Nitrogen speciation in upper mantle fluids and the origin of Earth's nitrogen-rich atmosphere

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Volatile elements stored in the mantles of terrestrial planets escape through volcanic degassing, and thereby influence planetary atmospheric evolution and habitability. Compared with the atmospheres of Venus and Mars, Earth's atmosphere is nitrogen-rich relative to primordial noble gas concentrations[1-3]. The compatibility of volatile elements in mantle minerals versus melts and fluids controls how readily these elements are degassed. However, the speciation of nitrogen in mantle fluids is not well constrained[4-6]. Here we present thermodynamic calculations that establish the speciation of nitrogen in aqueous fluids under upper mantle conditions. We find that, under the relatively oxidized conditions of Earth's mantle wedges at convergent plate margins[7-9], nitrogen is expected to exist predominantly as N_2 in fluids and, therefore, be degassed easily. In contrast, under more reducing conditions elsewhere in the Earth's upper mantle and in the mantles of Venus and Mars, nitrogen is expected predominantly in the form of ammonium (NH_4^+) in aqueous fluids. Ammonium is moderately compatible in upper mantle minerals[10,11] and unconducive to nitrogen degassing. We conclude that Earth's oxidized mantle wedge conditions—a result of subduction and hence plate tectonics—favour the development of a nitrogen-enriched atmosphere, relative to the primordial noble gases, whereas the atmospheres of Venus and Mars have less nitrogen because they lack plate tectonics.

Understanding the chemical evolution of Earth's atmosphere and hydrosphere is fundamental to understanding how Earth became habitable. A major process in forming planetary atmospheres is mantle degassing via volcanism, and the primary control on what elements are degassed by this process is their compatibility in mantle minerals relative to melts and fluids. The atmophile elements (for example, H–C–N, and noble gases) are mobilized within planetary interiors as dissolved species in supercritical aqueous fluids, which in turn can trigger partial melting. Such fluids in Earth's upper mantle are either indigenous or subducted volatiles directly associated with plate tectonics. However, recent empirical data show the martian mantle to be as 'wet' as Earth's[12], suggesting that aqueous fluids are prevalent within planetary interiors, irrespective of plate tectonics. Therefore, constraining the speciation of the atmophile elements in aqueous upper mantle fluids would enable the potential role of these fluids in degassing processes to be evaluated.

The deep Earth cycle of nitrogen is enigmatic because the speciation of nitrogen in mantle fluids is not well constrained[4-6]. Recent geochemical evidence suggests that degassing at mid-ocean ridges releases three times as much nitrogen as is subducted at convergent plate margins[13], consistent with deep storage of nitrogen in the mantle, and possibly the core[10,11,13-16]. Furthermore, Earth's atmosphere shows a distinct N_2 enrichment relative to the primordial noble gases when compared with the other telluric

planetary atmospheres (Fig. 1). The N_2-enriched nature of Earth's atmosphere is shown clearly in Fig. 1b, where the ratios of N_2 over ^{36}Ar, ^{20}Ne, ^{84}Kr and ^{130}Xe for Earth are all much higher than for Venus and Mars (see also Supplementary Methods). The N_2-to-noble gas enrichment in Earth's atmosphere relative to Venus and Mars requires a mechanism to fractionate nitrogen from the noble gases during volcanic degassing—importantly, by a process that does not apply to volcanic degassing on Mars and Venus.

