

1 **Revision 2**

2 **A petrological assessment of diamond as a recorder of the mantle nitrogen cycle**

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7 **Abstract:**

8 **Nitrogen is fundamental to the evolution of Earth and the life it supports, but for reasons poorly**  
9 **understood, it is cosmochemically the most depleted of the volatile elements. The largest reservoir in the**  
10 **bulk silicate Earth is the mantle, and knowledge of its nitrogen geochemistry is biased, because  $\geq 90\%$  of the**  
11 **mantle nitrogen database comes from diamonds. However, it is not clear to what extent diamonds record the**  
12 **nitrogen characteristics of the fluids/melts from which they precipitate. There is ongoing debate regarding**  
13 **the fundamental concept of nitrogen compatibility in diamond, and empirical global datasets reveal trends**  
14 **indicative of nitrogen being both compatible (fibrous diamonds) and incompatible (non-fibrous**  
15 **monocrystalline diamonds). A more significant and widely overlooked aspect of this assessment is that**  
16 **nitrogen is initially incorporated into the diamond lattice as single nitrogen atoms. However, this form of**  
17 **nitrogen is highly unstable in the mantle, where nitrogen occurs as molecular forms like  $N_2$ , or  $NH_4^+$ , both of**  
18 **which are incompatible in the diamond lattice. A review of the available data shows that in classic terms,**  
19 **nitrogen is the most common substitutional impurity found in natural diamonds because it is of very similar**  
20 **atomic size and charge to carbon. However, the speciation of nitrogen, and how these different species**  
21 **disassociate during diamond formation to create transient monatomic nitrogen, are the factors governing**  
22 **nitrogen abundance in diamonds. This suggests the counter-intuitive notion that a nitrogen-free (Type II)**  
23 **diamond could grow from a N-rich media that is simply not undergoing reactions that liberate monatomic N.**  
24 **In contrast, a nitrogen-bearing (Type I) diamond could grow from a fluid with a lower N abundance, in which**  
25 **reactions are occurring to generate (unstable) N atoms during diamond formation. This implies that**  
26 **diamond's relevance to nitrogen abundance in the mantle is far more complicated than currently**

27 **understood. Therefore, further petrological investigations are required to enable accurate interpretations of**  
28 **what nitrogen data from mantle diamonds can tell us about the deep nitrogen budget and cycle.**

29

## 30 **1. Introduction**

31 The importance of the geodynamic nitrogen cycle should not be understated. Nitrogen is fundamental to the  
32 evolution of Earth and the life it supports. This is demonstrated by the Earth's atmosphere being made up of roughly  
33 78 % nitrogen (Porcelli and Pepin, 2003), and nitrogen is a key element in the structure of molecules vital to life,  
34 including amino acids, proteins, and nucleic acids (Busigny and Bebout, 2013; references therein). It has also been  
35 suggested that oxidation of ammoniacal nitrogen in the mantle can generate water on the surface (Li and Keppler,  
36 2014), and that nitrogen may have played an important role in heating Earth's surface above the freezing point of  
37 water despite a faint young sun (Sagan and Chyba, 1997; Goldblatt et al., 2009). Therefore, an understanding of the  
38 geodynamic nitrogen cycle is fundamental to understanding the development of the habitable Earth (Canfield et al.,  
39 2010).

40 Placing firm constraints on the flux of nitrogen between the Earth's reservoirs is fundamental for quantitative  
41 models, but also very challenging. Empirical data used to trace the behavior of nitrogen in Earth's mantle across deep  
42 time (Ga timescales) come from geochemical studies of nitrogen-bearing mantle xenoliths and xenocrysts. The  
43 mantle mineral most widely used for this purpose is diamond (>90% of the mantle nitrogen database), in which  
44 nitrogen is the most common and abundant lattice-bound impurity, with concentrations ranging from below  
45 detection to >5000 ppm (**Fig.1a-c**). However, there are distinctions between mantle diamond-types. The  
46 monocrystalline diamonds typically contain less nitrogen than coated diamonds (average = 200-300 ppm),  
47 polycrystalline, garnet-bearing diamondites are also known to contain higher nitrogen abundances than  
48 monocrystalline diamonds (average = 600 ppm; see Mikhail et al., 2013), and sublithospheric diamonds are typically  
49 found to contain nitrogen below detection limits (average <20 ppm; Harte, 2010). The analysis of nitrogen in  
50 diamond by non-destructive FTIR is relatively simple, which has led to the nitrogen-abundance classification system  
51 (see Howell et al., 2012; references therein). Diamonds containing nitrogen are termed Type I, while Type II  
52 diamonds contain no detectable nitrogen (the lower limit depends upon the technique used; see Mikhail et al.,  
53 2014a). Kaiser and Bond (1959) were the first to show that differences in the FTIR spectra correlated with the  
54 detection of nitrogen by mass spectrometry, leading to the concept that nitrogen is a lattice-bound substitutional

55 impurity in Type I diamonds. However, it was unknown if nitrogen was a primary or secondary impurity (Milledge  
56 and Meyer, 1962). Our current understanding is that single N atoms substitute for single C atoms on a growth  
57 interface, and become incorporated into the lattice as point defects. As diamond formation in the mantle spans a  
58 large temporal and spatial range (from 0.6 to 3.5 Ga and <150 to >600 km depth; Gurney et al., 2010; Shirey et al.,  
59 2013), the carbon and nitrogen geochemistry of diamonds have been used to place constraints on the nature of deep  
60 volatile cycles through the mantle (see Cartigny et al. (2014) for a review).

