# The relationship between mantle pH and the deep nitrogen cycle

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## Abstract

Nitrogen is distributed throughout all terrestrial geological reservoirs (i.e., the crust, mantle, and core), which are in a constant state of disequilibrium due to metabolic factors at Earth's surface, chemical weathering, diffusion, and deep N fluxes imposed by plate tectonics. However, the behavior of nitrogen during subduction is the subject of ongoing debate. There is a general consensus that during the crystallization of minerals from melts, monatomic nitrogen behaves like argon (highly incompatible) and ammonium behaves like potassium and rubidium (which are relatively less incompatible). Therefore, the behavior of nitrogen is fundamentally underpinned by its chemical speciation. In aqueous fluids, the controlling factor which determines if nitrogen is molecular ($N_2$) or ammonic (inclusive of both $NH_4^+$ and $NH_3^0$) is oxygen fugacity, whereas pH designates if ammonic nitrogen is $NH_4^+$ and $NH_3^0$. Therefore, to address the speciation of nitrogen at high pressures and temperatures, one must also consider pH at the respective pressure–temperature conditions. To accomplish this goal we have used the Deep Earth Water Model (DEW) to calculate the activities of aqueous nitrogen from 1-5 GPa and 600-1000 °C in equilibrium with a model eclogite-facies mineral assemblage of jadeite + kyanite + quartz/coesite (metasediment), jadeite + pyrope + talc + quartz/coesite (metamorphosed mafic rocks), and carbonaceous eclogite (metamorphosed mafic rocks + elemental carbon). We then compare these data with previously published data for the speciation of aqueous nitrogen across these respective P-T conditions in equilibrium with a model peridotite mineral assemblage (Mikhail, S. Sverjensky, D.A. 2014. Nature. Geoscience 7, 816–819). In addition, we have carried out full aqueous speciation and solubility calculations for the more complex fluids in equilibrium with jadeite + pyrope + kyanite + diamond, and for fluids in equilibrium with forsterite + enstatite + pyrope + diamond.

Our results show that the pH of the fluid is controlled by mineralogy for a given pressure and temperature, and that pH can vary by several units in the pressure-temperature range of 1-5 GPa

and 600-1000 °C. Our data show that increasing temperature stabilizes molecular nitrogen and increasing pressure stabilizes ammonic nitrogen. Our model also predicts a stark difference for the dominance of ammonic vs. molecular and ammonium vs. ammonia for aqueous nitrogen in equilibrium with eclogite-facies and peridotite mineralogies, and as a function of the total dissolved nitrogen in the aqueous fluid where lower N concentrations favor aqueous ammonic nitrogen stabilization and higher N concentrations favor aqueous $N_2$.

Furthermore, we present thermodynamic evidence for nitrogen to be reconsidered as an extremely dynamic (chameleon) element whose speciation and therefore behavior is determined by a combination of temperature, pressure, oxygen fugacity, chemical activity, and pH. We show that altering the mineralogy in equilibrium with the fluid can lead to a pH shift of up to 4 units at 5 GPa and 1000 °C. Therefore, we conclude that pH imparts a strong control on nitrogen speciation, and thus N flux, and should be considered a significant factor in high temperature geochemical modeling in the future. Finally, our modelling demonstrates that pH plays an important role in controlling speciation, and thus mass transport, of Eh-pH sensitive elements at temperatures up to at least 1000 °C.

## 1. INTRODUCTION

Nitrogen is the dominant gas in Earth's atmosphere and is distributed in all terrestrial geological reservoirs, which are in a constant state of disequilibrium (see Busigny & Bebout, 2013; Bebout et al., 2013, 2016; Johnson & Goldblatt, 2015). The flux of nitrogen between the surface and interior is governed by volcanism (out-gassing) and subduction (in-gassing); this interplay ultimately controls atmospheric $N_2$ levels (see discussion in Barry & Hilton, 2016), which are intimately linked with biology (Stüeken et al., 2016; Zerkle & Mikhail, 2017). But to constrain the N flux and/or the partial pressure of atmospheric N over geologically-long (>Ga) timescales is difficult due to a lack of samples (e.g. Marty et al., 2013; Som et al., 2012; 2016). Consequently, in order to address these issues, workers must combine the evidence from sparse deep-time N datasets with experimental and theoretical (thermodynamic) models to estimate past nitrogen dynamics.

At present, there is no consensus for the direction (i.e., positive or negative ) or magnitude of the global N flux out of the Earth through time (Dauphas & Marty, 1999; Fischer et al., 2002; Marty & Dauphas, 2003; Busigny et al., 2003; Elkins et al., 2006; Philippot et al., 2007; Yokochi et al., 2009; Mohapatra et al., 2009; Halama et al., 2010, 2014; Palot et al., 2012; Mikhail et al., 2014; Mikhail & Sverjensky, 2014; Barry & Hilton, 2016; Zerkle & Mikhail, 2017). As a result, there is no

quantitative explanation for the discrepancy between calculated N-fluxes from different arc systems (see recent reviews by Busigny & Bebout, 2013; Bebout et al., 2013, 2016), and thus the nature of the deep nitrogen cycle remains a controversial topic (Zerkle & Mikhail, 2017).

To understand the pathways followed by N during subduction requires a first-order understanding of the partitioning behavior of nitrogen within specific minerals. For example, molecular nitrogen ($N_2^0$) and ammonia ($NH_3^0$) are both neutrally charged, and therefore highly incompatible in most mineral phases (Brooker et al., 2003). Conversely, ammonium ($NH_4^+$) is positively charged and has an ionic radius between those of $Rb^+$ and $K^+$, and thus should be compatible in K-bearing phases such as phengite, phlogopite, K-bearing clinopyroxene, K-hollandite, Phase-X ($(K)Mg_2Si_2O_7H$) (Honma & Itihara, 1983; Haendel et al., 1986; Busigny et al., 2003; Yokochi et al., 2009; Palya et al., 2011; Bebout et al., 2016). Ammonium has also been shown to dissolve as a trace component in K-absent mafic minerals (Li et al., 2013; Watenphul et al., 2010). Therefore, the behavior of nitrogen is predictably governed by the speciation of nitrogen where neutrally charged compounds are – thermodynamically speaking – highly incompatible (Blundy & Wood, 2003), an assertion that has been demonstrated experimentally (Brooker et al., 2003).

For high temperature aqueous systems, the speciation of N been constrained as a function of oxygen fugacity (Mikhail & Sverjensky, 2014; Li & Keppler, 2014), and both studies agree that most nitrogen in upper mantle fluids should be ammonic. The difference between these datasets is the nature of the ammonic nitrogen present. For example, at 5 GP, 1000 °C, and an oxygen fugacity of -1 log units relative to the Quartz-Fayalite-Magnetite buffer reaction (QFM) the speciation of nitrogen in equilibrium with olivine ($Fo_{90}$) was determined to be ammonia in quenched run products (using FTIR; Li & Keppler, 2014), but the predicted speciation of nitrogen in equilibrium with forsterite + enstatite is ammonium (Mikhail & Sverjensky, 2014). We note that this could be the result of quenching, where ammonium (a reactive ion) re-equilibrates to a stable state during cooling (pre-analysis). But the controlling factor, which designates if ammonic nitrogen is $NH_4^+$ and $NH_3^0$ is not oxygen fugacity, but rather pH – and more alkaline conditions favor $NH_3^0$. This implies that the pH of the fluid in equilibrium with olivine (Fo90; Li and Keppler, 2014) may be more alkaline than is predicted for pH of the fluid in equilibrium with forsterite + enstatite (where pH can be expressed as proportional to $\log[{}^aMg^{2+}/({}^aH^+)^2]$; Mikhail and Sverjensky, 2014). Overall, this result implies pH is a significant variable at high temperatures.

