Nitrogen Isotopes and Mantle Geodynamics: The Emergence of Life and the Atmosphere–Crust–Mantle Connection

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Nitrogen is the main diamond impurity. Studying diamond gives access to deep mantle nitrogen (150 to > 800 km).
IMAGE: FANUS VILJOEN

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Nitrogen shows unique features among the volatile elements. To be cycled, atmospheric di-nitrogen (N_2) needs to be reduced, which is efficiently done by bacterial processes. Crustal uptake of nitrogen and its eventual recycling into the mantle is thus primarily mediated by the biosphere. There is also a marked isotopic contrast between the mantle (^{15}N depleted) and the Earth's surface (^{15}N enriched). Although the cause of such disequilibrium is not fully understood, it provides insights into mantle–surface interactions over geological time, including recycling of surface sediments into the deep mantle.

KEYWORDS: nitrogen, ammonium, chemical geodynamics, degassing, recycling

INTRODUCTION

Owing to its strong triple covalent bond, atmospheric di-nitrogen (N_2) has often been described as an inert molecule, that is, behaving somewhat like the noble gases. Supposedly chemically inert and incompatible during mantle-melting processes, nitrogen would have degassed from the mantle and accumulated in the atmosphere over geological time. The potential recycling of sedimentary nitrogen into the mantle was not considered to be significant in any long-term process (e.g. Zhang and Zindler 1993). With only two stable isotopes and no radiogenic ones, nitrogen's chronology could not be inferred from its isotopic composition. Compared to the radiogenic noble gases, in particular xenon (Xe) and argon (Ar), nitrogen was thus seen, for many years, as a *useless* element in mantle geochemistry.

Despite its triple covalent bond, atmospheric N_2 is massively cycled by biological activity (at a rate of ~2 × 10^{14}g N/y; Galloway 2003), particularly by primary producers (e.g. phytoplankton, cyanobacteria, etc.). Without a strong return flux (denitrification and anaerobic ammonium oxidation, or anammox), present-day atmospheric nitrogen (~4 × 10^{21} g N) would be entirely sequestered within less than 100 million years (My). Nitrogen enters the rock cycle as organic matter matures, releasing the ammonium ion (NH_4^+). Having similar charge and ionic radius as potassium, ammonium then substitutes for – and follows the fate of – potassium in potassic minerals (e.g. clays and micas; Busigny and Bebout 2013 this issue). According to present-day estimates of the nitrogen content of the continental crust, nearly a fifth of surface nitrogen is now stored in the continental crust (Galloway 2003; Rudnick and Gao 2003; Busigny and Bebout 2013). The fraction of nitrogen that has been stored in K-rich minerals during Earth's history is likely to be greater when crustal recycling into the mantle is taken into account.

PRESENT-DAY NITROGEN DISTRIBUTION IN EARTH RESERVOIRS

The present-day distribution of nitrogen and its isotopes among the different terrestrial reservoirs (FIGS. 1, 2) illustrates the wide-scale ^{15}N-depleted homogeneity of the mantle ($\delta^{15}N \approx -5 \pm 2$ per mil [‰]) compared to the atmosphere ($\delta^{15}N$ = 0‰ by definition) and crust/sediments ($\delta^{15}N$ > 0‰). Fibrous diamonds (a relatively young type of diamond, <500 My old) and mid-ocean ridge basalts (MORB) (Marty and Dauphas 2003; Cartigny 2005 and references therein) show a distribution of $\delta^{15}N$ values that converge towards an endmember value of around –5‰. In detail, comparable isotope compositions of N (as well as of C and the noble gases) occur among worldwide fibrous diamonds (Canadian, Siberian, South African and West African cratons), mid-ocean ridge basalts (Atlantic, Pacific and Indian oceans) and volcanic gases (e.g. Oldoinyo Lengai volcano; Fischer et al. 2009). Another important result, inferred from the observation of near-constant $N_2/^{40}Ar^*$ ratios in MORB (where $^{40}Ar^*$ stands for ^{40}Ar corrected for atmospheric contamination), is that nitrogen and argon have comparable solubilities in basaltic melts. Presumably both are incompatible during partial melting (although this point needs confirmation in the case of nitrogen; see Busigny and Bebout 2013), so $N_2/^{40}Ar^*$ ratios should be representative of the mantle source value (Marty 1995). Coupled to He flux, $N_2/^{40}Ar^*$ ratios constrain the outgassing mantle flux to about 0.7 × 10^{11}g N/y (Marty 1995; Busigny et al. 2011 and references therein). Other outgassing fluxes, such as due to intraplate volcanism, are negligible (Sano et al. 2001). In addition, because ^{40}Ar results from the decay of ^{40}K over time (^{40}K half-life = 1.25 Gy), the calibration of N to ^{40}Ar lets us link nitrogen to non-volatile, mantle-recyclable potassium and to time. Thus $N_2/^{40}Ar^*$ ratios offer perspective for bringing chronological and quantitative dimensions to N systematics (Marty 1995; Marty and Dauphas 2003). Yet there are open questions in mantle N studies. For example, the origin of positive $\delta^{15}N$ values measured in some MORB samples (FIG. 1), generally associated with low $^{40}Ar/^{36}Ar$ ratios, might reflect contamination by surface material, source heterogeneity (in particular,

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from the occurrence of subducted nitrogen at mantle depths), contamination/assimilation of hydrothermally altered material/sedimentary N during magma emplacement within the crust, or isotope fractionation related to degassing.