61 To use the presence of nitrogen in diamond to constrain the extent and flux of the mantle's nitrogen reservoir(s)  
62 requires an understanding of the partitioning behaviour of nitrogen into diamond as a function of P-T-X. The most  
63 common method applied to constrain nitrogen uptake into diamond is reverse modeling of empirical data. This  
64 method assigns a fluid-diamond partition coefficient for nitrogen by fitting the co-variations of carbon-isotope values  
65 and nitrogen abundances to a curve for a given temperature (using theoretical equilibrium carbon-isotope  
66 fractionation factors that assume the speciation of carbon as methane or carbonate: Javoy et al., 1984; Boyd et al.,  
67 1987, 1992; Boyd and Pillinger, 1994; Bulanova et al., 2002, 2014; Cartigny et al., 1997, 1998a,b, 2001, 2003, 2004,  
68 2009; Klein-BenDavid et al., 2010; Harte et al., 1999; Hauri et al., 2002; Howell et al., 2013, 2015a; Gautheron et al.,  
69 2005; Hutchison et al., 1997; Mikhail et al., 2013, 2014a; Stachel and Harris, 2009; Palot et al., 2009, 2012, 2014;  
70 Thomassot et al., 2007, 2009), where T is independently determined using the degree of nitrogen aggregation  
71 and/or geothermometry on paired silicate inclusions (discussed by Stachel and Harris, 2008).

72 However, this approach has not explained how single atoms of nitrogen have been generated in the mantle for  
73 incorporation into the diamond lattice. As monatomic N is highly unstable, nitrogen would be expected to occur in  
74 other more stable forms (Mikhail and Sverjensky, 2014). Therefore, to interpret the meaning of the nitrogen data  
75 recorded in diamonds, and to model any possible equilibrium stable-isotope fractionation of  $^{15}\text{N}/^{14}\text{N}$  to explain the  
76 large range of  $\delta^{15}\text{N}$  data (Mikhail et al., 2014a) an understanding of the partitioning behaviour of nitrogen during  
77 diamond formation is required (e.g. Howell et al., 2015a). In this paper we evaluate the behavior of nitrogen during  
78 diamond formation, and show that the incorporation of nitrogen in to diamond is primarily controlled by diamond-  
79 forming reactions involving nitrogen in the growth medium.

80

## 81 **2. Nitrogen compatibility in diamond**

82 Considering the rules of trace element partitioning, first laid down by Goldschmidt (1937), the presence of  
 83 nitrogen as a structural constituent in diamond is not unexpected, because carbon and nitrogen have similar charges  
 84 and ionic radii. The first rule states that atoms of the same charge and radius will enter a crystal lattice with equal  
 85 ease. This provides the basis for modern elemental substitution models, and in the simplest sense remains an  
 86 accurate assumption, e.g. Ni substituting for Fe in olivine (Blundy and Wood, 2003). Any resulting charge imbalance  
 87 will require balancing via a double substitution. For example, in diopside at 11.5 GPa and 750 °C, monovalent  
 88 ammonium can be incorporated (up to 1000 ppm) through a double-substitution mechanism, with a trivalent ion  
 89 balancing the charge:  $(Ca^{2+})_{M2} + (Mg^{2+})_{M1} \Leftrightarrow (NH_4^+)_{M2} + (Al^{3+} \text{ or } Cr^{3+})_{M1}$  (Watenphul et al., 2010).

90 The compatibility of an element is most commonly expressed in one of two ways (for a more detailed discussions  
 91 see Blundy and Wood, 2003). Assuming a two-phase system (diamond + fluid) the relative partitioning of N and C  
 92 can be represented by a partition coefficient (D), which reflects the compatibility of N/C relative to fluids/melts  
 93 (Eq.1). However, due to the crystal symmetry of diamond, N can be incorporated on any crystallographic site. In  
 94 addition, C + N mix on the same sites, meaning a chemical control (i.e., stoichiometric constraint) will drive the  
 95 partitioning behavior ( $K_d$  – Eq.2). Therefore, the partitioning behavior could be considered as the ratio of partition  
 96 coefficients ( $K_d$  – Eq.2). This approach is similar to what is typically implemented for describing e.g. Fe-Mg exchange  
 97 equilibrium between e.g. olivine and silicate melts (Toplis, 2005). Note that if  $D_N$  or  $K_N \geq 1$ , the element is described  
 98 as compatible.