Here we investigate the effect of pH on the speciation of nitrogen under upper mantle P-T-$fO_2$ conditions as a function of system stoichiometry using a hypothetical host-rock mineralogy. As is

the case with $fO_2$, the pH of the system is governed by pressure, temperature and composition (P-T-X). In the case of nitrogen geochemistry for our study, this can be considered as the equilibrium between a fluid and a solid, therefore if all else is equal, the stoichiometry of the system can exert control on the pH and therefore the speciation and behavior of nitrogen. This is because different protonation reactions can buffer the pH of the fluid to different values (e.g., whether the protonation reactions are governed by the $\log[{}^{\alpha}Mg^{2+}/({}^{\alpha}H^{+})^{2}]$ or $\log[{}^{\alpha}Na^{+}/{}^{\alpha}H^{+}]$). Herein we investigate the role of a hypothetical mineralogy (for stoichiometry) on fluid pH by presenting the outputs from a series of thermodynamic calculations, and we discuss the implications of our findings in light of the deep-Earth nitrogen cycle, and mantle geochemistry.

## 2. METHODS

The speciation of aqueous ions, metal complexes, neutral species and minerals can be predicted by applying the Helgeson-Kirkham-Flowers (HKF) equations of state (Helgeson and Kirkham, 1974a,b, 1976; Helgeson et al., 1981; as revised in Tanger and Helgeson, 1988, and Shock and Helgeson, 1988). Prior to recent pioneering work (Pan et al., 2013; Facq et al., 2014; Sverjensky et al, 2014a) there was a historic limitation of pressure < 0.5 GPa, due to the fact that the dielectric constant of water was not known at higher pressures (Johnson et al., 1992; Shock et al., 1992). This precluded the application of the HKF equations of state to matters concerning aqueous fluids in deep Earth systems (e.g., lower crust, upper mantle, and subduction zones). However, the dielectric constant of water has recently been constrained ≤6 GPa (Sverjensky et al., 2014a), which enables an extension of the P-T range for the application of the HKF equations of state for aqueous species up to ≤6 GPa and ≤1200°C (Pan et al., 2013; Facq et al., 2014; Sverjensky et al., 2014a). As a result, it is now feasible to determine the speciation of aqueous ions, metal complexes, neutral species and minerals across conditions akin to the pressure and temperature pathway followed by a subducted-slab from Earth's surface to a depth of approximately 150 km using the Deep Earth Water (DEW) model. As previously described (Sverjensky et al., 2014b; Sverjensky & Huang, 2015; Mikhail & Sverjensky, 2014), the DEW model enables calculation of equilibrium constants involving aqueous species of all kinds as a function of temperature and pressure, and the incorporation of these equilibrium constants into aqueous speciation, solubility, and chemical mass transfer codes.

We have predicted the speciation of nitrogen as a function of P-T-$fO_2$-pH. Note, pH is a function of the activities of $Mg^{2+}$ and $Na^{+}$ in supercritical aqueous fluid in equilibrium with specific mineral

assemblages (Sverjensky et al., 2014). The pH values denoted by subducted oceanic crust in **Figs. 1a-d** were constrained by equilibrium with the model eclogite-facies mineral assemblages (jadeite + kyanite + $SiO_2$ representing metasediment, and jadeite + pyrope + talc + $SiO_2$ representing metamorphosed mafic rocks) at pressures of 1 and 5 GPa and temperatures of 600 to 1,000°C. The equilibrium between fluid and jadeite, kyanite, $SiO_2$ enables derivation of the following equations:

$$2NaAlSi_2O_6 + 2H^+ = Al_2SiO_5 + 3SiO_2 + 2Na^+ + H_2O \quad (2)$$

for which $$logK_2 = log\frac{a^2_{Na^+}}{a^2_{H^+}} \quad (3)$$

Assuming pure minerals and unit activities of the minerals and the water results in

$$pH = \frac{1}{2}logK_2 - loga_{Na^+} \quad (4)$$

For the mafic eclogite-facies mineral assemblages, equilibrium between the components of jadeite, garnet, talc and $SiO_2$ enables writing

$$Mg_3Si_4O_{10}(OH)_2 + 2NaAlSi_2O_6 + 2H^+ = Mg_3Al_2Si_3O_{12} + 5SiO_2 + 2Na^+ + 2H_2O \quad (5)$$

for which $$pH = \frac{1}{2}logK_5 - loga_{Na^+} \quad (6)$$

Noteworthy, $SiO_2$ is coesite at 5 GPa (600 & 1000 °C), but at 1 GPa $SiO_2$ is stable as either α-Qtz (600 °C) and β-$SiO_2$ (1000 °C). A range of values for the $a_{Na^+}$ from 0.01 to 1.0 were used in Eqns. (4) and (6) resulting in a range of estimated pH values. For example, at 5 GPa and 600 °C, the calculated pH values from Eqns. 4 and 6 are 3.1 - 5.1 and 3.2 - 5.2, for metasedimentary and mafic eclogites respectively. Because these two ranges are indistinguishable on this scale, we only plot the values from Eqn. 4 in **Figs. 1a-d** (subducted oceanic crust). The assumption of pure minerals introduces small uncertainties on the scale of the plots shown. For example, a decrease in the activity of jadeite in Eqn. (4) from 1.0 to 0.5 would produce a decrease in the pH in Eqn. (6) of 0.30, which is relatively small compared to the range of $Na^+$ activities assumed. Very low activities of jadeite would produce a bigger effect (e.g., if the activity of jadeite were reduced from 1.0 to 0.10, the pH would be decreased by 1.0 unit). Furthermore, by applying values of logK calculated as described above, together with the range of activities for the $Mg^{2+}$ and $Na^+$ corresponds to a range of pH values for the fluids. It should be emphasized that uncertainties caused by using the pure minerals and water are rather small on a logarithmic scale such as in **Figs. 1a-d** compared to the range of pH associated with the range of activities for either $Mg^{2+}$ or $Na^+$.

157 The boundaries between the various nitrogen species shown in **Figs. 1a-d** depend on the
158 stoichiometry of the equilibria, the magnitudes of the relevant equilibrium constants, and the
159 total dissolved nitrogen (Mikhail and Sverjensky, 2014). The latter dependence is a consequence of
160 equilibria between $N_2$, which has two moles of N, and reduced N-species, which have one mole of
161 N in each. As a consequence, the speciation of N in aqueous fluids at equilibrium is a function of
162 the total dissolved nitrogen in the fluid. In our calculations, we consider a large range of possible
163 nitrogen concentrations from 0.001 to 1 m N, corresponding to concentrations between 14 ppm
164 by mass and 1.4 wt.%. This range was selected in order to simulate a wide range of likely fluid
165 compositions that might be found in nature, but also to constrain the effect of N concentration
166 (order of magnitude scales).

