Implications of metallic iron for diamonds and nitrogen in the sublithospheric mantle

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Abstract: Recently published experimental data suggest that the Earth’s mantle below ~250 km is saturated in metallic Fe, reaching a concentration of ~1 wt.% Fe° throughout the lower mantle and buffering oxygen fugacity by Fe°+Fe3+ reactions. Metallic Fe in the mantle bears important implications for N, which behaves as a moderately siderophile element. Here, we propose that the trapping of N in (Fe, Ni) metal and Fe-carbides during diamond growth may account for the characteristically low N content of diamonds from the sublithospheric mantle. This model may also explain the origin of especially valuable, large, anhedral, flawless Type II (N-free) diamonds, like the Cullinan, that comprise a minor part of world diamond production. Partition coefficients of N (D_N) between diamond and metallic Fe within D_N = 0.0005–0.013 have been demonstrated in high-pressure experiments for diamond synthesis and in a natural sample of a N-poor lower mantle diamond with inclusions of Fe-nitrocarbide. More N is incorporated into diamond if it grows in the lithosphere, where there is no ambient Fe° to trap N. As a broader implication, the recognition of Fe° in the mantle and its affinity for N suggests metallic Fe should be a major host of mantle N. Retention of primordial mantle N in metallic Fe could explain the high N²⁶/Ar and low ^1⁵^N/^²⁴^N ratios of the mantle compared with the atmosphere.

Introduction

Most recent experiments on the Fe speciation in the mantle suggest that the mantle below ~250 km contains metallic Fe (Ballhaus 1995; Frost et al. 2004; Rohrbach et al. 2007; Rohrbach et al. 2011). Here, we explore the implications of this metallic Fe for the behaviour of mantle N based on new empirical and experimental data on its distribution between high-pressure mantle phases. Specifically, we propose an explanation for the origin of the low N concentrations that typify diamonds from the sublithospheric mantle.

The uppermost ~200 km of the mantle, sampled by xenoliths, massifs, and mantle melts, has a moderately oxidized character, with oxygen fugacities (fO₂) lying within a few log units of the fayalite–magnetite–quartz buffer (FMQ; O₂ + 3FeSiO₄ ↔ 2FeO.O₄ + 3SiO₂) (Frost and McCammon 2008; Stagno et al. 2013). Garnet peridotite xenoliths show decreasing fO₂ with depth, down to three log units below FMQ at 6 GPa in the deepest lithosphere of the Slave (Canada) and Kaapvaal (South Africa) cratons (Stagno et al. 2013). Theoretical calculations and experiments show that at ~250 km (8 ± 1 GPa), the fO₂ reaches the iron–wüstite buffer (IW; O₂ + 2FeO ↔ 2FeO), where (Fe, Ni) metal becomes stable (Ballhaus 1995; Frost et al. 2004; Rohrbach et al. 2007; Rohrbach et al. 2011) (Fig. 1). At this depth, majoritic garnet and subcalcic pyroxene incorporate appreciable Fe²⁺, to the extent that Fe²⁺ will disproportionate into Fe³⁺ and Fe⁰ (Rohrbach et al. 2011). As the Fe³⁺ is taken up by silicate minerals, the complementary Fe⁰ forms a stable metal phase, increasing its mode from the ~250 km saturation depth to ~0.5 wt.% at 660 km, i.e., at the base of the transition zone (Rohrbach and Schmidt 2011; Rohrbach et al. 2011). Below 660 km, MgSi-perovskite incorporates Fe³⁺, permitting a Fe⁰ content of ~1 wt.% throughout the lower mantle (Fig. 1) (Frost et al. 2004). No rock samples from below ~200 km are available as xenoliths, but metal saturation of the deeper mantle may be confirmed by diamonds. Diamonds derived from the sublithospheric mantle, including the lower mantle, sometimes contain inclusions of native Fe, Ni, Fe–Ni alloys (Fig. 2), and Fe-carbides (Hayman et al. 2005; Bulanova et al. 2010; Gurney et al. 2010; Kaminsky and Wirth 2010). In contrast, anhedral, flawless Type II (N-free) diamonds, like the Cullinan, that comprise a minor part of world diamond production, have a low N content of ~0.01 wt% (Kaminsky and Wirth 2010). As a model, we propose that the trapping of N in (Fe, Ni) metal and Fe-carbides during diamond growth may account for the characteristically low N content of diamonds from the sublithospheric mantle. This model may also explain the origin of especially valuable, large, anhedral, flawless Type II (N-free) diamonds, like the Cullinan, that comprise a minor part of world diamond production. Partition coefficients of N (D_N) between diamond and metallic Fe within D_N = 0.0005–0.013 have been demonstrated in high-pressure experiments for diamond synthesis and in a natural sample of a N-poor lower mantle diamond with inclusions of Fe-nitrocarbide. More N is incorporated into diamond if it grows in the lithosphere, where there is no ambient Fe° to trap N. As a broader implication, the recognition of Fe° in the mantle and its affinity for N suggests metallic Fe should be a major host of mantle N. Retention of primordial mantle N in metallic Fe could explain the high N²⁶/Ar and low ^1⁵^N/^²⁴^N ratios of the mantle compared with the atmosphere.
Fig. 1. Schematic mantle section, summarizing mineralogy, $f_{O_2}$ characteristics, and diamond nitrogen content. Mineralogy and phase changes are based on peridotitic “pyrolite” mantle composition (Irifune and Tsuchiya 2007). Relative $f_{O_2}$, compared with the IW buffer, changes character with depth beyond ~250 km as the mantle becomes saturated in metallic Fe (Rohrbach and Schmidt 2011; Stagno et al. 2013). The metal saturation depth and base of cratonic lithosphere are marked with dashed lines, as these are not fixed depths.