99 Eq.1 
$$D_N^{Diamond-Fluid} = \frac{N^{Diamond}}{N^{Fluid}}$$

100 Eq. 2 
$$K_{N-C}^{Diamond-Fluid} = \frac{N^{Fluid} \pm N^{Diamond}}{C^{Fluid} \pm C^{Diamond}}$$

101

## 102 2.1. Previous models

103 There is no consensus in the literature regarding the overall compatibility of nitrogen in diamond. Instead, there  
 104 are three contradictory arguments that are (confusingly) all supported by empirical datasets. These contradictory  
 105 arguments are as follows: [1] nitrogen is incompatible in diamond (Boyd et al., 1994; Cartigny et al., 2001), [2],  
 106 nitrogen is compatible in diamond (Stachel and Harris, 2009), and finally, [3] the compatibility of nitrogen in  
 107 diamond is redox-sensitive (Deines et al., 1989; Thomassot et al., 2007; Smith and Kopylova, 2014).

108 The evidence for nitrogen being incompatible: The global dataset for the abundance of nitrogen in diamond shows a  
109 distribution skewed towards zero for non-coated monocrystalline mantle diamonds (**Fig.1a-b**), and this pattern is  
110 characteristic of an incompatible element (Ahrens, 1954). If N is incompatible, the incorporation of nitrogen in  
111 diamond must be governed by a kinetic process rather than by equilibrium distribution, despite the similarity in  
112 charge and ionic radius between atomic N and C. This would mean that nitrogen-rich diamonds occur as a  
113 consequence of rapid disequilibrium growth and the N/C ratio of diamond approaches that of the precipitating fluid  
114 or melt. In contrast, Type II diamonds would be produced by slow growth under near-equilibrium conditions,  
115 regardless of the nitrogen content of the growth medium (Cartigny et al 2001). In addition, a recent study by Palot et  
116 al. (2013) that determined the co-variations for  $\delta^{13}\text{C}$  values and N-abundances in situ using SIMS, argued that these  
117 data are consistent with bulk-sample data (e.g. Cartigny et al., 2001), and concluded that nitrogen behaved  
118 incompatibly during diamond formation.

119 The evidence for nitrogen being compatible: Stachel and Harris (2009) argue that nitrogen is compatible in diamond  
120 irrespective of  $f\text{O}_2$ , citing the decreasing nitrogen contents from core to rim observed in high-pressure high-  
121 temperature (HPHT) synthetic diamonds grown under reducing conditions in Fe-Ni solvent catalysts (e.g. Reutsky et  
122 al 2008) and under more oxidizing conditions (de-carbonation of carbonate) in the presence of silicates (Pal'yanov et  
123 al 2002). The concept of nitrogen being compatible is also consistent with recent data from single populations of  
124 diamonds (e.g. Thomassot et al., 2007), and within single (zoned) diamonds (Smart et al., 2011; Palot et al., 2014;  
125 Petts et al., 2015). Thomassot et al. (2007) analyzed a suite of diamonds from a single peridotite xenolith (assumed  
126 to have formed in a single event) and found co-variations between the carbon-isotope values and nitrogen  
127 abundances that fit the equilibrium Rayleigh fractionation model outlined by Cartigny et al. (2001). These data result  
128 in a calculated  $K_{\text{N}}$  of 2 between diamond and a hypothetical methanogenic fluid; meaning nitrogen is twice as  
129 compatible in the diamond relative to the fluid. Similar studies used high spatial-resolution SIMS profiles within  
130 individual diamonds that showed pronounced oscillatory zoning and recorded co-variations of N contents vs.  $\delta^{13}\text{C}$   
131 (Smart et al., 2011; Palot et al., 2014; Petts et al., 2015). By applying the same reverse-modeling approach as Cartigny  
132 et al. (2001) and Thomassot et al. (2007) a  $K_{\text{N}}$  value of 5 was calculated for diamond precipitation from a carbonatitic  
133 fluid (Smart et al., 2011). Collectively, these two datasets suggest that nitrogen is compatible under both oxidizing  
134 and reducing conditions conducive to diamond-formation, assuming a simple two-phase relationship between  
135 diamond and fluid (i.e. not accounting for the possibility of ammonium partitioning into silicates or other phases).