167 Although nitrogen concentrations in aqueous fluids from the upper mantle are poorly known
168 (because aqueous fluids from the upper mantle are rarely sampled), the concentrations in
169 minerals are better constrained. We cite a range of nitrogen concentrations measured in mantle
170 rocks and minerals to demonstrate the possibility that aqueous fluids in the mantle might also
171 exhibit a wide range of nitrogen concentrations. For example, typical measurements of volcanic
172 xenoliths and basaltic samples are approximately 0.1-10 ppm by mass (whole rock from Marty,
173 1995, mineral separates from Fischer et al., 2005; basaltic glasses from Barry et al., 2012), and the
174 phlogopites ranges from 7.6 to 25.7 ppm by mass (Yokochi et al., 2009) and lithospheric and
175 sublithospheric diamonds contain between <1 to >10,000 ppm by mass N (Smart et al., 2011;
176 Mikhail et al. 2014). In fact, some very rare mantle xenoliths and diamonds contain fluid-inclusions
177 of pure $N_2$ (Andersen et al., 1995; Smith et al. 2014). Despite the fact that nitrogen is a trace
178 component in material from shallow depths, typically sampled by volcanoes (see Johnson and
179 Goldblatt et al., 2016 for a review), there are processes (i.e. metasomatism and melting) that can
180 generate localized nitrogen-enrichment and render nitrogen a major volatile element in the
181 mantle**.** Therefore, the concentrations used here (ca. 14 ppm by mass to 1.4 wt.%) are not
182 unrealistic, and enable us to investigate the speciation of nitrogen as a function of P, T, $fO_2$, pH,
183 and nitrogen concentration.

184

185 **3. RESULTS**

186 Superposed on **Figs. 1a-d** are fields representing the calculated (theoretical and empirical) oxygen
187 fugacities of peridotitic (Woodland et al. 1992; 1996, 2006; Ionov & Wood 1992; Wood & Virgo
188 1989, Canil et al. 1990, Brandon & Draper 1996, Frost and McCammon, 2008) and eclogitic rocks

189 (Simakov, 2006; Stagno et al., 2015) as well as the predicted range of pH values for aqueous fluids
190 in equilibrium with hypothetical mineral assemblages representing model peridotite (from Mikhail
191 & Sverjensky, 2014) and eclogite-facies mineral assemblages (this study).

192 The oxygen fugacities for peridotites in arc-mantle wedges (QFM to QFM + 2) vs. the oxygen
193 fugacity of peridotites from sub-cratonic lithospheric mantle (QFM to QFM -3) are taken from
194 Frost and McCammon (2008). The available data suggest eclogitic rocks cover a similar $fO_2$ range
195 to their peridotitic counterparts (Simakov, 2006; Stagno et al., 2015; Smart et al., 2016). We plot a
196 larger range for the $fO_2$ of eclogites in the **figures** (QFM to QFM - 4) to account for the observed
197 occurrence of carbides, nitrides and native metals in samples from the obducted Tibetan
198 ophiolites (≤ QFM - 4; Dobrzhinetskaya et al., 2009). In addition, the sediments subducted beneath
199 the Cyclades Greek islands are relatively oxidized (≥ QFM - 1; Ague and Nicolescu, 2014), having
200 stable carbonate phases. The range of $fO_2$ values for eclogites shown in **Figs. 1a-d** represents the
201 global range, and is not intended to represent any single geographical locality (i.e., data from
202 Tibetan and Greek obducted rocks are provided to illustrate the large range of $fO_2$ values in
203 measured subducted assemblages).

204 The pH values plotted here correspond to the calculated equilibrium between water and pure
205 forsterite + enstatite (model peridotite – Mikhail & Sverjensky, 2014) and hypothetical eclogite-
206 facies mineral assemblages; jadeite + kyanite + $SiO_2$ (metasediment – this study), jadeite + pyrope
207 + talc + $SiO_2$ (metamorphosed mafic rocks – this study), and carbonaceous eclogite-facies mineral
208 assemblages (metamorphosed mafic rocks + elemental carbon; this study). Importantly, the
209 relative proportions of the pure minerals do not influence the fluid chemistry, because the fluid
210 chemistry is set by the equilibrium constants (see methods). In our model, pH is expressed by the
211 $^{\alpha}H^{+}$ (fluid) and $^{\alpha}Na^{+}$ (eclogite – this study) and $^{\alpha}Mg^{2+}$ (peridotite; Mikhail & Sverjensky, 2014) (eq.4
212 and eq.6). We have applied a range of activities for $^{\alpha}Na^{+}$ and $^{\alpha}Mg^{2+}$ from 0.1 to 1 (e.g. eq.3). Our
213 calculations show the speciation of aqueous ammonic nitrogen in equilibrium with eclogite-facies
214 metasediments and mafic rocks (herein collectively referred to as eclogite-facies mineral
215 assemblage; this study) is predicted to differ from aqueous nitrogen in equilibrium with
216 peridotites under most of the conditions investigated (**Figs. 1a-d**). Under most conditions,
217 ammonium ($NH_4^{+}$) dominates in peridotite, and ammonia ($NH_3^{0}$) is dominant in the eclogite-facies
218 mineral assemblages; this is due to the eclogite-facies mineral assemblages buffering the fluid to
219 higher pH conditions (**Figs. 1a-d**).

For an oxygen fugacity of QFM -1 to -2, 600°C, and 1 or 5 GPa (**Figs 1a and 1c** respectively), the dominant nitrogen species in the fluid are predicted to be $NH_3^0$ or $NH_4^+$, depending on pressure and pH. At 1,000°C and 1 or 5 GPa (**Figs 1b and 1d** respectively), the dominant nitrogen species in the fluid is predicted to be $N_2^0$. This temperature range is relevant to modern arc systems. For example, Syracuse et al., (2010) calculated the thermal models for 204 slab temperatures in arc systems on the Pacific rim and found the range to be 301 to 987°C, with a mean of 789 ± 76°C. Thus, our results strongly suggest that the nitrogen speciation in eclogitic fluids in 'cold' subduction zones differs from those in 'hot' subduction zones. Note, the exact thermal regimes for hot and cold subduction zones are difficult to constrain, because there are a number of dependent and independent vairbales to consider which control the thermal-depth status of a subdcuted slab (age of slab, slab-dip, slab T beneath arc, Moho T beneath arc, velocity of subduction) and the temperature also varies significantly with distance from slab surface (in both directions; Syracuse et al., 2010). Furthermore, because geothermal gradients during subduction are non-linear, there are multiple degrees of freedom to explore. To examine this further, we direct the reader to Syracuse et al. (2010). Herein, we refer to cold subduction zones as those with a thermal gradient (at the slab surface) of <10 ºC/km.

