamond, contain trace amounts of boron and are prized for their blue colors. Since boron is a quintessential crustal element, it is completely unexpected in diamond-forming fluids at mantle depths. Despite the mineralogical/geochemical interest in type IIb diamonds, almost nothing is known about how they form chiefly because of their rarity (≤0.02% of all diamonds) and high gem value.

To investigate the type of mantle host rock, the depth of origin (lithospheric vs. convecting mantle), and the source of boron, the high-volume diamond grading stream of the Gemological Institute of America was systematically screened to find type IIb diamonds with inclusions. Over a period of about two years, 46 prospective samples were identified and examined optical microscopy, X-ray diffraction, and infrared/Raman spectroscopy; a few diamonds were also analyzed for carbon isotopic composition and polished for electron probe microanalysis of inclusions.

The examined inclusions represent retrogressed high-pressure minerals, from metabasic to metaperidotitic hosts in the lowermost mantle transition zone (MTZ) to lower mantle (LM). These include former CaSiO3-perovskite, majorite, bridgmanite, stishovite, calcium-ferrite-type phase, and ferropericlase. The variably light carbon isotope compositions and inclusion mineralogy indicate diamond growth in deeply subducted oceanic lithosphere (crust and mantle). Some inclusions are found to have coexisting fluid (CH4 ± H2) that suggests the original high-pressure minerals interacted with hydrous media. We propose that the boron resided in serpentinized oceanic lithosphere. During subduction, the serpentine was metamorphosed to dense hydrous magnesium silicates (DHMS) that retained some boron. Upon breakdown in the MTZ/LM, these DHMS yielded boron-bearing hydrous fluids conducive to diamond growth.
Ice-VII inclusions in ultradeep diamonds

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We present the first evidence for inclusions of ice-VII in diamonds from southern Africa, China, North- and South-America [1]. Combining synchrotron X-ray diffraction, X-ray fluorescence and IR spectroscopy, we show the presence of ice-VII as inclusions in diamonds that have formed at depth > 410 km to about 800 km in the Earth's mantle. What is now crystalline ice-VII, a high pressure polymorph of water-ice, was a component of an aqueous fluid entrapped in the diamonds that were growing in the deep mantle. Because of the confinement by the host diamonds, the inclusions retain high pressures. The same holds for inclusions of magnesian calcite, halite, and ilmenite found in the same diamond specimens. These inclusions reflect the presence of aqueous and carbonaceous fluids in the mantle transition zone and the shallow lower mantle.

Using their current residual pressures and the equations of state, we can reconstruct their recovery paths [2,3]. Further, we can use the intersection of modelled recovery paths to better constrain the encapsulation pressure and temperature of these inclusions in diamonds.

Mantle metasomatism and diamond-forming fluids

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Diamonds and the fluids that form them are important players in the deep carbon cycle that transforms carbon between mantle and surface reservoirs. However, the role of the high-density fluids (HDFs) that are found in micro-inclusions in diamonds is not limited to diamond formation. Examination of literature data on metasomatized rocks suggests that some may have formed by interaction of peridotites and eclogites with HDF-like melts. For example, silicic HDFs can explain the evolution of an orthopyroxene-rich vein in a garnet hartzburgite from Bulfontein, SA [1]. The composition that was added to the harzburgite and turned it into an orthopyroxene+olivine+phlogopite+garnet+carbonate+sulfide vein (green ellipse in the figure) lies at the extent of the array of silicic to low-Mg carbonatitic HDFs found in fibrous diamonds (pink diamonds). A silicic HDF (blue diamond) that contributed the added component would evolve into more carbonatitic compositions (arrow).

Saline melts found in diamonds carry chloride, carbonate and silicate components, similar to saline hydrous fluids found in harzburgites xenoliths from Pinatubo, Philippines [2]. The higher water content in Pinatubo is, most probably, the result of lower temperatures and shallower level, but it attests for the role of saline fluids in metasomatism at the arc environment.