136 The evidence for nitrogen compatibility being redox sensitive: Several studies have proposed that the compatibility  
137 of nitrogen in diamond is redox-sensitive (Deines et al., 1989; Thomassot et al., 2007). The most recent model argues  
138 that nitrogen is compatible in diamond only in the absence of Fe<sup>0</sup> or Fe-Ni alloys (Smith and Kopylova, 2014). This is  
139 largely based on the observation that the decrease in average nitrogen abundance in diamonds with increasing  
140 depth of origin can be correlated (crudely) with the predicted increasing mole fraction of Fe<sup>0</sup> in peridotitic mantle  
141 with depth (Frost et al., 2004; Rohrbach et al., 2007). Smith and Kopylova (2014) cite experimental data for diamond  
142 synthesis in a sealed capsule with a strong redox gradient where one end contained Fe-metal and the other  
143 contained carbonate (Palyanov et al. 2013). The diamonds in contact with Fe<sup>0</sup> contained 100–200 ppm N, whereas  
144 the diamonds in the carbonate-melt portion contained 1000–1500 ppm N. However, despite one potential exception  
145 (Howell et al., 2015b), there is little evidence to justify modeling diamond-formation in the mantle in equilibrium  
146 with a metallic solvent catalyst, especially considering that the theoretical metal saturation in the mantle is only 1wt  
147 % Fe<sup>0</sup> (Frost et al., 2004). Therefore, the application of the study by Smith and Kopylova (2014) to natural systems is  
148 limited. The total nitrogen abundance of the charges used in all diamond-synthesis experiments is unknown (i.e.  
149 never reported). Ergo, it is not possible to determine D<sub>N</sub> or K<sub>N</sub> values during experimental diamond formation using  
150 the existing published datasets.

151

### 152 **3. A new petrological assessment of the incorporation of nitrogen in mantle diamonds**

153 The preceding review demonstrates, quite surprisingly, that the compatibility of nitrogen in diamond remains a  
154 highly debated topic. Thomassot et al. (2007) and Smart et al. (2011) show convincing data that indicate nitrogen is  
155 compatible in diamond, with K<sub>N</sub> values of 2 and 5 during diamond precipitation from CH<sub>4</sub>-rich and CO<sub>3</sub><sup>2-</sup>-rich fluids  
156 respectively (at 1200°C). However, these conclusions do not explain why the global distribution of nitrogen  
157 concentrations for in non-coated monocrystalline diamonds is skewed towards zero (akin to incompatible behavior;  
158 **Fig.1a-b**), whereas the distribution for the fibrous growth of coated diamonds is Gaussian, peaking at *ca* 800 ppm  
159 (akin to compatible behavior; **Fig.1c**). Equally perplexing are the low nitrogen concentrations observed in diamonds  
160 from the deeper parts of the mantle (see Harte (2010) and references therein). Despite the question of nitrogen  
161 compatibility in diamond being contested, we propose it to be a moot point for the following reasons. According to  
162 Goldschmidt's (1937) rules for element compatibility, nitrogen is of the similar atomic size and charge to carbon,  
163 making N compatible in the diamond lattice, as is borne out by nitrogen being the most common substitutional

164 impurity in diamond. However, nitrogen is incorporated into diamond in a monatomic state, even though it does not  
165 occur in the mantle in this highly unstable form (Mikhail and Sverjensky, 2014; Li and Keppler, 2014). Nitrogen is  
166 stable under equilibrium conditions as a variety of molecules, where each nitrogen complex exhibits radically  
167 different chemical affinities. Therefore, the real focus of investigation should be into understanding how these  
168 various nitrogen species behave, and which potential chemical reactions can disassociate these compounds to  
169 produce (unstable) monatomic N during diamond formation.

170 Historically, nitrogen has been considered an atmophile element and accordingly grouped with the noble gases.  
171 Atmophile elements are defined as 'those elements that remain mostly on or above the surface because they are, or  
172 occur in, liquids and/or gases at temperatures and pressures found on the surface' (Goldschmidt, 1937). However,  
173 under conditions of high P and T, nitrogen can behave like a noble gas ( $N_2$ ), a siderophile element ( $Fe_3N$ , TiN, BN), an  
174 alkali metal ( $NH_4^+$ ) or an organic reactant (e.g. nitrosyl;  $NO\cdot$ ). In fact, in samples from the lower crust and the upper  
175 mantle, nitrogen has been found as molecular  $N_2$  (Andersen et al., 1995; Smith et al., 2014), ammonium (implied by  
176 Yokochi et al., 2009), metallic nitride ( $Fe_3N$ , TiN, BN; Dobrzhinetskaya *et al.* 2009), an impurity in carbide (Kaminsky  
177 & Wirth, 2011) and as a lattice-bound component within diamond ( $NC_4$ ; Kaiser & Bond, 1959). Recent experimental  
178 and theoretical data have shown that pressure, temperature, redox state, pH, and the molar abundance of nitrogen  
179 can have significant effects on the speciation of nitrogen, with redox being the most important (Li and Keppler, 2014;  
180 Mysen et al., 2014; Mikhail and Sverjensky, 2014; Roskosz et al., 2006). For conditions relevant to most (by sample  
181 mass) diamond formation (1000-1300°C and 4-7 GPa across a  $LOGfO_2$  range of QFM +2 to -4), nitrogen will be stable  
182 in diamond-forming fluids as ammoniac ( $NH_4^+/NH_3^0$ ) or molecular ( $N_2$ ) forms (**Fig.2 & 3**).