A significant difference between cold and hot subduction regimes are shown more distinctly in **Figs.2a-b & 3a-b.** We calculated a full aqueous speciation model at 5.0 GPa between 600 and 1,000°C at QFM - 2 for aqueous nitrogen in fluids in equilibrium with a model eclogite consisting of jadeite + pyrope + kyanite + coesite, +diamond and a model peridotite consisting of forsterite + enstatite + pyrope + diamond. The latter is a more complex chemical system than has previously been considered (Mikhail & Sverjensky, 2014). Results are shown for high (0.1 m N ≈ 1.4 wt% N) and low (0.001 m N ≈ 14 ppm by mass N) nitrogen concentrations. Unreactive aqueous nitrogen ($N_2^0$ + $NH_3^0$) progressively increase in N concentration and then dominate over reactive nitrogen ($NH_4^+$) in fluids in equilibrium with the eclogite-facies assemblage while temperature increases from 600-1000°C (**Fig.2a-b**). For the model peridotite assemblage the relationship is similar for high nitrogen concentrations, where molecular aqueous nitrogen ($N_2$) progressively increases in abundance and then dominates over reactive nitrogen ($NH_4^+$), but importantly, ammonia is always less dominant than what we find for the eclogite-facies eclogites assemblage (**Fig.3b**). However, for low N concentrations in equilibrium with the peridotite assemblage, ammonium is the most abundant species across all temperatures investigated (**Fig.3a**). Therefore, the hottest subduction zone fluids at QFM-2 are predicted to be dominated by $N_2$ at higher N concentrations in both eclogite-facies (**Fig.2b**) and model peridotite (**Fig.3b**) assemblages, but at the lowest N-

253 concentrations, $N_2$ is minor for both eclogite (**Fig.2a**) and peridotite (**Fig.3a**) with ammonia and
254 ammonium dominating, respectively. Note, the difference in domination for ammonia and
255 ammonium between the eclogite and peridotite simulations is the function of differing pH values
256 for the fluids at high tempertures (**Fig.1**).

257

258 **4. DISCUSSION**

259 **4.1 Limitations of the approach**

260 This study examines the role of pH in the deep-Earth nitrogen cycle at temperatures from 400-
261 1000°C and pressures of 1-5 GPa (**Figs. 1-3**). We have calculated the pH for aqueous fluids in
262 equilibrium with hypothetical eclogite-facies and metasediments with a simple bulk chemistry.
263 However, our approach does not consider some important and classically considered electron-
264 doner elements (i.e., $Fe^{2+,3+}$, $S^{-2,+6}$) nor do we consider the role of alkali metals besides $Na^+$ ($K^+$,
265 $Rb^+$, $Cs^+$). Furthermore, under water-saturated conditions at 1000 °C and 1 GPa, peridotites and
266 eclogites would likely melt (Grove et al., 2006). The DEW model does not (presently) take melting
267 into account, and therefore we can only show the predicted speciation of aqueous nitrogen in
268 equilibrium with solid mineral phases. If a melt phase were present, the partitioning of ions could
269 be affected, and therefore the pH values of the aqueous fluids could also be affected. Therefore,
270 we acknowledge that our approach represents a simplification. Nonetheless, our approach does
271 allow for robust constraints to be applied based on the effect of pH on the speciation of aqueous
272 nitrogen at high temperatures and pressures. The modeling detailed here shows how changes in
273 pH as a function of mineralogy are not only possible, but are predicted to be large (orders of
274 magnitude – **Fig.1a.d**), and this approach has been further reinforced by a recent study employing
275 a different (theoretical) modeling approach (Galvez et al., 2016). Ergo, large changes in $fO_2$ are
276 predicted, which is consistent with empirical data and conventional understanding. However, we
277 also predict large variations in pH, which also overlap with speciation changes for nitrogen
278 between three distinct species ($NH_4^+$-$NH_3^0$-$N_2^0$).

279

280 **4.2 Ammonia and Ammonium**

281 Our results show, that nitrogen can occur either in a neutral or positively charged state at high
282 temperatures in the mantle, where molecular vs. ammonic is dependent on $fO_2$ (i.e. Mikhail &
283 Sverjensky, 2014), but ammonia vs. ammonium is dependent on pH (this study). For example, at

700°C, 5 GPa, and a LOG$fO_2$ -2 (ΔQFM) >80% of the nitrogen in equilibrium with Jadeite + Pyrope + Kyanite + $SiO_2$ + Diamond will be at $NH_4^+$ but neutrally charged nitrogen becomes dominant with increasing temperature, where $NH_4^+$ drops off to 10% and $N_2^0$ and $NH_3^0$ make up 60 and 30 % of the fluid, respectively, at 1000°C (**Fig.2a**). At 1000°C and 5 GPa (**Fig. 1d**), aqueous nitrogen in fluids under equilibrium with eclogite are predicted to be more alkaline than in peridotite, and there are a wide range of conditions where $NH_3^0$ will be the dominant nitrogen species (**Fig. 1d**). As a futher additional complexity influencing the behavior of nitrogen in upper mantle fluids, the total amount of nitrogen in the fluids also affects the speciation (**Figs.2-3**). For example, in **Fig. 1a**, the speciation of nitrogen in eclogitic fluids at QFM – 2, ranges from $NH_3^0$ in low-N fluids to $N_2$ in high-N fluids.

We note that the dominance of $NH_3^0$ in our hypothetical eclogite-facies and metasediments must be considered a gross simplification for the sake of constraining the first-order level effect of pH. Nonetheless, this result can be viewed as an upper limit, where the addition of $H^+$ would hydrolyze $NH_3^0$ to $NH_3^+$. We further note that there are other reactions (in nature) which can produce $H^+$ ions and convert $NH_3^0$ to $NH_4^+$. For example, such reactions require coupling with a reaction that produces $H^+$ ions during subduction (e.g., the carbonation of calcium shown in equation 7):

$$Ca^{2+} + CO_2 + H_2O = CaCO_3 + 2H^+ \quad (7)$$

Therefore, we can model the incorporation of neutrally charged ammonia into K-bearing minerals through pH-dependent reactions such as:

$$Muscovite + NH_3^0 + H^+ = NH_4^+ - Mica + K^+ \quad (8)$$

Because some carbonation reactions generate $H^+$ ions (e.g. Eq.7), the pH of fluids in equilibrium with eclogites may not inherently destabilize ammonium, but instead the stability of ammonium over ammonia in nature may depend on the bulk chemistry of the more complex natural system(s). Therefore, future empirical work may indeed link the carbon cycle with the nitrogen cycle, on a more genetic basis. To take this further requires extensive experimental and theoretical interrogation in the near future to examine the pH shift and the dramatic effect on N specation (shown here). However, where conditions permit and ammonium is stabilized, the secondary $H^+$-producing reactions (e.g., Eq.7) are not required for nitrogen to exchange for potassium directly (Eq.9):

$$Muscovite + NH_4^+ = NH_4^+ - Mica + K^+ \quad (9)$$

Our data also show that fluid mobilization from the sedimentary package into the mantle (eclogite or peridotite) will result in transitions between $N_2^0$, $NH_3^0$, and $NH_4^+$, where the nature of these transitions will vary depending on whether or not the reaction is driven by pH, $fO_2$, or even the N concentration in the fluid (**Fig.2-3**). In short, the fluid pathway and bulk compositions (i.e., slab-mantle systems, slab-ambient mantle, and mantle wedge-ambient mantle) will determine the aqueous N-speciation (**Fig.1a-d**). Therefore, it is conceivable that nitrogen can behave like a highly incompatible and volatile element (e.g., a noble gas) or a large-ion lithophile element (e.g., $K^+$ & $Rb^+$) in the same dynamic upper-mantle wedge system (see **Fig.4**). This means some arc systems can out-gas + in-gas, some will solely in-gas, and others will solely out-gas nitrogen depending upon the bulk rock geochemistry of the system. We argue that these data strongly imply that cold subduction zones favor mass transfer of N into the mantle, but hot subduction zones do not (**Fig.2**). This notion partly explains why efforts to determine a global N flux using specific geographical localities have been thwarted by contradictory (but equally correct) results (e.g.,. Fischer et al., 2002; Busigny et al., 2003; Elkins et al., 2006; Barry & Hilton, 2016). In fact, we argue that contrasting results should actually be expected.

