The relationship between mantle pH and the deep nitrogen cycle

Sami Mikhail[1,2] Peter H. Barry[2], Dimitri A. Sverjensky[3]

[1]The School of Earth and Environmental Sciences, The University of St. Andrews, St. Andrews, UK, email: sm342@st-andrews.ac.uk

[2]St Andrews Centre for Exoplanet Science, The University of St. Andrews, UK

[3]The Department of Earth Sciences, The University of Oxford, Oxford, UK

[4]The Department of Earth and Planetary Sciences, Johns Hopkins University, Baltimore, M.D., USA

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 $\log[{}^{a}Mg^{2+}/({}^{a}H^{+})^{2}]$; 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:

$$2NaAlSi_2O_6 + 2H^+ = Al_2SiO_5 + 3SiO_2 + 2Na^+ + H_2O \tag{2}$$

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

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

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

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

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

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

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^+.

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

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

3. Results

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

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

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

The pH values plotted here correspond to the calculated equilibrium between water and pure forsterite + enstatite (model peridotite – Mikhail & Sverjensky, 2014) and hypothetical eclogite-facies mineral assemblages; jadeite + kyanite + SiO_2 (metasediment – this study), jadeite + pyrope + talc + SiO_2 (metamorphosed mafic rocks – this study), and carbonaceous eclogite-facies mineral assemblages (metamorphosed mafic rocks + elemental carbon; this study). Importantly, the relative proportions of the pure minerals do not influence the fluid chemistry, because the fluid chemistry is set by the equilibrium constants (see methods). In our model, pH is expressed by the $^{\alpha}H^{+}$ (fluid) and $^{\alpha}Na^{+}$ (eclogite – this study) and $^{\alpha}Mg^{2+}$ (peridotite; Mikhail & Sverjensky, 2014) (eq.4 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 calculations show the speciation of aqueous ammonic nitrogen in equilibrium with eclogite-facies metasediments and mafic rocks (herein collectively referred to as eclogite-facies mineral assemblage; this study) is predicted to differ from aqueous nitrogen in equilibrium with peridotites under most of the conditions investigated (**Figs. 1a-d**). Under most conditions, ammonium (NH_4^{+}) dominates in peridotite, and ammonia (NH_3^{0}) is dominant in the eclogite-facies mineral assemblages; this is due to the eclogite-facies mineral assemblages buffering the fluid to 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-concentrations, N_2 is minor for both eclogite (**Fig.2a**) and peridotite (**Fig.3a**) with ammonia and ammonium dominating, respectively. Note, the difference in domination for ammonia and ammonium between the eclogite and peridotite simulations is the function of differing pH values for the fluids at high tempertures (**Fig.1**).

4. Discussion

4.1 Limitations of the approach

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

4.2 Ammonia and Ammonium

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

700°C, 5 GPa, and a LOGfO_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):

$$Ca^{2+} + CO_2 + H_2O = CaCO_3 + 2H^+ \tag{7}$$

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

$$Muscovite + NH_3^0 + H^+ = NH_4^+ - Mica + K^+ \tag{8}$$

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):

$$Muscovite + NH_4^+ = NH_4^+ - Mica + K^+ \tag{9}$$

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 $\Delta^{15}N_{NH3-N2}$ 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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Figures:

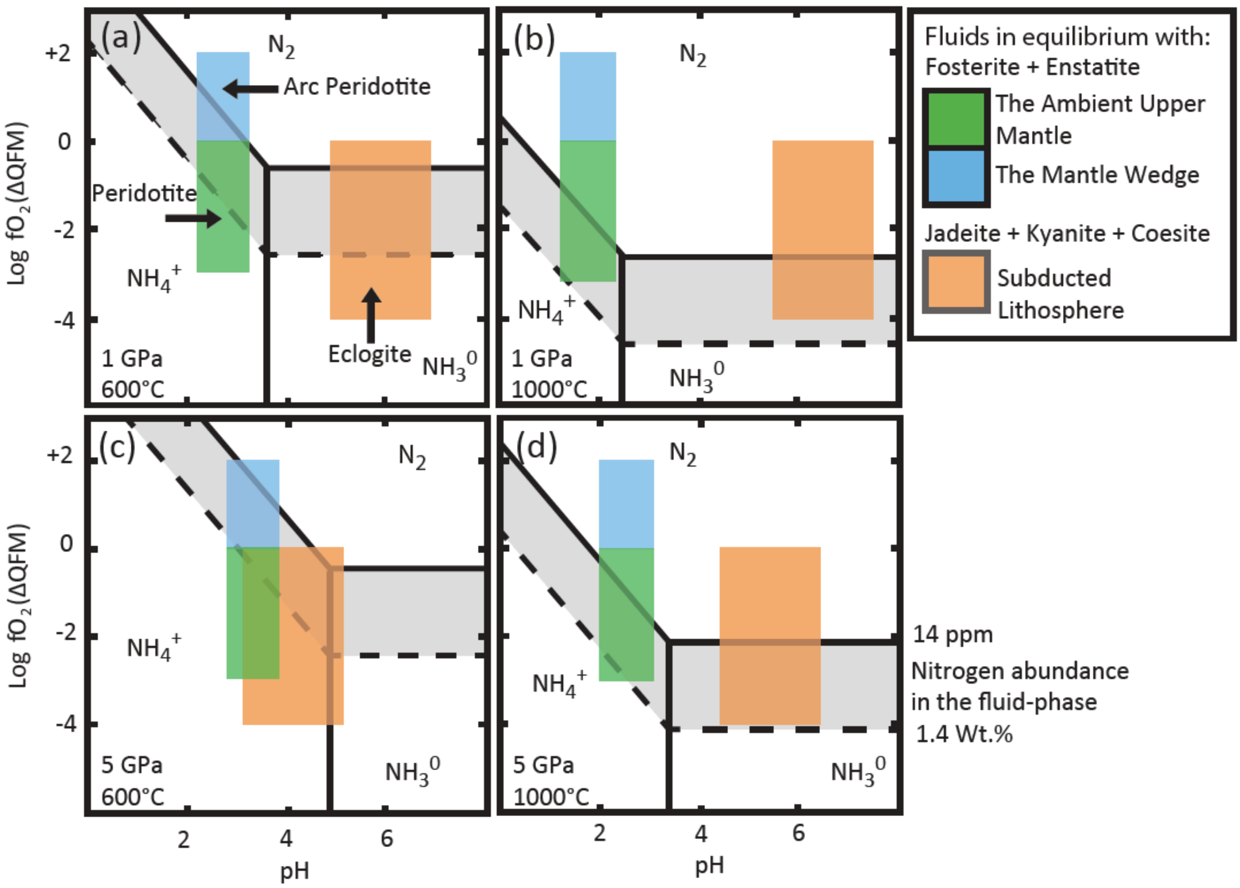

Figure 1: Calculated logfO_2-pH diagrams for nitrogen speciation in supercritical aqueous fluids using the Deep Earth Water (DEW) model (see methods). The colored boxes show where predicted compositions of upper mantle (peridotite; green), mantle wedge (arc peridotite; blue) and subducted oceanic crust (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 logfO_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).