183 None of the nitrogen molecules listed above are compatible in diamond, because they are far too large to fit  
184 within the diamond lattice (or neutrally charged and therefore inert, as is the case for  $N_2$  and  $NH_3$ ). Therefore, the  
185 only state in which nitrogen can be partitioned into diamond is as monatomic  $N^{-3}$ , which as noted above is not a  
186 stable form of nitrogen. This requires that nitrogen is incorporated into diamond when monatomic N is produced by  
187 coupled oxidation/reduction and acidity/basicity reactions involving  $N_2$  or  $NH_4^+$  and  $CO_2$  or  $CH_4$ . Three simplified  
188 ideal reactions are shown in equations 3-5, where  $CO_2$  is interchangeable with  $CO_3^{2-}$  (but would require a different  
189 mass balance). Noteworthy, the " $NC_4$ " molecule is not an independent species, but instead represent diamond  
190 containing N as a point defect in the crystal structure:

191 Oxidation/reduction reactions:



194    Acidity/basicity reaction:



196            For the above reactions to form diamond requires that the nitrogen-bearing species in the diamond-forming  
197 medium to become unstable at upper mantle conditions. This means they will react during diamond-formation, thus  
198 enabling monatomic nitrogen to partition into diamond following oxidation of  $\text{NH}_4^+$ (Eq3),the reduction of  $\text{N}_2$  (Eq.4),  
199 or dehydrogenation of  $\text{NH}_4^+$  (Eq.5). Equilibrium constants for the stability of ammonium/molecular nitrogen under  
200 conditions conducive to diamond formation show that the transition between ammoniac and molecular nitrogen at  
201  $1200^\circ\text{C}$  occurs when  $\text{LOG}f\text{O}_2$  is between  $\Delta\text{QFM} = 0$  and  $-2$  (Li and Keppler, 2014). These conditions are very similar to  
202 those under which carbonate/methane transitions to diamond (Stagno et al., 2010; Sverjensky et al., 2014; Frost and  
203 McCammon, 2008) (Fig.2). In short, diamond formation can occur under conditions where ammonium is  
204 thermodynamically stable, which would inhibit nitrogen partitioning into diamond. Our model implies that nitrogen  
205 uptake into diamond is not a kinetically driven process based upon N being compatible in the diamond lattice, but  
206 instead requires coupled oxidation/reduction (Eq.3-4) or acid/base (Eq.5) reactions to liberate monatomic N from  
207 ammonium or molecular nitrogen during diamond formation. In this model, the formation of Type II diamond can  
208 occur under a variety of conditions, and requires no single mechanism/environment for formation. From a  
209 petrological standpoint it is not necessary for Type II diamonds to precipitate in N-free domains or from N-poor  
210 fluids; it is only required that Type II diamond precipitate in the absence of monatomic nitrogen. Diamond growing  
211 in equilibrium with  $\text{Fe}_3\text{N}$ ,  $\text{TiN}$ ,  $\text{NH}_4$ ,  $\text{NH}_3$ , or  $\text{N}_2$  would be Type II (because these nitrogen molecules are incompatible  
212 in the diamond lattice).

213            Diamonds that are thought to grow in the lower parts of the upper mantle, the transition zone, and the lower  
214 mantle (based on their mineral inclusion assemblages) are commonly found to be Type II (see Harte (2010) and  
215 references therein). One possible explanation could be that nitrogen becomes more compatible in other mineral  
216 phases that are present at these reduced depths in the mantle (such as Fe-alloys, and K-bearing minerals such as K-  
217 hollandite). In a sense, this is a similar process to that used in industrial HPHT diamond synthesis of Type II  
218 diamonds; the reduction of nitrogen in the presence of native metals such as Fe, Cr, or Ti (nitrogen getting /  
219 nitriding; Stachel and Harris, 2009). Tentative evidence for this process in nature comes from an unusual suite of Fe-



220 carbide inclusions within a diamond from the Amazon craton (Juina, Brazil; Kaminsky and Wirth, 2011). The Fe-  
221 carbide has a high N content (termed nitro-carbide; 73 000–91 000 ppm N) while the host diamond contains only  
222 44ppm nitrogen. This would give a  $K_{N \text{ diamond-carbide}}$  of only 0.0005. However, Mikhail et al., (2014c) also described  
223 several Fe-carbide inclusions from two Southern African diamonds (from Jagersfontein, Kaapvaal craton, South  
224 Africa) in which neither the diamond nor the syngenetic carbide inclusions contained detectable nitrogen.  
225 Interestingly, a recent study by Tsuno and Dasgupta (2015), demonstrating the effect of S on the stability of diamond  
226 in equilibrium with Fe-Ni alloys, undermines the argument for co-existing nitride formation. They found that the  
227 presence of S results in the assemblage diamond + sulfide, whereas in the absence of S the assemblage is Fe-carbide  
228 (cementite) + Fe-Ni alloy (Lord et al., 2009). As sulfides are the most common inclusion in diamond (Shirey et al.,  
229 2013), it is likely that the formation of sulfide precludes the formation of nitrides, as it does for carbides. Although  
230 this aspect is the subject of debate and ongoing study, it is important to note that the existence of lithospheric Type II  
231 diamonds (i.e. those formed at more typical depths of 120-200 km) and the lack of metallic inclusions in almost all  
232 sub-lithospheric diamonds demonstrate that the presence of native metals and exceedingly reduced conditions are  
233 not required to explain the formation of Type II diamonds in the sub-lithospheric mantle. In addition, there is  
234 evidence that sub-lithospheric diamond-formation occurs in equilibrium with relatively oxidizing subducted  
235 carbonate melts in the sublithospheric mantle, ergo, inhibiting carbide or nitride stability during ‘deep’ diamond-  
236 formation (Walter et al., 2008, 2011; Thompson et al., 2014).