In short, we propose that nitrogen should not have a single label regarding geochemical behavior. Nitrogen should not be considered lithophile, siderophile, or volatile, but instead nitrogen should always be viewed as a most dynamic *chameleon* element whose behaviour in aqueous fluids is effectively determined by a combination of temperature, pressure, oxygen fugacity, pH, and N concentration (i.e. mole fraction).

## 5. Broader Implications

### 5.1 Nitrogen Isotope Fractionation

The results discussed above have implications for the isotopic evolution of subducted nitrogen during devolatilization of the slab and/or mantle, because the magnitude and direction of $\Delta^{15}N$ for $NH_3^0$-$N_2^0$, $NH_4^+$-$N_2^0$, and $NH_4^0$-$NH_3^0$ differ dramatically. For example, at 600°C the predicted $\Delta^{15}N_{NH3\text{-}N2}$ is -4‰, $\Delta^{15}N_{NH4\text{-}N2}$ is +2‰, and $\Delta^{15}N_{NH4\text{-}NH3}$ is +8‰ (Hanschmann, 1981). Therefore, the evolution of the $\delta^{15}N$ value of subducted nitrogen cannot be modeled with a single fractionation factor ($\Delta^{15}N$), because during progressive devolatilization of the slab in the mantle the magnitude and direction of $\Delta^{15}N$ depends on upon the coupled $fO_2$-pH conditions for a given temperature, which should not be considered uniform across different mantle-wedge systems. Furthermore, because the stability of the K-bearing phases is a function of P-T-$X_K$, it is unlikely to be constant with depth on a global scale (because the large P-T variability of arc systems globally; Syracuse et

al., 2010). Therefore, the magnitude and direction of $\Delta^{15}N$ during devolatilization of nitrogen from the slab or mantle is difficult to constrain. Importantly, if the reaction in question is $\Delta^{15}N_{NH3\text{-}N2}$ where the direction is for a $^{15}N$-depleted residuum, this may explain why some eclogitic diamonds show mantle-like negative $\delta^{15}N$ values alongside crustal organic carbon-like light $\delta^{13}C$ values (Cartigny et al., 1997, 1998).

**5.2 The pH of mantle fluids**

In low-temperature geochemistry, Eh and pH are both considered important variables for predicting and expressing the nature of given chemical environments (i.e., for a recent review on low-T nitrogen see Stüeken et al., 2016). Traditionaly, only Eh is considered in high temperature geochemistry, and because mineral charge-balances reflect the electron exchange where most minerals receive their negative charge in the form of $O^-$ anions, this parameter is commonly expressed as the fugacity of oxygen ($fO_2$). Furthermore, traditional models for the speciation of volatile elements in mantle fluids have long been constructed based on mixtures of neutral gases ($CO_2$, $CH_4$, $H_2$ and $H_2O$; commonly termed COH-fluids; e.g. Zhang. & Duan, 2009). Thus, the role of dissolved aqueous ions or species derived from silicate rock components have been overlooked or ignored (see Sverjensky & Huang, 2015). Because oxygen fugacity is considered of primary importance there have been numerous theoretical and empirical approaches to predicting and quantifying the fugacity of oxygen in the mantle during accretion and differentiation (Wade and Wood, 2005; Wood et al., 2006; Frost et al., 2008), in upper mantle peridotites (Wood & Virgo 1989; Woodland et al. 1992; 1996, 2006; Ionov & Wood 1992; Canil et al. 1990; Brandon & Draper 1996; Cottrell and Kelley, 2013; Rohrbach et al., 2007), lower mantle peridotites (Frost et al., 2004), in eclogites (Simakov, 2006; Stagno et al., 2015; Smart et al., 2016), in the mantle wedge of arc systems (Lecuyer and Ricard, 1999; Parkinson and Arculus, 1999; Wood, et al., 1990), and within other telluric bodies in the Solar System (Herd, 2008).

DEW model predictions now suggest pH should also be considered a significant dimension in high temperature mineralogical composition and mantle geochemistry (Sverjensky et al., 2014b; Sverjensky & Huang, 2015; Mikhail & Sverjensky, 2014; and this study), although other modeling approaches are being pioneered that have lead to the same conceptual conclusion (Galvez et al., 2016). In hindsight, the importance of high temperature pH is not a surprising result. It is well established that at lower temperatures (< ca. 400 °C) fluid-rock interaction can exert large shifts in fluid pH, which can have dramatic effects. For example, pH as a variable has been explored by experimental means to understand why some economically viable REE deposits show significant

REE fractionation leading to economically viable HREE-enrichment (Migdisov et al., 2009; Williams-Jones et al., 2012).

The most important finding of this contribution is the expected variability of the pH values of fluids in equilibrium with peridotite- and eclogite-facies assemblages across several units, even for temperatures up to 1000 °C (**Fig.1b & d**). In the case of carbon (Sverjensky et al., 2014b; Galvez et al., 2016) and nitrogen (this study) the large pH shift as a function of mineral chemistry will significantly affect the speciation and behaviour of these important elements (in the mantle and in subduction zones), and should therefore have influenced which species of pH sensitive compounds were and are degassed into planetary surface environments. Finally, our theoretical study raises several pressing questions:

[1] Is there stratification of aqueous fluid pH with depth in the bulk silicate Earth following pressure effects on $Mg^{+}/Na^{+}$ phase equilibria and phase transitions (coesite-α-Qtz-β-$SiO_2$; Fig.1a-b)?

[2] How much (if at all) has the pH of aqueous mantle fluids changed through time?

[3] How does the pH of aqueous mantle fluids vary between the different inner solar system planets (as is the case for $fO_2$)?

[4] How accurate is the large pH shift as a function of mineralogical composition predicted in this study (**Fig.1a-d**)?

[5] Which reactions or elemental fractionations can be used to retrospectively constrain the pH of a metasomatized high temperature environment using data from silicate/oxide minerals or melt inclusions?

## 6. Conclusions

We have calculated the speciation of aqueous nitrogen in equilibrium with a model eclogite-facies mafic mineral assemblage and a model carbonaceous eclogite-facies mafic mineral assemblage using the DEW model. We find nitrogen to be an extremely dynamic element whose speciation and behaviour is determined by a combination of temperature, pressure, oxygen fugacity, N concentration, and pH. Our modeling results show that increasing temperature stabilizes molecular nitrogen and increasing pressure stabilizes ammonic nitrogen – but the nitrogen concentration also exerts a governing control (**Figs.2-3**). These show that the pH of aqueous fluids is controlled by mineralogy for a given pressure and temperature and can vary by up to 4 units at 5

GPa and 1000 °C (**Fig.1**). This finding clearly demonstrates that pH plays an important role in controlling speciation, and thus mass transport, of Eh-pH sensitive elements (such as nitrogen) up to at least 1000 °C.