The enrichment of N_2 in Earth's atmosphere relative to Venus and Mars might be addressed through consideration of a number of scenarios. We focus on the speciation of nitrogen in high-pressure, supercritical aqueous fluids. Other possible explanations of the differences and similarities between Earth, Venus and Mars are considered in detail in the Supplementary Methods. For example, the size of the planet, distance from the sun, presence of a geodynamo, or the loss of primordial noble gases from Earth during the moon-forming impact cannot explain the data in Fig. 1. This is because the primordial noble gas data for the three planets are similar; for example, $^{20}Ne/^{84}Kr$ ratio of Earth's atmosphere falls alongside the venusian and martian values (Supplementary Fig. 1). In addition, the loss of Earth's early atmospheric N_2 and the primordial noble gases during the proposed moon-forming impact event would manifest as a distinct geochemical signature in Earth's atmosphere—for example, highly fractionated primordial noble gas ratios relative to the atmospheres of Mars and Venus[1]. Earth's atmosphere does show lower total concentrations of noble gases and molecular nitrogen relative to Venus, but there is no indication of fractionation of heavy/light primordial noble gases relative to the venusian and martian atmospheres (that is, $^{20}Ne/^{36}Ar$ and $^{20}Ne/^{83}Kr$ ratios; Supplementary Fig. 1). Noble gas partitioning into bridgmanite could fractionate nitrogen from the noble gases in the lower mantles of Earth and Venus[17], and a difference for nitrogen partitioning during core-formation between the planets[14] could account for differences between the planets. However, in both scenarios Mars should be an outlier to the Earth and venusian systems owing to its smaller size, which is not the case (Fig. 1). Herein we investigate the role and relationship between the redox state of supercritical aqueous fluids under upper mantle conditions between different tectonic settings to explain the N_2 enrichment in Earth's atmosphere.

Recent experiments have shown ammonium to be moderately compatible in mantle minerals such as clinopyroxene and other K-bearing minerals (depending on f_{O_2}; refs 10,11), and oxidation in the upper mantle could preferentially release nitrogen from these minerals as highly volatile and incompatible N_2, which is degassed to the atmosphere[10]. However, the potential role of supercritical aqueous fluids in the oxidation, release and transport of nitrogen has not been examined because of a lack of data on nitrogen speciation in such fluids under representative upper mantle

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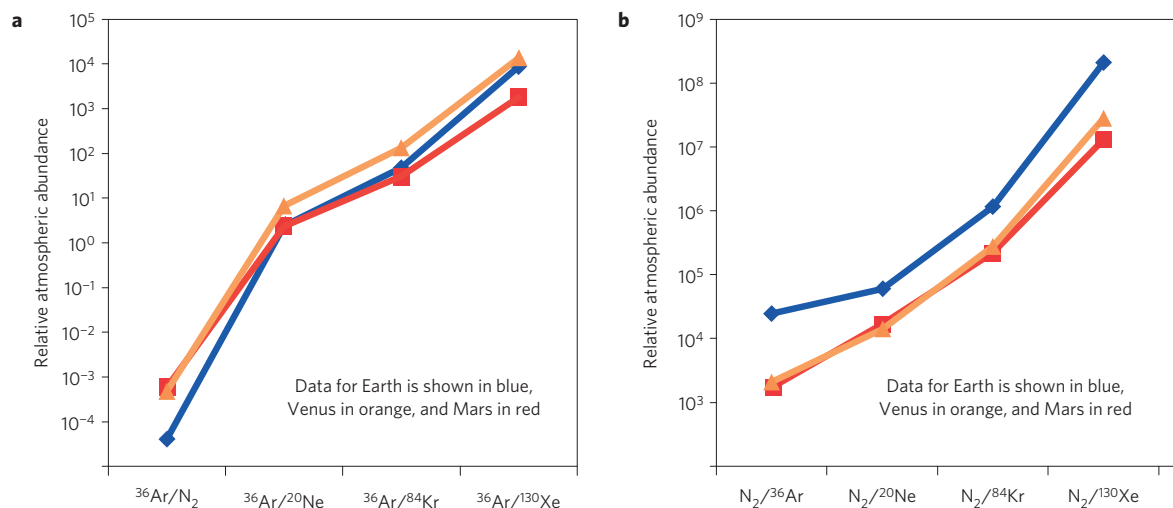
Figure 1 | Earth's atmosphere shows an enrichment of N$_2$ relative to the primordial noble gases of the martian and venusian atmospheres. a, The abundance of primordial atmospheric ^{36}Ar relative to the atmospheric abundances of N$_2$ and the primordial noble gases of Earth, Mars and Venus. **b**, The abundance of atmospheric N$_2$ relative to the abundance of the primordial noble gases of Earth[1], Mars[1,2] and Venus[1,3]. Molecular and the primordial noble gases are listed in order of their relative abundances[1].