Sublithospheric diamonds, grown in this metal-saturated environment, have low average nitrogen contents ($[N]_{avg}$) and high proportions of Type II diamonds. The increase in metallic Fe up to ~1 wt.% in the lower mantle is further correlated with lower $[N]_{avg}$ and a greater proportion of Type II diamonds. Diamond characteristics for lithospheric (17% Type II, number of samples ($n$) = 917), asthenospheric (63% Type II, $n$ = 65), and lower mantle (81% Type II, $n$ = 155) diamonds are calculated from data sources compiled in supplementary Table S1. Non-conv., non-convecting; Cpx, clinopyroxene; Opx, orthopyroxene; HP, high pressure.

These inclusions testify to the presence of Fe$^6$ in the sublithospheric mantle.

If the mantle below ~250 km does have a stable Fe$^0$ component, this has significant implications for the behaviour of mantle N. Partitioning of N into ambient metallic phases could explain why diamonds from the sublithospheric mantle have low N contents. Moreover, given the marked solubility of N in metallic Fe, especially compared with other mantle minerals, (Fe, Ni) metal could be a major mantle N reservoir, even though it may constitute no more than ~1 wt.% of the lower mantle.

**Siderophile character of N**

The presence of metallic Fe in the mantle will affect the behaviour of N because N is moderately siderophile. Owing to its small atomic size, N can occupy the interstitial lattice sites in metallic Fe, which allows it to dissolve in molten and crystalline iron as well as to form Fe-nitride compounds (Ringwood and Hibberson 1991). The solubility of N in metallic Fe is up to several orders of magnitude higher than in silicate melt, depending on pressure, temperature, and $f_{O_2}$ (Hashizume et al. 1997; Miyazaki et al. 2004; Roskosz et al. 2013). In experiments with silicate melt of simplified CI chondrite composition and (Fe, Ni) metal, at 2200–2700 °C and $f_{O_2}$ near IW, N solubility varies from a few ppm to a plateau of 0.6–0.8 wt.% in the silicate, and from 0.035 to 18 wt.% in the metal, as pressure increases from atmospheric up to 18 GPa (a depth of ~530 km) (Roskosz et al. 2013). At pressures >1 GPa, the partition coefficient between the metal and silicate melts is 18 ± 10, which has been shown to be capable of drawing considerable N into the Earth’s metallic core during segregation of the early Earth (Marty 2012; Roskosz et al. 2013). This siderophile behaviour for N is also supported by first principles molecular dynamic modelling (Zhang and Yin 2012).