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**References Cited:**

Ague, J.J., Nicolescu, S. 2014. Carbon dioxide released from subduction zones by fluid-mediated reactions. *Nature Geoscience.* 7, 355–360

Andersen, T., Burke, E.A.J., Neumann, E. 1995. Nitrogen-rich fluid in the upper mantle: fluid inclusions in spinel dunite from Lanzarote, Canary Islands. Contributions to Mineralogy and Petrology. 120, 20-28

Barry, P.H., Hilton, D.R., Halldórsson, S.A., Hahm, D., & Marti, K. 2012. High precision nitrogen isotope measurements in oceanic basalts using a static triple collection noble gas mass spectrometer. *Geochemistry, Geophysics, Geosystems*. 13(1).

Barry, P.H., Hilton, D.R. 2016. Release of subducted sedimentary nitrogen throughout Earth's mantle. *Geochemical Perspectives Letters.* 2, 148-159

Bebout, G.E, Fogel, M.L, Cartigny, P. 2013. Nitrogen: Highly volatile yet surprisingly compatible. Elements. 9, 333-338

Bebout, G., Lazzeri, K., Geiger, C.A. 2016. Pathways for nitrogen cycling in Earth's crust and upper mantle: A review and new results for microporous beryl and cordierite. *American Mineralogist,* 101, 7-24.

444 Blundy, J., Wood, B.J. 2003 Partitioning of trace elements between crystals and melts. Earth and
445 Planetary Science Letters, 210, 383–397

446 Brandon A.D, Draper D.S. 1996. Constraints on the origin of the oxidation state of mantle overlying
447 subduction zones: an example from Simcoe, Washington, USA. *Geochimica Cosmochimica et Acta,*
448 60, 1739–1749

449 Brooker, R.A., Du, Z., Blundy, J., Kelley, S.P., Allan, N.L., Wood, B.J., Chamorro, E.M., Wartho, J.A.,
450 Purton, J.A. 2003. The 'zero charge' partitioning behaviour of noble gases during mantle melting.
451 Nature, 423 738–741

452 Busigny, V., Bebout, G.E. 2013. Nitrogen in the silicate Earth: Speciation and isotopic behaviour
453 during mineral-fluid interactions. Elements, 9, 353–358

454 Busigny, V., Cartigny, P., Philippot, P., Ader, M., Javoy, M. 2003. Massive recycling of nitrogen and
455 other fluid-mobile elements (K, Rb, Cs, H) in a cold slab environment: evidence from HP to UHP
456 oceanic metasediments of the Schistes Lustres nappe (western Alps, Europe). Earth and Planetarty
457 Science Letters. 215, 27–42

458 Busigny, V., Cartigny, P., Philippot, P. 2011. Nitrogen isotopes in ophiolitic metagabbros: A re-
459 evaluation of modern nitrogen uxes in subduction zones and implication for the early Earth
460 atmosphere. *Geochimica et Cosmochimica Acta* 75, 7502–7521.

461 Busigny, V., Lebeau, O., Ader, M., Krapez, B., Bekker, A. 2013. Nitrogen cycle in the late archean
462 ferruginous ocean. Chemical Geology, 362 115–130

463 Canil, D., Virgo, D., Scarfe, C.M. 1990. Oxidation state of mantle xenoliths from British Columbia,
464 Canada. Contributions to Mineralogy and Petrology, 104, 453–62

465 Cartigny, P., Boyd, S.R., Harris, J.W., Javoy, M. 1997. Nitrogen isotopes in peridotitic diamonds
466 from Fuxian, China: the mantle signature. Terra Nova, 9, 175–179

467 Cartigny, P., Harris, J.W., Javoy, M. 1998. Eclogitic Diamond Formation at Jwaneng: No room for a
468 recycled component. Science, 280, 1421–1424

469 Cottrell, E., Kelley, K.A. 2013. Redox heterogeneity in mid-ocean ridge basalts as a function of
470 mantle source. Science, 340, 1314–1317

471 Dauphas, N., Marty, B. 1999. Heavy nitrogen in carbonatites of the Kola Peninsula: A possible
472 signature of the deep mantle. *Science,* 286, 2488-2490

473 Dobrzhinetskaya, L.F., Wirth, R., Yang, J., Hutcheon, I.D., Weber, P.K., Green, H.W. 2009. High-
474 pressure highly reduced nitrides and oxides from chromitite of a Tibetan ophiolite. Proceedings of
475 the National Academy of Sciences, 106, 19233–19238

476 Elkins, L.J., Fischer, T.P., Hilton, D.R., Sharp, Z.D., McKnight, S., Walker, J. 2006. Tracing nitrogen in
477 volcanic and geothermal volatiles from the Nicaraguan volcanic front. Geochimica et
478 Cosmochimica Acta. 70, 5215-5235

479 Facq, S., Daniel, I., Sverjensky, D. A. 2014. *In situ* Raman study and thermodynamic model of
480 aqueous carbonate speciation in equilibrium with aragonite under subduction zone conditions.
481 *Geochim. Cosmochim. Acta,* 132, 375–390

482 Fischer, T.P., Hilton, D.R., Zimmer, M.M, Shaw, A.M., Sharp, Z.D., Walker, J.A. 2002. Subduction
483 and recycling of nitrogen along the Central American margin. *Science,* 297, 1154-1157

484 Fischer, T.P., Takahata, N., Sano, Y., Sumino, H., Hilton, D.R., 2005. Nitrogen isotopes of the
485 mantle: insights from mineral separates. Geophysical Research Letters. 32.
486 doi:10.1029/2005GL022792

Frost, D.J., McCammon, C.M. 2008. The Redox State of Earth's Mantle. Annual Reviews in Earth and Planetary Sciences, 36, 389–420

Frost, D.J., Liebske, C., Langenhorst, F., McCammon, C.A., Trønnes, R.G. 2004. Experimental evidence for the existence of iron-rich metal in the Earth's lower mantle. *Nature* 248:409–12

Frost, D.J., Mann, U., Asahara, Y., Rubie, D.C. 2008. The redox state of the mantle during and just after core formation. Phil. Trans. R. Soc. A, 366, 4315–4337

Galvez, M.E., Connolly, J.A.D., Manning, C.E. 2016. Implications for metal and volatile cycles from the pH of subduction zone fluids. Nature. 539, 420–424

Grove, T.L., Chatterjee, N., Parman, S.W., Medard, E. 2006. The influence of $H_2O$ on mantle wedge melting. Earth and Planetary Science Letters. 249, 74-89

Haendel, D., Muhle, K., Nitzsche, H.M., Stiehl, G., Wand, U. 1986. Isotopic variations of the fixed nitrogen in metamorphic rocks. Geochim. Cosmochim. Acta, 50, 749–758

Halama, R., Bebout, G., John, T., Scambelluri, M. 2014. Nitrogen recycling in subducted mantle rocks and implications for the global nitrogen cycle. Int. J. Earth Sci. 103: 2081-2099

Halama, R., Bebout, G.E., John, T., Schenk, V. 2010. Nitrogen recycling in subducted oceanic lithosphere: The record in high-and ultrahigh-pressure metabasaltic rocks. Geochimica et Cosmochimica Acta. 74, 1636–1652

Hanschmann G. 1981. Berechnung von Isotopieeffekten auf quantenchemischer Grundlage am Beispiel stickstoffhaltiger Moleküle. ZFI Mitteilungen 41, 19-31

Harlow, G.E., Davis, R. 2004. Status report on stability of K-rich phases at mantle conditions. Lithos, 77, 647–653

Helgeson H. C., Kirkham D. H. 1974a. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: I. Summary of the thermodynamic/electrostatic properties of the solvent. Am. J. Sci. 274, 1089–1198.