pressure, temperature, f_{O_2} and pH conditions[4–6,15,16]. In this study, we have applied recent advances extending the revised Helgeson–Kirkham–Flowers equations of state for aqueous species to upper mantle conditions[18–20] to calculate the speciation of nitrogen as a function of P–T–f_{O_2}–pH in equilibrium with supercritical aqueous fluids at pressures of 1 and 5 GPa and temperatures of 600 and 1,000 °C (Fig. 2—see Methods). The boundaries between the nitrogen species in Fig. 2 define the speciation of nitrogen in aqueous upper mantle fluids under a wide range of relevant mantle P–T–f_{O_2}–pH conditions for the first time.

Our results (Fig. 2) are in good agreement with available experimental data, which show the N-species in supercritical aqueous fluids to be molecular under very oxidizing conditions (Ni–NiO buffer) and ammonium under very reducing conditions (Fe–FeO buffer)[5,6]. However, our theoretical calculations are also able to distinguish the stability fields of aqueous NH$_4^+$ and NH$_3$, which results in a boundary between NH$_4^+$ and N$_2$ that depends on both log f_{O_2} and pH, something that has not yet been constrained by high-pressure–temperature experiments. Superposed on these diagrams are fields representing likely ranges of pH and f_{O_2} in aqueous planetary mantle fluids (Methods). We note also that any fluids present beneath mid-ocean ridge and ocean island settings are also more likely to be much more CO$_2$-rich than the fluids considered here[7]. It can be seen in Fig. 2 that supercritical aqueous fluids in Earth's mantle wedge at 1,000 °C are clearly in the field of predominance of N$_2$. However, the rest of Earth's upper mantle at this temperature, and the venusian and martian upper mantles, would mainly host aqueous fluids near or below the boundary between molecular nitrogen and ammonium, depending on the nitrogen concentration and pH of the fluids (Fig. 2).

The relatively oxidizing conditions of the mantle wedge beneath arc systems (log f_{O_2} = ΔQFM 0 to +2) relative to ambient mantle (log f_{O_2} = ΔQFM < 0) (refs 7–9) are, so far as known, unique to Earth[7–9,21–23]. They are the direct consequence of subduction-zone plate tectonics injecting oxidizing fluids into the mantle wedge[22,23]. Without plate tectonics, the mantles of Earth and Venus would probably be identical in terms of their petrology (and redox state). Our results do not address the speciation of the fluids in the subducting sediments/eclogite, but do demonstrate that if aqueous fluids from a subducting slab, or from the ambient mantle, equilibrate with the mantle wedge they should contain nitrogen chiefly as N$_2$ (Fig. 2). Any aqueous fluids in the rest of

Earth's upper mantle and the other terrestrial planetary mantles will contain a mixture of N$_2$ and NH$_4^+$, or solely NH$_4^+$, enabling storage of nitrogen as NH$_4^+$ in silicate minerals[10,11]. Consequently, degassing of Earth's upper mantle wedges should have contributed to an enrichment of N$_2$ in Earth's atmosphere, but would not have occurred on Venus and Mars. This process would increase the N$_2$/noble gas ratio of Earth's atmosphere because the partitioning behaviour of ^{20}Ne, ^{36}Ar, ^{84}Kr and ^{130}Xe are insensitive to f_{O_2} and pH.