During diamond growth, the same tendency of N to partition into metallic Fe phases is evident. Synthetic diamonds grown in (Fe, Ni) metal contain less N than those synthesized in silicate-carbonate melts, due to stronger partitioning of N into the metal. Experiments to grow diamond by reactions between metallic Fe and carbonate sealed in a single vessel have shown this tendency clearly. Palyanov et al. (2013) conducted experiments to simulate the redox interaction between mantle with metallic Fe and subducted, carbonate-bearing crust. Experimental runs used a Fe or Fe$_3$C pellet embedded in (Mg, Ca) carbonate, within a platinum capsule. Run products revealed diamond growth both in the metal-rich and carbonate-rich regions, on either side of the redox front. Notably, the diamonds in contact with metallic Fe contained only 100–200 ppm N, while those in the carbonate melt portion contained 1000–1500 ppm N (Palyanov et al. 2013). Other synthetic diamonds grown either in (Fe, Ni) alloy or silicate-
carbonate melts show similar results (Pal'yanov et al. 2002; Spivak et al. 2008; Babich et al. 2012). This implies that the diamond-melt distribution coefficient \( D_N = (\text{mole fraction N in diamond})/(\text{mole fraction N in growth medium}) \) is lower for metallic Fe than for silicate or carbonate melts.

The distribution coefficient of N between synthetic diamond and metallic Fe can be constrained from experiments, which typically run at pressures of 5–7 GPa. It should be noted that absolute N concentration of synthetic diamonds should not be expected to coincide with natural diamonds because it depends on the bulk N content of the starting materials. Synthetic diamonds are often grown in Fe or (Fe, Ni) metal. The addition of N-bearing phases has allowed some experiments to produce diamonds with higher N concentrations. In one set of experiments, up to 0.5 wt.% Ba(N₃)₂ was added to the starting materials to synthesize high-N diamonds, resulting in diamonds containing up to 1600–2400 ppm N (Yu et al. 2008). Even in experiments with high nickel contents in the metal (Niₓ,Feₓ)metal, which will significantly reduce its N solubility (Simmons 1996), the N concentration of the metal remains higher than that of the synthesized diamonds (Pal'yanov et al. 2010). A more extreme experiment, with a catalyst consisting entirely of Feₙ,N, which effectively contains 250 000 ppm N, yielded diamonds with 1350–3300 ppm N (Borzdov et al. 2002). These experiments in Feₙ,N imply \( D_N \) values of 0.005–0.013. Relative incompatibility of N in synthetic diamonds compared with metallic Fe (i.e., \( D_N < 1 \)) is further illustrated by the fact that slowing the diamond growth rate, which allows the N partitioning to approximate equilibrium more closely, yields diamonds with lower N concentrations (Spivak et al. 2008). Relative incompatibility of N is also supported by the fact that the morphologically dominant diamond faces have higher N concentrations (Burns et al. 1999). Although successive growth layers accumulate slowly on dominant crystal faces, growth steps on dominant faces advance more rapidly than they do on subordinate faces, so dominant faces have less opportunity to reject incompatible impurities during growth (Sunagawa 1984).

Natural diamonds also provide evidence of N partitioning into Fe⁶ phases. For example, a lower mantle diamond from Juina, Brazil, was found to contain inclusions of Fe-carbides (Fe⁶ with interstitial C⁰) with appreciable N contents. The N concentration was 73 000–91 000 ppm in some inclusions, while the host diamond contained merely 44 ppm N (Kaminsky and Wirth 2011). These values give a very low \( D_N \) of 0.0005 between the diamond and the Fe⁶ phase. Higher pressure in the lower mantle compared with laboratory diamond synthesis will achieve higher N solubility in the metal and lead to lower \( D_N \) values (Roskosz et al. 2013). The N contents of other reported metallic Fe inclusions in sublithospheric diamonds have not been analyzed. During routine analysis with X-ray spectroscopy in an electron microscope or electron microprobe, N is among the light elements that are generally not analyzed, so it is plausible that high N has gone unnoticed in other studied metallic Fe or Fe-carbide inclusions.

**Consequences of metallic Fe in the sublithospheric mantle**

**Low N content of sublithospheric diamonds**

If the mantle below ~250 km is saturated in metallic Fe, and N tends to partition into this metal, a difference in N content between lithospheric and sublithospheric diamonds should be expected. Such a contrast is indeed observed (Fig. 3) and has long been an unexplained curiosity (Davies et al. 1999; Hutchinson et al. 1999; Kaminsky et al. 2001; McCammon 2001; Stachel et al. 2002, 2005; Bulanova et al. 2010; Palot et al. 2012). Lithospheric diamonds, which comprise the majority of mined diamonds, grow in the subcontinental lithospheric mantle of old, thick continental regions (cratons) at depths of 140–200 km (Boyd and Gurney 1986; Meyer 1987). The top of the depth interval corresponds to the graphite–diamond transition, while the bottom corresponds to the base of the cratonic lithosphere. The depth of origin is inferred from studies of diamond inclusions and diamondiferous xenoliths. Lithospheric diamonds contain garnet, clinopyroxene, orthopyroxene, olivine, Mg-chromite, rutile, coesite, as well as sulfides, and these correspond to peridotitic and eclogitic host rocks (Stachel and Harris 2008).