Helgeson H. C., Kirkham D. H. 1974b. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures: II. Debye–Hückel parameters for activity coefficients and relative partial molal properties. Am. J. Sci. 274, 1199–1261.

Helgeson H. C., Kirkham D. H. 1976. Theoretical prediction of the thermodynamic properties of aqueous electrolytes at high pressures and temperatures. III. Equation of state for aqueous species at infinite dilution. Am. J. Sci. 276, 97–240.

Helgeson H. C., Kirkham D. H., Flowers G. C. 1981. Theoretical prediction of the thermodynamic behavior of aqueous electrolytes at high pressures and temperatures. IV. Calculation of activity coefficients, osmotic coefficients, and apparent molal and standard and relative partial molal properties to 5 kb and 600 C. Am. J. Sci. 281, 1241–1516.

Herd, C.D.K. 2008. Basalts as probes of planetary interior redox state. In Oxygen in the Solar System (eds. G. J. MacPherson, D. W. Mittlefehldt and J. H. Jones). Mineralogical Society of America, Chantilly, VA.

Honma, H., Itihara, Y. 1983. Distribution of ammonium in minerals of metamorphic and granitic rocks. Geochim. Cosmochim. Acta, 45, 983–988

Ionov D.A, Wood B.J. 1992. The oxidation state of subcontinental mantle: oxygen thermobarometry of mantle xenoliths from central Asia. *Contrib. Mineral. Petrol.* 111:179–93

Johnson, B., Goldblatt, C. 2015. The nitrogen budget of Earth. *Earth-Science Reviews* 148, 150-173

529 Johnson J. W., Oelkers E. H., Helgeson H. C. 1992. SUPCRT92: a software package for calculating
530 the standard molal thermodynamic properties of minerals, gases, aqueous species, and reactions
531 from 1 to 5000 bars and 0 to 1000 C. Comput. Geosci. 18, 899–947

532 Lécuyer, C., Ricard, Y. 1999. Long-term fluxes and budget of ferric iron: implication for the redox
533 states of the Earth's mantle and atmosphere. *Earth Planet. Sci. Lett.* 165:197–211

534 Li, Y., Keppler, H. 2014. Nitrogen speciation in mantle and crustal fluids. Geochimica Cosmochimica
535 et Acta, 129, 13–32

536 Li, Y., Wiedenbeck, M., Shcheka, S., Keppler, H. 2013. Nitrogen solubility in upper mantle minerals.
537 Earth Planetary Science Letters. 377, 311–323

538 Lyons, T.W., Reinhard, C.T., Planavsky, N.J. 2014. The rise of oxygen in Earth's early ocean and
539 atmosphere. *Nature.* 506, 307-315

540 Marty, B., Dauphas, N. 2003. The nitrogen record of crust-mantle interaction and man tle
541 convection from Archean to present. Earth Planet. Sci. Lett., 206, 397–410

542 Marty, B., Zimmermann, L., Pujol, M., Burgess, R., Philippot, P. 2013. Nitrogen isotopic
543 composition and density of the Archean atmosphere. Science, 342, 101–104

544 Marty, B. 1995. Nitrogen content of the mantle inferred from $N_2$-Ar correlation in oceanic basalts.
545 Nature, 377, 326–329

546 Migdisov A.A., Williams-Jones A.E., Wagner T. 2009. An experimental study of the solubility and
547 speciation of the Rare Earth Elements (III) in fl uoride- and chloride-bearing aqueous solutions at
548 temperatures up to 300 ºC. Geochimica et Cosmochimica Acta, 73, 7087-7109

549 Mikhail, S. Sverjensky, D.A. 2014. Nitrogen speciation in upper mantle fluids and the origin of
550 Earth's nitrogen-rich atmosphere. Nature. Geoscience 7, 816–819

551 Mikhail, S., Verchovsky, A.B., Howell, D., Hutchison, M.T., Southworth, R., Thomson, A.R.,
552 Warburton, P., Jones, A.P., and Milledge, H.J. 2014. Constraining the internal variability of the
553 stable isotopes of carbon and nitrogen within mantle diamonds. Chemical Geology, 366, 14–23

554 Mohapatra, R., Harrison, D., Ott, U., Gilmour, J., Trieloff, M. 2009. Noble gas and nitrogen isotopic
555 components in Oceanic Island Basalts. Chemical Geololgy, 266, 29–37

556 Palot, M., Cartigny, P., Harris, J.W., Kaminsky, F.V., Stachel, T., 2012. Evidence for deep mantle
557 convection and primordial heterogeneity from nitrogen and carbon stable isotopes in diamond.
558 Earth Planet. Sci. Lett. 357–358, 179–193

559 Palya, A.P., Buick, I.S., Bebout, G.E. 2011. Storage and mobility of nitrogen in the continental crust:
560 Evidence from partially melted metasedimentary rocks, Mt. Stafford, Australia. Chem. Geol., 281,
561 211–226

562 Pan, D., Spanu, L., Harrison, B., Sverjensky, D.A., Galli, G. 2013. The dielectric constant of water
563 under extreme conditions and transport of carbonates in the deep Earth. Proc. Nat. Acad. Sci. 110,
564 6646–6650

565 Parkinson, I.J. Arculus, R.J. 1999. The redox state of subduction zones: insights from arc-
566 peridotites. *Chem. Geol.* 160, 409–423

567 Rohrbach, A., Ballhaus, C., Golla-Schindler, U., Ulmer, P., Kamenetsky, V.S., Kuzmin, D.V. 2007.
568 Metal saturation in the upper mantle. *Nature,* 449, 456–458.

569 Shock, E.L., Oelkers, E.H., Johnson, J.W., Sverjensky, D.A., Helgeson, H.C. 1992. Calculation of the
570 thermodynamic and transport properties of aqueous species at high pressures and temperatures:
571 effective electrostatic radii to 1000 C and 5 kb. Faraday Soc. Trans. 88, 803–826

572 Shock, E.L., Helgeson, H.C. 1988. Calculation of the thermodynamic and transport properties of
573 aqueous species at high pressures and temperatures: Correlation algorithms for ionic aqueous
574 species and equation of state predictions to 5 kb and 1000 °C. Geochimica et Cosmochimica Acta
575 52: 2009-2036.

576 Simakov, S.R. 2006. Redox state and peridotites from sub-cratonic upper mantle and a connection
577 with diamond genesis. Contrib Mineral Petrol., 151, 282–296

578 Sleep, N.H., Windley, B.F. 1982. Archean plate tectonics: constraints and inferences. *Journal of*
579 *Geology*. 90, 363–379

580 Smart, K.S., Chacko, T., Stachel, T., Muehlenbachs, K., Stern, R.A., Heaman, L.M. 2011. Diamond
581 growth from oxidized carbon sources beneath the Northern Slave Craton, Canada: a $\delta^{13}C$–N study
582 of eclogite-hosted diamonds from the Jericho kimberlite. Geochimica et Cosmochimica Acta. 75,
583 6027-6047

584 Smart, K.S., Tappe, S., Simonetti, A., Simonetti, S.S., Woodland, A.B., Harris, C. *In Press*. Tectonic
585 significance and redox state of Paleoproterozoic eclogite and pyroxenite components in the Slave
586 cratonic mantle lithosphere, Voyageur kimberlite, Arctic Canada. Chemical Geology. DOI:
587 http://dx.doi.org/10.1016/j.chemgeo.2016.10.014

588 Smith, E.M., Kopylova, M.G., Frezzotti, M.L., and Afanasiev, V.P. 2014. N-rich fluid inclusions in
589 octahedrally-grown diamond. Earth and Planetary Science Letters, 393, 39–48

590 Som, S.M., Buick, R., Hagadorn, J.W., Blake, T.S., Perreault, J.M., Harnmeijer, J.P., Catling, D.C.
591 2016. Earth's air pressure 2.7 billion years ago constrained to less than half of modern levels.
592 *Nature Geosci,* advance online publication.