In a companion abstract (Elazar et al., this volume) we report the finding of potassium-rich microinclusions in garnets in an eclogite xenolith from Robert Victor, SA. Their composition falls close to that of silicic to low-Mg carbonatitic HDFs in diamonds. Their lower potassium and higher aluminum content suggests derivation by higher degree of partial melting compared with the diamond forming fluids. All of the above observations support the important role of HDF-like melts and fluids in mantle processes.

Inclusions in diamonds constrain thermo-chemical conditions of the Kaapvaal cratonic mantle

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Mineral and fluid/melt inclusions in diamonds, which are encapsulated and isolated during a metasomatic event, offer the opportunity to constrain changes in the sub-continental lithospheric mantle that occurred during individual thermo-chemical events. Fibrous diamonds from the Group I De Beers Pool kimberlites, South Africa (SA), trapped incompatible-element enriched saline high-density fluids (HDFs) and peridotitic mineral microinclusions. Their substitutional nitrogen resides almost exclusively in A-centers. With regard to the elevated thermal conditions that prevailed in the SA lithosphere during and following Karoo volcanism at ~180 Ma, this low-aggregation state of nitrogen suggests a short mantle residence time, constraining the time of saline metasomatism to be close to the eruption of the kimberlites at ~85 Ma.

Thermometry of mineral microinclusions yield temperatures between 875-1080 °C (at 5 GPa). These temperatures overlap with conditions recorded by touching inclusion pairs, which represent the mantle ambient conditions just before eruption, and are altogether lower by 150-250°C compared to P–T gradients recorded by peridotite xenoliths from the same locality. In addition, the oxygen fugacity calculated for the saline HDF compositions (\(\Delta\log f_{O_2}(FMQ)\) = -2.5 to -1.3) are higher by about a log unit compared with that recorded by xenoliths at 4-7 GPa.

We conclude that enriched saline HDFs mediated the metasomatism that preceded Group I kimberlite eruptions in the southwestern Kaapvaal craton, and that their ‘cold and oxidized’ nature reflects their derivation from a deep subducting slab. To reconcile the temperature and oxygen fugacity discrepancy between inclusions in diamonds and xenoliths, we argue that xenoliths did not equilibrate during the last saline metasomatic event or kimberlite eruption. Thus the P-T-\(f_{O_2}\) gradients they record express pre-existing lithospheric conditions that were likely established during the last major thermal event in the Kaapvaal craton (i.e. the Karoo magmatism at ca. 180 Ma).
Mixing of Saline and Carbonatitic Fluids To Form Peridotitic Panda Diamonds

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Diamonds containing fluid inclusions provide the most direct samples of upper mantle fluids. In eclogites, diamond can form by pH drop during fluid-rock interaction. However, in peridotites, the cause of the chemical evolution of the fluids and minerals, including the wide range of observed salinities involved, are still unclear. Here we used new experimental calibrations of the Deep Earth Water model involving organic and inorganic complexes of the major rock-forming elements to show that fluid mixing can cause diamond formation in the peridotitic environment.

Models of the saline and carbonatitic fluid inclusion compositions consistent with the chemistry of measured solid inclusions in Panda diamonds were used to simulate the irreversible, chemical mass transfer when a carbonatitic fluid infiltrates harzburgite containing a saline fluid at 950°C and 4.5 GPa. Simultaneous oxidation of aqueous hydrocarbons in the peridotitic fluid and reduction of the organic acid anion formate as well as bicarbonate in the carbonatitic fluid during mixing and reaction with harzburgite resulted in the formation of diamond, olivine, and garnet, and increases in the logfO₂ and pH. Olivine was predicted to become more Fe-rich and garnet more Ca and Fe-rich with reaction progress, in agreement with reported temporal trends in the composition of mineral inclusions from octahedral cores to coated rims on Panda diamonds. Aqueous phase concentrations of all elements changed consistent with measured trends in fluid inclusion compositions from saline to less saline. For comparison, we also simulated a saline fluid infiltrating a harzburgite containing a carbonatitic fluid. Diamond again formed, but the compositional trends of the silicate minerals and the trend of salinity with reaction progress were all in the opposite direction to data from the Panda diamonds. Overall, our study strongly suggests that mixing of fluids containing carbon from both reduced and oxidized sources, and simultaneous reaction with harzburgite can cause precipitation of diamond, without the need for triggering by temperature or pressure changes, while adding Ca and Fe to the sub-lithospheric mantle.
**Effect of water on the MgCO$_3$–Fe reaction and the fate of carbonates in the reduced mantle**