In contrast, sublithospheric diamonds are distinguished by higher-pressure mineral inclusions, derived from greater depths. These diamonds make up a small and variable proportion (~1%) of mine production (Gurney et al. 2010). Below 250 km, the first higher-pressure mineral inclusion is majoritic garnet which becomes increasingly stable through the deeper mantle to 410 km depth (Fig. 1). Diamonds hosting majorite are referred to as “asthenospheric” (Stachel et al. 2005). At the transition zone (410–660 km), first wadsleyite, then ringwoodite are formed, which are high-pressure polymorphs of olivine, (Mg, Fe)₂SiO₄. Although they are destabilized and reverted upon decompression, wadsleyite and ringwoodite inclusions can still be recognized by geochemical means and are interpreted as sourced from the transition zone (Kaminsky 2012). Below 660 km, in the lower mantle, ferropericlase, MgSi-perovskite, and CaSi-perovskite are the principal inclusions phases (Kaminsky 2012), although their abundances and compositions may also reflect localized redox reactions (Pal'yanov et al. 2013). Metallic Fe inclusions have also been reported, mainly in sublithospheric diamonds (Gurney et al. 2010), although limited occurrences of metallic Fe inclusions in lithospheric diamonds are also known (Bulanova 1995; Davies et al. 1999b). A more detailed overview of sublithospheric diamond inclusions is given by Kaminsky (2012).

Sublithospheric diamonds, including those formed in the “asthenosphere”, transition zone, and lower mantle, are markedly depleted in N compared with those from the lithosphere. Substitutional N is the most common impurity in diamond and is routinely analyzed with infrared spectroscopy. Figure 3 shows the N content of diamonds with mineral inclusions, used to identify host rock paragenesis. On average, the N content of lithospheric diamonds is 150–200 ppm for peridotitic and 300–400 ppm for eclogitic diamonds (Cartigny 2005; Stachel and Harris 2009). Taken together, the lithospheric diamonds in Fig. 3 average 253 ppm (90% are within 0–700 ppm). Type II diamonds, those
Fig. 3. Nitrogen concentration distributions for inclusion-bearing diamonds. (A) Peridotitic and (B) eclogitic lithospheric diamonds have more N than (C) sublithospheric diamonds. Data sources as listed in supplementary Table S1: peridotitic and eclogitic (Stachel and Harris 2009); sublithospheric (Deines et al. 1991; Stachel and Harris 1997; Davies et al. 1999a; Hutchison et al. 1999; McDade and Harris 1999; Stachel et al. 2002; Hayman et al. 2005; Tappert et al. 2005a, 2005b, 2009; Bulanova et al. 2010; Palot et al. 2012).

with N contents below the detection limit of infrared spectroscopy (~10 ppm), make up ~24% of peridotitic diamonds and ~10% of eclogitic diamonds (Stachel and Harris 2009; Gurney et al. 2010). Not shown in Fig. 3 are fibrous diamond coats and cuboids. This less common, dendritic growth habit of lithospheric diamond typically has N contents within 600–1400 ppm (Cartigny 2005).

In sharp contrast to lithospheric diamonds, the average for sublithospheric diamonds lies at 33 ppm (90% are within 0–100 ppm) for the data compiled in Fig. 3. Moreover, sublithospheric diamonds are dominated by Type II diamonds, which make up 73% of the 243 samples in Fig. 3. Subdivision of sublithospheric dia-

monds into lower mantle and asthenospheric–transition zone fur-

ther resolves this pattern. Figure 1 shows that lower mantle diamonds contain less nitrogen (81% Type II) than those from the asthenosphere–transition zone (63% Type II). It is also worth noting the crystal lattice configuration of N in sublithospheric dia-

monds tends to be highly aggregated to B centres (McCammon 2001; Hayman et al. 2005; Tappert et al. 2009). The subset of sub-
lithospheric diamonds in Fig. 3 with detectable N are, on average, 90% aggregated to B centres. The high aggregation state is consist-
tent with the high temperatures (Taylor et al. 1990) of the sub lithospheric mantle. In comparison, lithospheric diamonds have a range of aggregation states, averaging about 40% B centres, and only 5% of these reach beyond the 90% B mark (Stachel 2007).