237

#### 238 **4. Implications for diamond-formation**

239 Despite the similarity in charge and ionic radius between N and C, data from extensive studies of natural  
240 diamonds and HPHT experiments provide conflicting evidence regarding the compatibility of nitrogen in diamond  
241 (e.g. Deines et al., 1989; Cartigny et al., 2001; Thomassot et al., 2007; Stachel and Harris, 2009; Smart et al., 2011;  
242 Smith and Kopylova, 2014). It is clear that when the matter is considered from a petrological standpoint, the  
243 behavior of nitrogen during diamond formation is complex. For nitrogen to be in an atomic form, capable of  
244 incorporation into the diamond lattice during growth, requires coupled oxidation/reduction (Eq.3-4) or acid/base  
245 (Eq.5) reactions during diamond formation to liberate N in the monatomic state. This fundamental concept  
246 undermines our entire thinking about diamond as a recorder of mantle nitrogen. For example, it is possible to argue  
247 that a Type II diamond could have grown from a fluid with a high nitrogen concentration, where conversely a Type I

248 diamond can precipitate from a fluid with a much lower N content - a counter-intuitive notion. Ergo, the nitrogen  
249 abundance of mantle diamonds is potentially controlled by the  $fO_2$  conditions during diamond formation, and not  
250 just the nitrogen concentration of the diamond-forming fluid. By inference, using the global datasets (**Fig. 1a-c**) we  
251 predict that the formation of the fibrous overgrowths of coated diamonds may require a large redox gradient that  
252 transitions across the stability of ammonium and molecular nitrogen (which is dependent upon P, T, and X),  
253 generating abundant monatomic nitrogen that is readily incorporated into the fibrous diamond. Conversely, the  
254 formation of non-fibrous monocrystalline diamond occurs across a large range of redox states, that do not  
255 necessarily cross the boundary between nitrogen species, meaning many samples may grow under conditions where  
256 ammonium or molecular nitrogen are completely stable species during diamond formation (and are dissolved in the  
257 fluid). This model explains why the distribution of nitrogen concentrations in non-fibrous monocrystalline diamonds  
258 is skewed towards zero (akin to an incompatible element; **Fig.1a-b**) and the distribution for the fibrous overgrowths  
259 of coated diamonds is Gaussian (akin to a compatible element; **Fig.1c**).

260 It is important to reiterate the point that broad statements regarding the compatibility of nitrogen in diamond  
261 are too simplistic. Atomic nitrogen is compatible, whereas molecular nitrogen, ammonium/ammonia and metallic  
262 nitrides are not. Therefore, we need to understand the effects of the mantle P-T-X- $fO_2$  conditions on the speciation of  
263 nitrogen over the range relevant to diamond formation. The diversity of stable nitrogen molecules under this range  
264 of mantle conditions can exhibit radically different solubility, stability, and partitioning behavior in fluids and melts,  
265 meaning a general view on nitrogen compatibility in diamond is irrelevant and it needs to be considered on a case-  
266 by-case basis. Therefore, a much more pertinent question is 'what is the behavior of nitrogen in the mantle, and how  
267 is diamond formation recording it?'

#### 268 **4.1 N in HPHT Synthetic Diamonds**

269 This review of N behavior during natural diamond growth raises obvious questions when it comes to synthetic  
270 diamond growth. When diamonds are synthesized under HPHT conditions from metal solvents (e.g. FeNi alloy), they  
271 commonly contain substitutional N unless special steps are taken (i.e. the addition of N getters such as Ti<sup>0</sup>). The  
272 source of the N is assumed to be atmospheric contamination (i.e. N<sub>2</sub>; Boyd et al., 1988). If we consider the redox  
273 reactions above (eq. 3-5) which affect N speciation, then it is likely that the N<sub>2</sub> will be subjected to very reducing  
274 conditions within the HPHT capsule (in equilibrium with C<sup>0</sup> and a Fe-Ni alloy). This means that N<sub>2</sub> will be converted

275 to iron nitride or  $\text{NH}_4$ , during which time monatomic N will be generated, which can be incorporated into the  
276 diamond lattice.