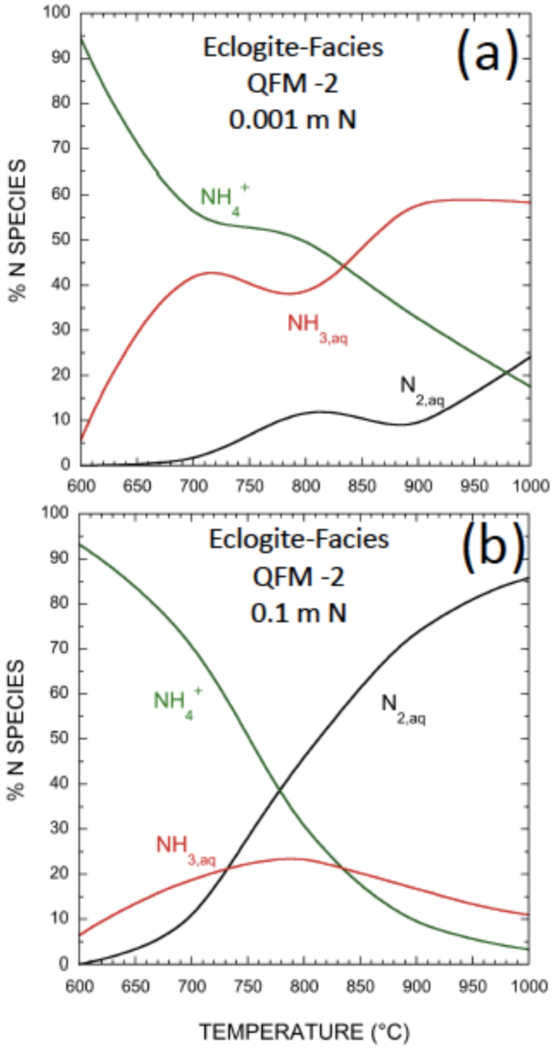

Figure 2: Aqueous speciation of nitrogen in fluids in equilibrium with a model eclogite-facies mineral assemblages at 5 GPa, and QFM -2, and temperatures ranging from cold to hot subduction zone conditions. (a) Jadeite + Pyrope + Kyanite + diamond in equilibrium with fluid containing 0.001 m N, and (b)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

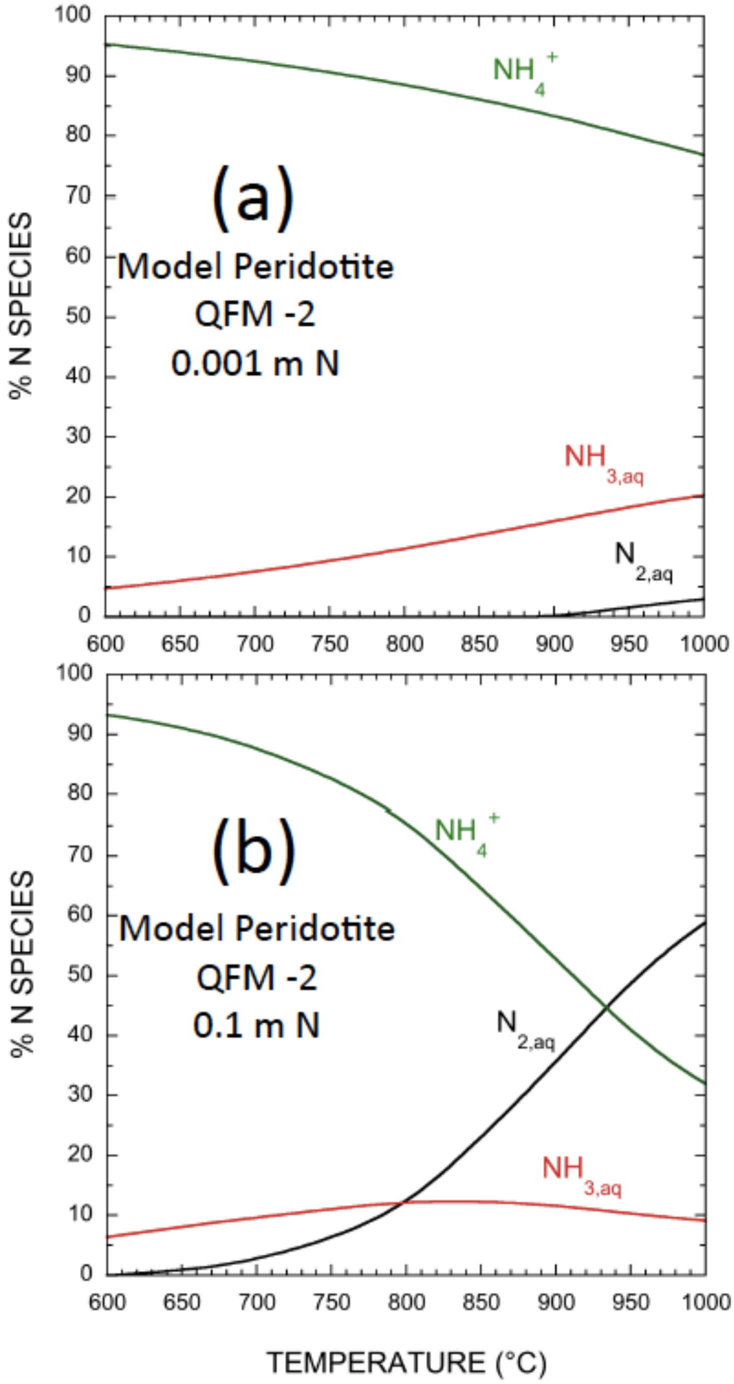

Figure 3: Aqueous speciation of nitrogen in fluids in equilibrium with a model peridotite mineral assemblages at 5 GPa, QFM -2, and temperatures ranging from cold to hot subduction zone conditions. (a) Forsterite + Enstatite + Pyrope/Clinochlore + diamond in equilibrium with fluid containing 0.001 m 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).