593 Som, S.M., Catling, D.C., Harnmeijer, J.P., Polivka, P.M., Buick, R. 2012. Air density 2.7 billion years
594 ago limited to less than twice modern levels by fossil raindrop imprints. *Nature,* 484, 359-362.

595 Stagno, V., Frost, D.J., McCammon, C.A., Mohseni, H., Fei, Y. 2015. The oxygen fugacity at which
596 graphite or diamond forms from carbonate-bearing melts in eclogitic rocks. Contrib. Mineral.
597 Petrol., 169, 16

598 Stüeken, E.A., Kipp, M.A., Koehler, M.C., Buick, R. 2016. The evolution of Earth's biogeochemical
599 nitrogen cycle. Earth-Science Reviews, 160, 220–239

600 Sverjensky, D.A., Huang, F. 2015. Diamond formation due to a pH drop during fluid–rock
601 interactions. Nature Communications, 6, 8702

602 Sverjensky, D.A., Harrison, B., Azzolini, D. 2014. Water in the deep Earth: The dielectric constant
603 and the solubilities of quartz and corundum to 60 kb and 1,200 °C. *Geochim. Cosmochim. Acta*
604 129, 125–145

605 Sverjensky, D.A., Stagno, V., Huang, F. 2014. Important role for organic carbon in subduction-zone
606 fluids in the deep carbon cycle. *Nat. Geosci.* 7, 909–913

607 Syracuse, E.M., van Keken, P.E., Abers, G.A. 2010. The global range of subduction zone thermal
608 models, *Phys. Earth Planet. Inter.*, 51, 1761–1782

609 Tanger, J.C., Helgeson H.C. 1988. Calculation of the thermodynamic and transport properties of
610 aqueous species at high pressures and temperatures: Revised equations of state for the standard
611 partial molal properties of ions and electrolytes. Amer. J. Sci. 288: 19-98.

Wade, J., Wood, B.J. 2005. Core formation and the oxidation state of the Earth. *Earth Planet. Sci. Lett*. 236, 78–95

Watenphul, A., Wunder, B., Wirth, R., Heinrich, W., 2010. Ammonium-bearing clinopyroxene: a potential nitrogen reservoir in the Earth's mantle. Chem. Geol. 270, 240–248

Williams-Jones, A.E., Migdisov, A.A., Samson, I.M. 2012. Hydrothermal Mobilization of the Rare Earth Elements – a Tale of "Ceria" and "Yttria". Elements, 8, 355–360

Wood, B.J., Virgo, D. 1989. Upper mantle oxidation state: ferric iron contents of lherzolite spinels by 57Fe Mössbauer spectroscopy and resultant oxygen fugacities. Geochim Cosmochim Acta 53, 1277–1291

Wood, B.J., Bryndzia, L.T., Johnson, K.E. 1990. Mantle oxidation state and its relationship to tectonic environment and fluid speciation. Science, 248, 337–345

Wood, B.J., Walter, M.J., Wade, J. 2006. Accretion of the Earth and segregation of its core. *Nature*. 441, 825–833

Woodland, A.B., Kornprobst, J., Wood, B.J. 1992. Oxygen thermobarometry of orogenic lherzolite massifs. J Petrol, 33, 203–230

Woodland, A.B., Kornprobst, J., McPherson, E., Bodinier, J-L., Menzies, M.A., 1996. Metasomatic interactions in the lithospheric mantle. Petrologic evidence from the Lherz massif, French Pyrenees. *Chem. Geol.* 134, 83–112

Woodland, A.B., Kornprobst, J., Tabit, A. 2006. Ferric iron in orogenic lherzolite massifs and controls of oxygen fugacity in the upper mantle. *Lithos,* 89, 222–241

Yokochi, R., Marty, B., Chazot, G., Burnard, P., 2009. Nitrogen in peridotite xenoliths: lithophile behaviour and magmatic isotope fractionation. Geochim. Cosmochim. Acta 73, 4843–4861

Zhang, C., Duan, Z.A. 2009. A model for C–O–H fluid in the Earth's mantle. *Geochim. Cosmochim. Acta,* 73, 2089–2102

**Figures:**

**Figure 1:** Calculated log$fO_2$-pH diagrams for nitrogen speciation in supercritical aqueous fluids using the Deep Earth Water (DEW) model (see methods). The colored boxes show where predicted compositions of upper mantle (peridotite; green), mantle wedge (arc peridotite; blue) and subducted oceanic crust (eclogite; orange) are predicted to plot under these $fO_2$ – pH conditions. The boundaries between nitrogen-species represent a range of total dissolved nitrogen. For the purposes of examining nitrogen speciation under redox conditions appropriate to silicate mantles with a peridotitic bulk composition, we have expressed the log$fO_2$ relative to the quartz-fayalite-magnetite mineral buffer (expressed as ΔQFM in log units). The range of $fO_2$ values for eclogites shown above represents the global range, and is not intended to represent any single geographical locality The fields for the oxidation state of peridotitic mantle domains and eclogitic mantle domains are described in the text. The pH values represent the equilibrium with jadeite + kyanite + $SiO_2$ and a range of total dissolved Mg concentrations (see methods).

**Figure 2:** Aqueous speciation of nitrogen in fluids in equilibrium with a model eclogite-facies mineral assemblages at 5 GPa, and QFM -2, and temperatures ranging from cold to hot subduction zone conditions. (a) Jadeite + Pyrope + Kyanite + diamond in equilibrium with fluid containing 0.001 m N, and (b) Jadeite + Pyrope + Kyanite + diamond in equilibrium with fluid containing 0.1 m N.

**Figure 3:** Aqueous speciation of nitrogen in fluids in equilibrium with a model peridotite mineral assemblages at 5 GPa, QFM -2, and temperatures ranging from cold to hot subduction zone conditions. (a) Forsterite + Enstatite + Pyrope/Clinochlore + diamond in equilibrium with fluid containing 0.001 m N, and (b) Forsterite + Enstatite + Pyrope/Clinochlore + diamond in equilibrium with fluid containing 0.1 m N. Note, the minerals are pyrope at 800 °C and above, clinochlore at 600 and 700 °C (data from Mikhail & Sverjensky, 2014).

**Figure 4:** A cartoon showing the likely pathways followed by nitrogen during subduction. This cartoon illustrates that there are two options for nitrogen, degassing of neutrally charged $NH_3^0$ and $N_2^0$, or re-gassing of the mantle with lattice-bound $NH_4^+$ transported by the mineralogical conveyer belt of K-bearing minerals shown as colored arrows (phengite, phlogopite, K-bearing clinopyroxene, Phase-X and K-Hollandite). The depth-related stability for the K-bearing phases shown were taken from Harlow and Davies (2004).