## 277 **5. Broader implications and future directions**

### 278 **5.1 Stable isotope fractionation**

279 The use of stable isotopes to trace subducted material through the mantle is widespread, and based on the  
280 thermodynamic principle that equilibrium stable isotope fractionation is large at low temperatures and decreases  
281 greatly as a function of T (Urey, 1947). Therefore, the light element stable isotope ratios (e.g. carbon and nitrogen)  
282 are fractionated in Earth's surficial reservoirs, primarily the atmosphere and hydrosphere, by much larger factors  
283 than are possible in the mantle. This makes the stable isotopes of light atmophile elements powerful tracers of  
284 material subducted through the mantle (Hilton et al., 2002). However, because carbon isotopes can be significantly  
285 fractionated in the mantle under open-system Rayleigh conditions (Cartigny et al., 2001), or reducing conditions  
286 involving Fe-carbides (Mikhail et al., 2014c), the use of diamonds' carbon isotopes alone cannot conclusively ascribe  
287 a mantle origin to the diamond-forming carbon (Cartigny et al., 1997). As nitrogen is present in most diamonds, the  
288  $^{15}\text{N}/^{14}\text{N}$  ratios in diamond have been coupled with the  $^{13}\text{C}/^{12}\text{C}$  ratios to verify or challenge the conclusions based  
289 solely on carbon-isotope data (Javoy et al., 1984; Boyd et al., 1987, 1992; Boyd and Pillinger, 1994; Cartigny et al.,  
290 1997, 1998a,b, 2001, 2003, 2004, 2009; Harte et al., 1999; Bulanova et al., 2002, 2014; Hauri et al., 2002; Howell et  
291 al., 2015a; Gautheron et al., 2005; Hutchison et al., 1997; Thomassot et al., 2007, 2009; Petts et al., 2015; Palot et al.,  
292 2009, 2012; 2014; Klein-BenDavid et al., 2010; Mikhail et al., 2013, 2014a). However, it is unclear whether the  
293  $^{15}\text{N}/^{14}\text{N}$  ratio in diamond records the  $^{15}\text{N}/^{14}\text{N}$  ratio of the diamond-forming fluids. The model presented here implies  
294 that partitioning of nitrogen into diamond can occur *via* three main reactions, involving either  $\text{N}_2$  or  $\text{NH}_4$  (Eq.3-5).  
295 Due to significant differences in the vibrational frequencies for nitrogen bonds in reduced and oxidised species (e.g.  
296 C-N, bonds, N-H bonds, and N-N bonds; Richet et al., 1977), deviations from the typical  $^{15}\text{N}/^{14}\text{N}$  ratios in mantle-  
297 derived rocks and within single minerals (e.g. diamond) may be a consequence of redox and pH changes in upper-  
298 mantle fluids (Petts et al., 2015). Instead of requiring special mechanisms such as tectonic injection of isotopically  
299 heterogeneous crustal sources (Boyd and Pillinger, 1994; Mikhail et al., 2014a) or primordial heterogeneities (Javoy  
300 et al., 1986; Cartigny et al., 1997; Palot et al., 2012), the observed variations in the nitrogen isotopic compositions of  
301 diamonds and other mantle materials might be the result of intra-mantle equilibrium (Petts et al., 2015) or kinetic  
302 (Yokochi et al., 2009; Li et al., 2009) stable-isotope fractionation associated with changes in fluid chemistry during

303 metasomatic reactions in the mantle. Therefore, qualitative understandings of equilibrium stable-isotope  
304 fractionation factors for nitrogen isotopes during the reactions shown in Eq. 3-5 are required.