The proposed presence of metallic Fe throughout most of the sublithospheric mantle and its demonstrated ability to scavenge N presents a straightforward solution for the low N content of sublithospheric diamonds. Figure 1 illustrates this inverse correlation between the metal content of the ambient mantle and the N content of diamonds. We propose that metallic Fe acts to trap N during diamond growth. N partitions into the Fe-carbide or metal-

cal Fe phase and little is taken up in the diamond lattice. This partitioning is demonstrated not only in synthetic diamonds (Borzdov et al. 2002; Yu et al. 2008; Babich et al. 2012; Palyanov et al. 2010, 2013), but is also manifested directly in the lower mantle diamond with a $D_N$ of 0.0005 between the diamond and the included Fe-carbonitride phase described by Kaminsky and Wirth (2011). Thus the characteristically low N content of sublithos-

pheric diamonds may well be a consequence of diamond growth in a mantle setting with metallic Fe, in a system buffered by Fe$^{0}$–Fe$^{2+}$. Conversely, lithospheric diamonds grow in the absence of metallic Fe, in host rocks whose oxygen fugacity is generally governed by Fe$^{2+}$–Fe$^{3+}$ buffering.

This model also explains the slightly lower N content in lower mantle diamonds, sourced from below 660 km, compared with “asthenospheric” and transition zone diamonds. The 660 km depth corresponds to the onset of ferropericlase stability and an increase in metallic Fe content (Rohrbach and Schmidt 2011). This increase in metal content is responsible for a boost in the capacity of the ambient mantle to trap N during diamond formation (Fig. 1).

Occasionally, metallic Fe may also occur in the lithosphere. Native (Fe, Ni) inclusions have rarely been found in the centre of lithospheric diamonds (Bulanova 1995; Davies et al. 1999b). Some of these diamonds may also exhibit low N contents, like the N-free polycrystalline diamond aggregate with garnet, Fe-carbide, (Fe, Ni) metal, and FeS inclusions reported by Jacob et al. (2004). However, these occurrences are seen as small, anomalous perturba-

tions in the overarching pattern of Fe oxidation state, $f_O^2$ buffering, and diamond formation described earlier in the text (Fig. 1).

Model of diamond growth in the sublithospheric mantle

Rohrbach and Schmidt (2011) outlined a model of redox melting and freezing in the deep mantle based on the response of C to the imposed oxygen fugacity. In the presence of Fe$^0$, mobile carbonate melts are reduced and immobilized. The carbon is initially in-

corporated into the metallic phase, making Fe-carbides, but converted to diamond when additional C can no longer be accommodated by the Fe$^{0}$ at hand (Rohrbach and Schmidt 2011). Diamond growth in this metal-saturated system occurs by the reduction of carbonates, imposed by the ambient mantle oxygen fugacity that is buffered by Fe$^{2+}$–Fe$^{3+}$ reactions (Palyanov et al. 2013).

Diamond growth will cease when either all the available car-

bonate is reduced or the local Fe$^{0}$ is exhausted. If the Fe$^{0}$ is ex-

hausted, Fe should be present as Fe$^{2+}$ and Fe$^{3+}$ in silicates and ferropericlase, and C will be present as diamond (Rohrbach and Schmidt 2011; Palyanov et al. 2013). Any additional carbonate en-
When carbonatic diamond-forming melt with traces of N percolates through the metal-saturated sublithospheric mantle, N will partition into the metallic Fe or Fe-carbide phases. The effectiveness of this process is ensured by the low melt/solid ratio and the restriction of both metallic Fe (Rohrbach et al. 2011) and the melt to interstices and grain boundaries. If the diamond-forming melt is equilibrated with an equal mass of Fe\(^0\), the N concentration of the diamond-forming melt may be reduced by a factor of \(18 \pm 10\), using the experimental \(D_N\) for metallic Fe and silicate melt (Roskosz et al. 2013). A reduction in N concentration of this magnitude for the diamond-forming melt agrees with the factor of eight decrease in average N concentration of sublithospheric diamonds compared with lithospheric diamonds (Fig. 3).