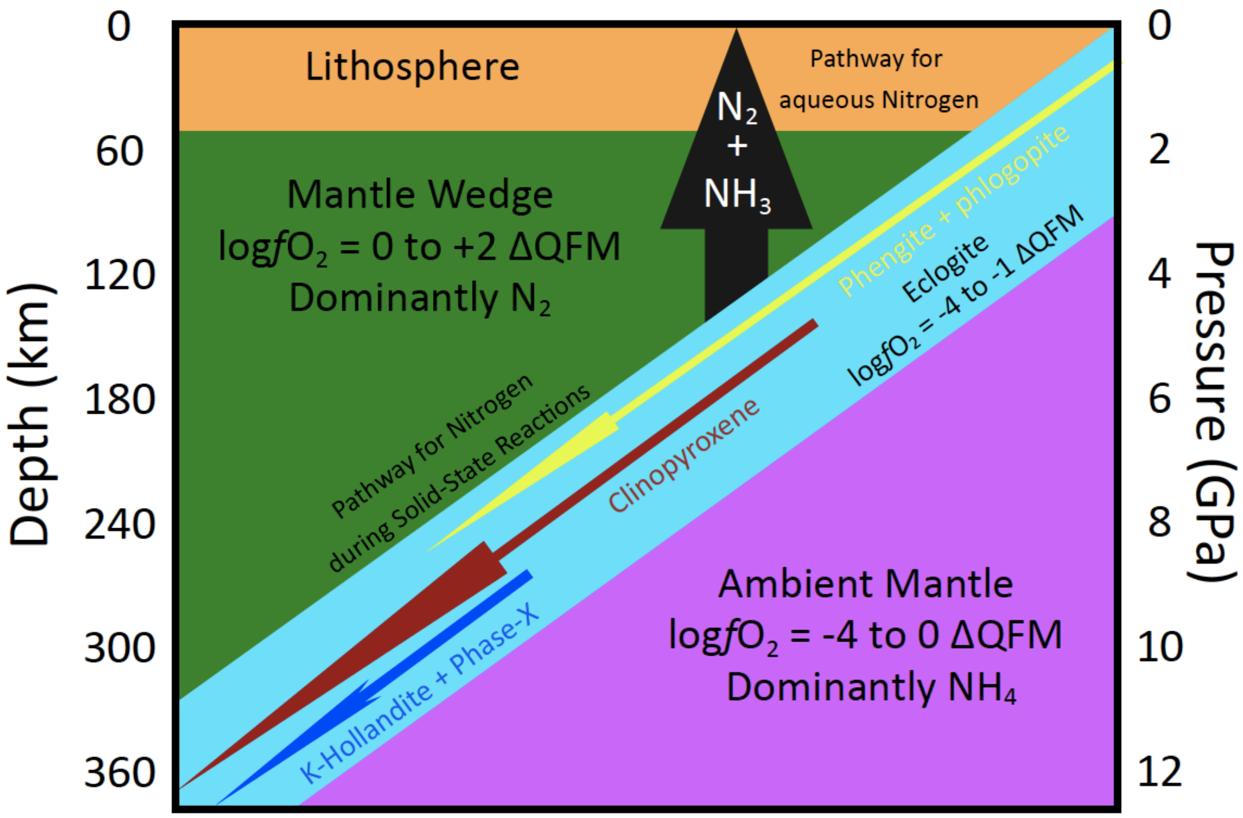

Figure 4: A cartoon showing the likely pathways followed by nitrogen during subduction. This cartoon illustrates that there are two options for nitrogen, degassing of neutrally charged NH_3^0 and N_2^0, or re-gassing of the mantle with lattice-bound NH_4^+ transported by the mineralogical conveyer belt 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).