## 305 **5.2 The mantle nitrogen budget**

306 Mantle diamonds show a decrease in average nitrogen abundance with increasing depth of formation. This could  
307 reflect a decrease in the nitrogen content of the silicate Earth with depth, as would be predicted if nitrogen were to  
308 behave like a noble gas, or if nitrogen is more compatible in other phases with increasing depth. Several lines of  
309 direct and indirect evidence show that nitrogen does not necessarily behave like a noble gas, and that the mantle is a  
310 significant reservoir for nitrogen: [1] Nitrogen shows the largest depletion (relative to chondrites) in the bulk silicate  
311 Earth + atmosphere compared with the enrichment levels of other volatile elements, including the noble gases (H, C,  
312 N, Ne, Ar, Kr, and Xe; Marty, 2012; Halliday, 2013), [2] The calculated flux for nitrogen between the surface and  
313 interior (subduction vs. volcanism) implies that more nitrogen is being out-gassed from the interior than is being  
314 returned into the mantle (Busigny et al., 2011), and [3] the solubility of nitrogen in enstatite and forsterite  
315 demonstrates that the reduced parts of the upper mantle can store >50 times more nitrogen than the surface  
316 reservoirs (including the atmosphere; Li and Keppler, 2013; Watenphul et al., 2010). Collectively, these data strongly  
317 imply the existence of a deep reservoir. Paradoxically, diamond is the mantle mineral with the highest average  
318 nitrogen abundance, but may not be the largest reservoir of mantle nitrogen. By far the most important storage  
319 mechanism for nitrogen in the mantle is probably through the exchange equilibria between positively charged  
320 ammonium cations ( $\text{NH}_4^+$ ) and positively charged alkali metals (e.g.  $\text{Rb}^+$  &  $\text{K}^+$ ). This implies that the mantle N-H cycle  
321 could follow the same pathways as alkali metals. Thus, based on the stability of the known K-bearing phases (Harlow  
322 and Davies, 2004) it is likely that ammonium-bearing mantle phases are stable throughout the entire silicate portion  
323 of the Earth. The nature of the deep nitrogen reservoir therefore depends upon the stability of ammonium in the  
324 mantle. The mole fraction of ammoniac/total nitrogen is predicted to decrease with increasing temperature (e.g. **Fig.3**  
325 **a & b**). However, there the mole fraction of ammoniac/total nitrogen should increase with increasing pressure (e.g.  
326 **Fig.3 b & d**), albeit this relationship is known with a limitation of only 4 GPa for  $\Delta P$  and maximum T of only 1400°C  
327 (Mikhail & Sverjensky, 2014; Li & Keppler, 2014). What is now required are data on the solubility and partitioning of  
328 ammoniac nitrogen between fluids, melts, and high-pressure K-bearing phases, to address the depletion of nitrogen  
329 relative to the other volatile elements, and by inference to express (mechanically) why average nitrogen abundance  
330 in diamonds decreases with increasing depth of formation. Addressing this question will provide a more robust

331 understanding of the fluxing of nitrogen during subduction, and the N-H storage capacity of planetary silicate  
332 mantles as a whole.

## 333 **6 Summary**

334 Nitrogen is initially incorporated into the diamond lattice as single nitrogen atoms, a form of nitrogen which is  
335 highly unstable. However, the stable forms of nitrogen in the mantle are dominated by  $N_2$ , and  $NH_4^+$ , both of which  
336 are incompatible in the diamond lattice. A review of the available data shows that in classic terms, nitrogen is the  
337 most common substitutional impurity found in natural diamonds because it is of very similar atomic size and charge  
338 to carbon. However, the speciation of nitrogen, and how these different species disassociate during diamond  
339 formation to create transient monatomic nitrogen, are the factors governing nitrogen abundance in diamonds. Our  
340 model suggests a counter-intuitive notion; nitrogen-free diamond could grow from a N-rich media that is simply not  
341 undergoing reactions to liberate monatomic N from  $N_2$ , or  $NH_4^+$  during coupled oxidation/reduction or acid/base  
342 reactions during diamond-formation (Eqs.3-5). In contrast, a nitrogen-bearing diamond could grow from a fluid with  
343 a lower N abundance, in which reactions are occurring to generate (unstable) N atoms during diamond formation are  
344 occurring.

345 The most logical conclusion we can derive is that, at present, we do not understand how diamonds are recording  
346 the mantle nitrogen cycle. However, we believe diamonds still represent our best tool for investigating numerous  
347 aspects of the mantle C-N cycle, especially when considering carbon and nitrogen stable isotope data. However,  
348 further investigations into the speciation, partitioning, and equilibrium stable-isotope fractionation of nitrogen will  
349 enable a more accurate interpretation of the nitrogen data from mantle diamonds, and lead to a better  
350 understanding of the Earth deep volatile cycles and fluxes.

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360

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563 **Figure 1.** Histogram showing the distribution of nitrogen contents (ppm) of mantle diamonds. Data from multiple  
564 sources (Boyd et al., 1987, 1992; Bulanova et al., 2002, 2014; Cartigny et al., 1997, 1998a, 1998b, 2001, 2003, 2004;  
565 2009; Gautheron et al., 2005; Harte et al., 1999; Howell et al., 2015a; Hauri et al., 2002; Javoy et al., 1984; Klein-  
566 BenDavid et al., 2010; Mikhail et al., 2013, 2014a, 2014b; Palot et al., 2009; 2012, 2014; Smart et al., 2011;  
567 Thomassot et al., 2007, 2009)

568

569 **Figure 2.** A schematic representation of the aqueous speciation of nitrogen and carbon and the solid state of carbon  
570 as a function of redox state at 5 GPa and 1200 °C (\*denotes calculations are in equilibrium with diamond). Data for  
571 aqueous nitrogen speciation from Mikhail and Sverjensky (2014), Mysen et al., (2014), and Li and Keppler (2014),  
572 data for aqueous carbon speciation from Sverjensky et al. (2014) and Frost and McCammon (2008), and the data for  
573 solid carbon speciation are from Stagno et al. (2010) and Rohrbach and Schmidt (2011).

574

575 **Figure 3.** Diagrams showing the aqueous speciation of a fluid with 1 wt.% nitrogen as a function of the fluid P, T,  $fO_2$ ,  
576 and pH (a-d) using data from Mikhail and Sverjensky (2014).