As long as there is Fe\(^0\) available to reduce carbonate to diamond, there are Fe\(^0\)-bearing phases to take up N preferentially. As the Fe\(^0\) is consumed, we should expect decreasing ability of metallic Fe or Fe-carbide to uptake N, due to a combination of N-saturation and oxidative consumption of these phases. This expected behaviour is consistent with the actual N zonation recorded in successive growth layers of diamond. Sublithospheric diamonds tend to show higher N concentrations in the rim of the crystal than the core, opposite to the typical trend exhibited by lithospheric diamonds (Davies et al. 1999a; Bulanova et al. 2010). In addition to the effect of N partitioning into metallic Fe, the incorporation of N into diamond will also depend on diamond growth rate as well as other factors affecting the N content of the melt, such as the crystallization of other minerals (Cartigny et al. 2001; Babich et al. 2012). These factors can also promote low N concentrations, independently from the effect of metallic Fe, in both lithospheric and sublithospheric diamonds.

If the metallic Fe content of the sublithospheric mantle provides favourable conditions for the growth of N-free diamonds, a sublithospheric origin may tentatively be assigned to those Type II (N-free) diamonds that do not contain mineral inclusions. Particularly, there is a special subset of Type II diamonds that are often large, inclusion-free, highly resorbed, generally anhedral, and of high quality, whose paragenesis remains enigmatic (Gurney and Helmstaedt 2012). Some of the largest and most valuable diamonds, like the famous Cullinan diamond, belong to this variety (Janse 1995). Often, they can be visually identified with confidence based on their unique characteristics (Bowen et al. 2009). The generally large size of these Type II diamonds is demonstrated for the Letšeng mine, where they increase in proportion from 18% of 2 carat (0.4 g) diamonds to 68% of diamonds larger than 10.8 carats (2.16 g) (Bowen et al. 2009). Characteristics of these unique diamonds may be consistent with growth in the sublithospheric mantle, although they differ somewhat from Type II diamonds with sublithospheric inclusions (Moore 2009).

The redox buffering capacity by Fe\(^{3+}\)-Fe\(^{2+}\) in metal-saturated mantle is large (Rohrbach and Schmidt 2011), providing a favourable environment to reduce a large amount of carbonate in one location and grow large diamonds. For example, 1 kg of mantle with 1 wt.% Fe\(^0\) could potentially reduce ~1 g of C to diamond (Rohrbach and Schmidt 2011). If grown as described here, the 621.2 g Cullinan diamond (Janse 1995) would require the reducing capacity of ~620 kg of mantle with 1 wt.% Fe\(^0\). Considering a 3.5–5.5 kg/m\(^2\) mantle density range, the Cullinan would therefore require a redox reaction within 110–180 m\(^3\) of mantle. This demands reactant/product transport distances of at least 3.0–3.5 m. The relatively high temperatures afforded by the sublithospheric mantle may ensure high diffusion rates to promote the growth of large crystals. High temperatures, combined with low diamond N concentrations, would also permit significant dislocation mobility (DeVries 1975; Field 1992) to help account for the predominance of bulk plastic deformation features (Gurney and Helmstaedt 2012) and polygonized dislocation networks (De Corte et al. 2006) in these unique Type II diamonds.

### Metallic Fe as a host of mantle N

The proposed ~1 wt.% metallic Fe content in the mantle and its ability to incorporate N has wide implications for the overall N budget of the mantle. Two longstanding problems surrounding mantle N are the nature of the phase(s) that host N and the reason for the high N/\(^{36}\)Ar ratio of the mantle compared with the atmosphere. The first problem has been approached from the perspective of an oxidized upper mantle, where N is expected to occur as NH\(^4\)+ substituting for K in silicates (Marty and Dauphas 2003). However, it is not clear what minerals should host the bulk of mantle N, and there are deficiencies in attempting to account for mantle N as being hosted in NH\(^4\)+-bearing silicates alone. For example, clinopyroxene has been shown experimentally to be capable of hosting up to 500–1000 ppm NH\(^4\)+ in the upper mantle, but this provides a capacity for merely 10\(^{22}\) mol of N (Goldblatt et al. 2009; Watenuhl et al. 2010). This figure is dwarfed by the estimated 3.6 ± 1.8 × 10\(^{26}\) mol of N residing in the bulk mantle (Marty 2012). Other experiments have demonstrated modest N solubility in silicate minerals at 3.5 GPa, with up to 10 ppm in forsteritic olivine and up to 100 ppm in enstatite (Li et al. 2013). The dominant lower mantle mineral phases, MgSi-perovskite, ferropericlase, and CaSi-perovskite, present no obvious N storage solutions. However, given the known extreme N solubility in (Fe, Ni) metal, up to ~12 wt.% for Fe-rich (Fe, Ni) alloys (Roskosz et al. 2013), the metallic Fe content of the mantle may serve as a significant host for mantle N.