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Thermodynamic calculations, experiments and metallic iron inclusions in diamonds suggest that mantle becomes metal-saturated at the depths ≥250 km [1, 2]. Subduction of carbonates beyond this depth will result in the redox reaction with Fe\(^0\) in silicate rocks. The carbonate–Fe\(^0\) system is a simplified model of this interaction and has been studied up to 150 GPa [3]. Here we investigated effect of H$_2$O-fluid on the MgCO$_3$–Fe\(^0\) reaction in the hydromagnesite(hMgs)–Fe\(^0\) system at 6 and 16 GPa and peridotite–CO$_2$–H$_2$O–Fe system at 6 GPa using multianvil apparatus.

The formation of (Fe,Mg)O (Mws), graphite and Fe$_7$C$_3$ was observed in both systems. Additionally, in the silicate-containing system, Mws reacts with pyroxene with formation of olivine, and increase of CaO and FeO content in garnet. This reactions lead to the change of the modal composition of the initial peridotite from the typical four mineral garnet lherzolite to the olivinite.

The kinetic calculations show that the reaction rate constant in the hMgs–Fe\(^0\) system increases by two orders of magnitude in comparison with the anhydrous system. The observations in peridotite–CO$_2$–H$_2$O–Fe\(^0\) system indicate a pronounced effect of water on the rate of mass transfer in the mantle silicates. Our results suggest the carbonates in the presence of water will be completely or largely consumed during typical subduction time to the mantle transition zone of 8–12 Ma (5 cm/yr), and their preservation during subduction to the lower mantle is possible only in the case of ‘coldest’ subduction PT-profiles.

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Modelling the temperature history of mantle lithosphere using FTIR maps of diamonds

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FTIR maps of diamond plates, cut through the centre of growth, contain abundant information about changing defect concentrations from core to rim. These data can, in principle, be interpreted in terms of the variation in conditions of diamond growth and the temperatures experienced by the diamond during the period of mantle residence between growth and exhumation. Many diamonds show multiple growth zones that can be observed by cathodoluminescence. Importantly, the combination of nitrogen concentration and nitrogen aggregation measured by FTIR can be used to determine whether the growth zones are of similar or very different ages (Kohn et al., 2016).

In this study, we use automated fitting of several thousand individual spectra within each FTIR map to define a model temperature for each pixel using the Python program, QUIDDIT. We then use a two-stage aggregation model to constrain potential temperature-time histories for each diamond. To take full advantage of the temperature history recorded by zoned diamonds, radiometric ages of inclusions are required. If the growth ages of each zone and the date of exhumation are well-known, then a model temperature can be calculated for each zone.

The combination of zone-specific ages and improved quality and processing of FTIR spectra is able to provide unique new insights into the thermal history of diamond-bearing lithospheric mantle. For the first time we will be able to use the N defects in diamonds to work out whether a particular location in the lithosphere has heated or cooled over long periods of geological time. The implications for the mechanism of formation of lithosphere will be discussed.

We will illustrate the approach using examples of zoned diamonds from Murowa (Zimbabwe), Argyle (Australia), Diavik (Canada), Venetia (South Africa) and Orapa (Botswana).