Exactly when the process of enrichment of Earth's N$_2$/noble gas ratio relative to Venus and Mars occurred is not clear. The single dataset available suggests the ^{36}Ar/N$_2$ ratio of the Earth's atmosphere between 3 and 3.5 Ga was comparable to the modern atmosphere[24]. If correct, this would suggest that our mechanism of N$_2$ enrichment on Earth occurred in the early Archaean, its relative impact has been severely reduced since the late Archaean, and that plate tectonics was well established in the early Archaean. However, temporal constraints on the onset of subduction-zone plate tectonics on Earth are controversial, with suggestions covering almost half of geologic time from about 2–4.4 Ga (see ref. 25 and references therein). Our model also implies that the oxidation of the mantle wedge pre-dates the Great Oxidation Event (GOE; ref. 25) of the Earth's atmosphere at 2–2.4 Ga (ref. 26; numerous mechanisms for the oxidation of the mantle wedge pre-GOE are suggested elsewhere[22,23]).

Despite the above uncertainties, our results suggest that the mantle wedge beneath arc volcanoes on Earth may have acted as a 'nitrogen-pump' out of Earth's mantle which specifically resulted in N$_2$ enrichment relative to the primordial noble gases. Over geologic time, the convective flow of the mantle can be expected to have brought deep material containing NH$_4^+$ in mafic minerals into the mantle wedge, where it can be efficiently degassed as N$_2$ in ascending supercritical aqueous fluids generated during subduction-related magmatism and metasomatism. For example, it has been estimated that, using present-day subduction rates and an average crustal thickness of 70 km, roughly 40% of the Earth's mantle could have been cycled through mantle wedges over 2.5 billion years[27].

Owing to the lack of data for volcanic degassing over geologic time, we are unable to quantify the relative importance of the N$_2$/noble gas mantle wedge mechanism to that of other parts of the deep N-cycle. However, we can make a simple calculation of how long it would take to produce the Earth's atmospheric N$_2$ enrichment relative to the primordial noble gases compared with the venusian and martian atmospheres. Assuming all volcanism being equal in
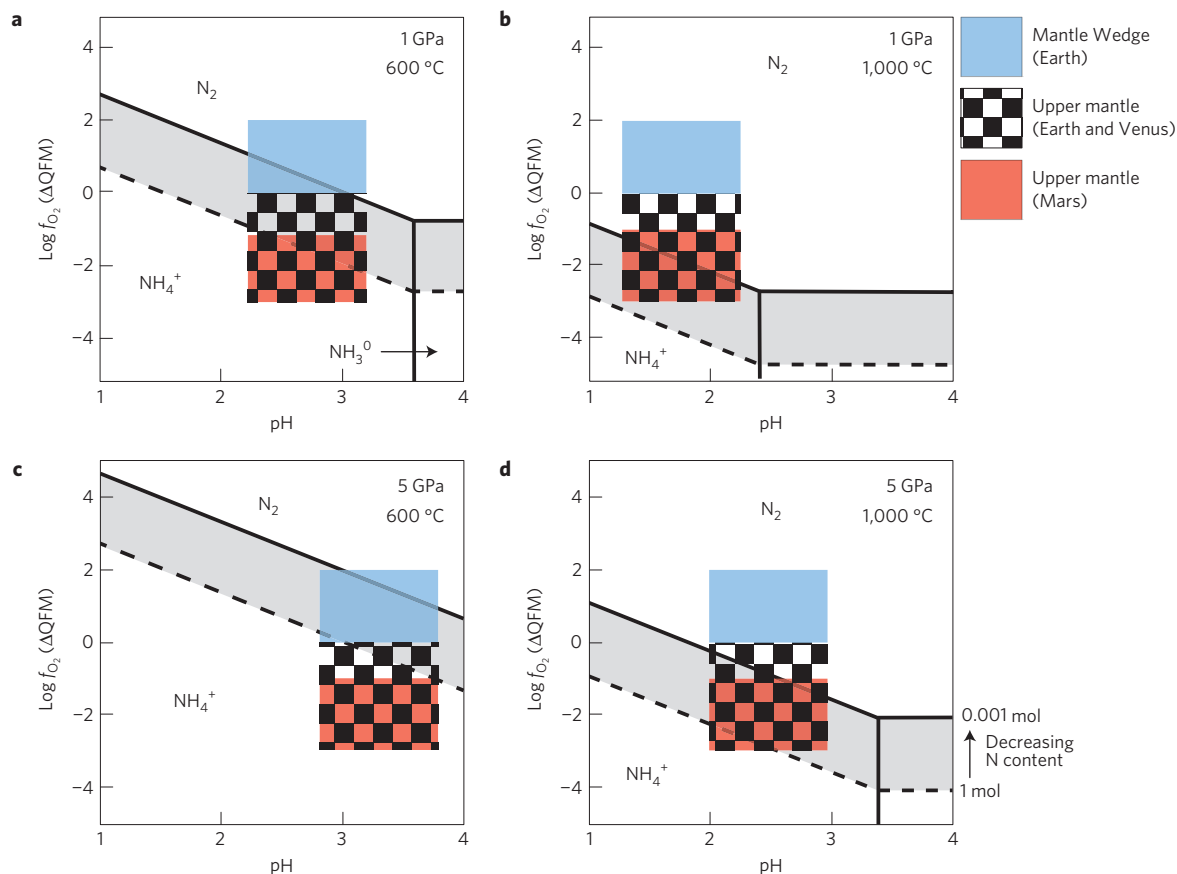
Figure 2 | Calculated log f_{O_2}–pH diagrams for nitrogen speciation in supercritical aqueous fluids at different temperatures and pressures using the Deep Earth Water (DEW) model[20]. The boundaries between N-species represent a range of total dissolved N. For the purposes of examining N speciation under redox conditions appropriate to planetary mantles, we have expressed log f_{O_2} relative to the quartz–fayalite–magnetite mineral buffer (expressed as ΔQFM in log units). For the mantles of Earth, Mars and Venus, the oxidation states are based on data from refs 7–9, whereas the pH values represent equilibrium with forsterite and enstatite and a range of total dissolved Mg concentrations (Methods). The grey area shows the effect of nitrogen concentration on the position of the molecular/ammonium boundary, where the lower (dashed line) denotes 1 mol of nitrogen and the upper (solid line) denotes 0.001 mol of nitrogen.