Experimental data are not available to allow quantification of the distribution of N between the metallic Fe and other mantle minerals at sublithospheric conditions. However, if N in the dominant mantle minerals remains incompatible during partial melting, and the metal–silicate melt distribution coefficient is 18 ± 10 (Roskosz et al. 2013), the distribution coefficient between metallic Fe and other mantle minerals will be ~18 ± 10. Considering a bulk mantle N concentration of 1 ppm (Marty 2012), a ~1 wt.% Fe\(^0\) content in the mantle could readily dissolve the entire N budget of the mantle (Frost et al. 2004; Rohrbach et al. 2007; Roskosz et al. 2013).

If significant amounts of N are dissolved in metallic Fe phases, and we observe N escaping the mantle as N\(_2\) gas (Marty 1995; Smith et al. 2014), it is implied that the liberation of N from upwelling mantle is controlled by oxygen fugacity and the destabilization of Fe\(^0\). Metallic Fe not only provides a storage solution for mantle N, it also lends insight into the notably higher N/\(^{36}\)Ar ratio of the mantle compared with the atmosphere. The difference is often explained in the framework of N recycling by subduction. Current models contend that both N\(_2\) and Ar is not (Matsuda et al. 1993). As an alternative, the fractionation of N/\(^{36}\)Ar could have been accomplished by retention of N in metallic Fe in the mantle early in Earth history, while \(^{36}\)Ar was degassed to the atmosphere. Therefore, Fe\(^0\) in the mantle provides a facility to retain N so that extensive N recycling is not required.

An early establishment of the N budget of the mantle, as opposed to accumulating recycled N over time, is supported by several lines of evidence. Firstly, N isotopes incorporated in old
lithospheric, cratonic diamonds match present-day upper mantle values (Cartigny 2005), indicating that this reservoir was established prior to 3.5–3.2 Ga (Gurney et al. 2010). Secondly, the early establishment of mantle N would be in agreement with the 4.0 Ga 40K–40Ar age of the mantle (Halliday 2013). These elements are linked because N correlates with 40Ar, which is a radioactive decay product of 40K. Specifically, 15N/14N ratios between mid-ocean ridge basalt, ocean-island basalt mantle samples, and the atmosphere are similar and reflect comparable long-term N/K ratios in the mantle (Marty and Dauphas 2003). Thus, if bulk mantle 40K and 40Ar contents are 4.0 Ga old, an early establishment of mantle N rather than buildup over geologic time via subduction of NH4 and (K) is preferred.

If we accept that N was retained in the mantle in metallic Fe, this may provide a convenient explanation for the low 15N/14N in the upper mantle [15N = −5‰, where 15N = (15N/(15N+14N)]sub/sup/LamN = 1]000 (Marty and Dauphas 2003) in comparison with the atmosphere. N taken up by the metal should be isotopically light and thus induce isotopic fractionation (Dauphas et al. 2004; Kerrich and Jia 2004). The retention of isotopically light N in metallic Fe eliminates the need to explain this signature with extensive, early subduction of uniquely low 15N biogenic, Archean N (Marty and Dauphas 2003), which is not well supported by evidence (Cartigny and Ader 2003; Kerrich and Jia 2004).

Concluding remarks

A better understanding of the depth-dependent mantle minerology based on ultra-high-pressure experiments (Frost et al. 2004; Rohrbach et al. 2007; Roskosz et al. 2013) has enabled us to explain why diamonds sourced from the sublithospheric mantle have distinctly low N contents compared with diamonds from the cratonic lithosphere. The difference may be attributed to the presence of metallic Fe below ~250 km in the sublithospheric mantle, which could preferentially incorporate N during diamond growth. We also speculate that the sublithospheric mantle may be the birthplace for the unique, inclusion-free, high-quality variety of Type II diamonds. If these Type II diamonds comprise a sizable part of production of many mines (Gurney and Helmlstaedt 2012), then sublithospheric diamonds are more prominent than we currently admit. These possibilities call for experimental and theoretical confirmation.

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