nature between the planets (for example, rifting and hotspots), and the Earth being exceptional in having arc systems, we use an empirical nitrogen flux from the Central American volcanic arc system of 0.63×10^{10} mol yr^{-1} (ref. 28; accounting for the N released from the mantle and discounting sedimentary input at the arc). To apply this flux globally over 1–2 Ga, it must be amplified to represent the global flux (factor of 20 or 10, respectively), to produce the Earth's N$_2$ enrichment. Overall, our results suggest the uniqueness of Earth's habitable outer layer has been strongly influenced by subduction-zone plate tectonics. In contrast, the atmospheres, and potentially the habitabilities, of Venus and Mars have evolved along different paths through geologic time because they lack plate tectonics.

Finally, our calculations raise several broader issues. First, on the basis of the diagrams in Fig. 2, the behaviour of nitrogen and the noble gases are clearly not equivalent in aqueous upper mantle fluids in the terrestrial planets. Therefore, estimations of volatile abundances and fluxes based on N$_2$/noble gas systematics may underestimate planetary volatile budgets[15,16,24,29]. Second, our results demonstrate the importance of the pH of deep planetary fluids controlled by the silicate environment. For example, on the basis of experimental data NH$_3$ was proposed to be the dominant reduced N-species[5]. But when pH is considered we find NH$_4^+$ dominates in equilibrium with forsterite + enstatite (Fig. 2). These results highlight the need to understand both the redox state and pH of fluids regarding the speciation of other volatile elements under mantle conditions (for example, carbon). Our work also points to

the necessity of plate tectonics for the possible evolution of habitable Earth-like environments on other telluric planets residing in the habitable zone of their stars, such as Keppler-186f (ref. 30).

Methods

The equilibrium constants used to construct the diagrams were calculated from the standard Gibbs free energies of the aqueous species using the Helgeson–Kirkham–Flowers aqueous species equation of state[18–20]. Such calculations have traditionally been limited to an upper pressure of 0.5 GPa because they depend on the dielectric constant of water, for which there has not been a characterization above 0.5 GPa. We have taken advantage of recent advances in theoretical aqueous geochemistry, resulting in the development of the Deep Earth Water (DEW) model[18–20], that now enable theoretical calculation of equilibrium constants involving aqueous ions, metal complexes, neutral species and minerals to 6 GPa and 1,200 °C. In the present study, the DEW model was used to calculate equilibrium constants involving aqueous N-bearing species and equilibrium constants involving minerals and aqueous ions for reactions controlling pH in deep fluids.

The boundaries between the various nitrogen species considered in the model are shown in Fig. 2 and clearly depend on the stoichiometry of the equilibria, the magnitudes of the relevant equilibrium constants, and the total dissolved nitrogen in the fluid. Because the nitrogen content of upper mantle aqueous fluids is not well constrained, we have considered a very large range of possible nitrogen concentrations, with activities of 0.001–1. A range of pH values is plotted corresponding to equilibrium between water and pure forsterite + enstatite and activities of Mg^{2+} from 0.1 to 0.001 and a range of estimated likely f_{O_2} values. Although the pH values seem low in comparison with those at 25 °C and 1 bar, neutral pH in such high-pressure fluids (from the dissociation constant for water) is about 4.1 at 1 GPa and 2.6 at 5 GPa. The boundary lines between the

different N-species shown in Fig. 2 were calculated from the equilibrium constants in the following way. For example, the boundary between N_2 and NH_4^+ was obtained by considering the equilibrium reaction

$$\frac{2}{3}N_{2,aq} + \frac{4}{3}H^+ + 2H_2O = \frac{4}{3}NH_4^+ + O_{2,g}$$
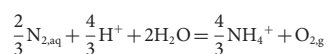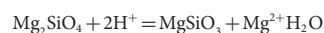
for which the equilibrium constant corresponds to

$$\log K = \log \frac{a_{NH_4^+}^{\frac{4}{3}} f_{O_{2,g}}}{a_{N_{2,aq}}^{\frac{2}{3}} a_{H^+}^{\frac{4}{3}} a_{H_2O}^2}$$

Rearrangement of the expression for the equilibrium constant, assuming that $a_{H_2O} = 1.0$, results in the following expression:

$$\log f_{O_{2,g}} = -\frac{4}{3}pH + \log K - \frac{2}{3}\log \frac{a_{NH_4^+}^{\frac{4}{3}}}{a_{N_{2,aq}}^{\frac{2}{3}}}$$

This equation corresponds to the line with a slope of $-4/3$ in Fig. 2, with a range of intercepts given by the value of $\log K$ (fixed at a given pressure and temperature) and an assumed range of the activities of the aqueous N-species from 0.001 to 1.0.

The ranges of pH values of supercritical aqueous fluids in the upper mantle shown in Fig. 2 were calculated using a model for the predominant minerals in the upper mantle. Assuming equilibrium between an aqueous fluid and Mg-rich olivine and orthopyroxene enables the following reaction to be written:

$$Mg_2SiO_4 + 2H^+ = MgSiO_3 + Mg^{2+} H_2O$$

for which the equilibrium constant can be expressed as

$$\log K = \log \frac{a_{Mg^{2+}}}{a_{H^+}^2}$$

assuming that the minerals and the water are pure. This equation can be rearranged to give

$$pH = \frac{1}{2}\log K - \frac{1}{2}\log a_{Mg^{2+}}$$

Using values of $\log K$, again calculated as described above, together with a range of values for the $a_{Mg^{2+}}$ 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 Fig. 2 in comparison to the range of pH associated with the range of $a_{Mg^{2+}}$ values.

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Author contributions

S.M. conceived the idea and collated the planetary datasets, D.A.S. performed the thermodynamic calculations, and both authors contributed equally to the writing of the manuscript.

Additional information

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Competing financial interests

The authors declare no competing financial interests.