The key question, however, is the potential fractionation of N isotopes during the genesis and evolution of mantle fluids or melts leading to both fibrous diamonds and MORB. In a model in which nitrogen is not highly incompatible, one would expect isotope (and elemental) fractionation to occur, leading to mantle products (i.e. diamonds and MORB) possibly differing in their N isotope signature by several per mil from their original mantle value(s). At less than 200 kilometres depth, the oxygen fugacity appears high enough (fayalite–magnetite–quartz buffer [FMQ] values = 0 to –2 log units; see Figure 2 in Frost and McCammon 2008) to allow nitrogen to be stable as either N_2 or ammonium (Watenphul et al. 2009), both likely behaving incompatibly during partial melting. In addition, the fractionation of nitrogen isotopes seems limited to the per mil level at high temperature, unless nitride species are present (Richet et al. 1977: Busigny and Bebout 2013). If the scale of nitrogen isotope fractionation related to melting bears little upon the concept of mantle-nitrogen unsteady state (since degassing and recycling fluxes differ in isotope composition, as described below), an understanding of such fractionation is a prerequisite for any quantitative modelling of the secular evolution of the concentration and isotopic composition of mantle nitrogen.

The quantities of N stored in the primitive mantle and in the core are uncertain. Marty and Dauphas (2003) proposed that positive δ^{15}N values from lavas associated with mantle plumes (about +2‰ for ocean island basalts; Fig. 1) represent recycled crustal nitrogen rather than primordial nitrogen. For reasons described below, primordial nitrogen is anticipated to be more depleted in ^{15}N than present-day mantle nitrogen, possibly as low as $\delta^{15}N \approx -40‰$. Whether or not plume lavas sample a primitive mantle region remains an open question from a nitrogen isotope perspective. It may well be possible that the deep mantle is heterogeneous for nitrogen isotopes, as it is for helium and neon isotopes.

The atmosphere (3.9×10^{21}g N) is the main reservoir of nitrogen at the Earth's surface and, by convention, has a δ^{15}N value of 0‰. Crustal nitrogen (in sedimentary and crystalline rocks) represents approximately one fifth of the surface inventory (~1.1×10^{21}g N) and has a mean δ^{15}N value of about +6‰ (see also Thomazo and Papineau 2013 this issue). From this crustal nitrogen content, we can infer an average net flux of nitrogen from the atmosphere to the crust of 2×10^{11}g N/y (averaged over 4.5 Gy; the flux value would be twice as high if averaged over the last 2.3 Gy). This flux is a thousand times lower than the present-day rate of sequestration of nitrogen from the atmosphere. Other reservoirs, such as oceanic nitrate and land and marine biomasses, are negligible (Galloway 2003). Importantly, estimates of the amount of crustal nitrogen are uncertain because bulk/upper-crust N inventories

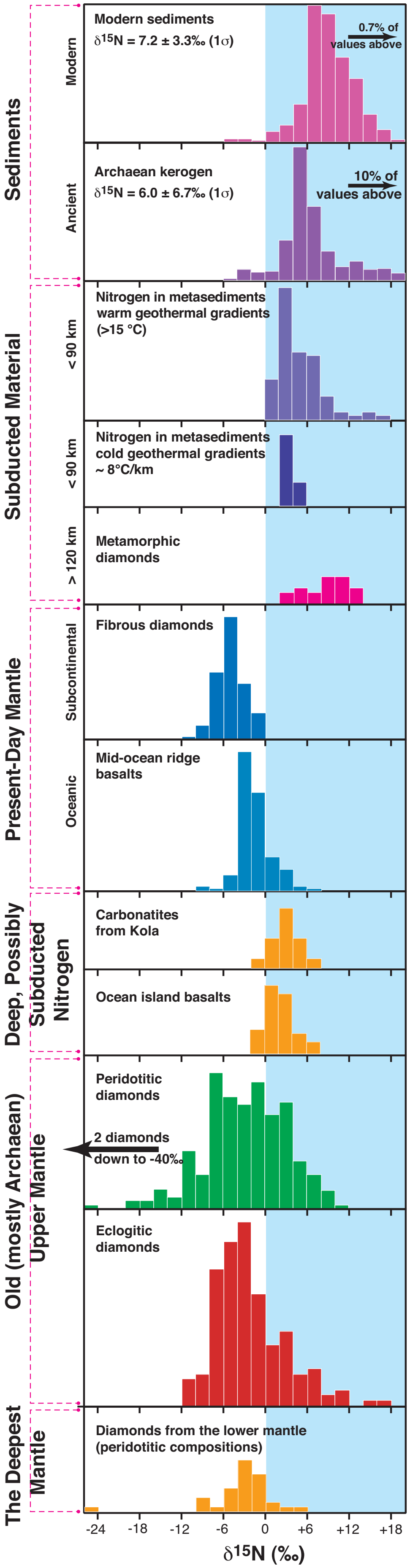

Figure 1 Comparative histograms of δ^{15}N values for modern and ancient sediments, subducted nitrogen (warm and cold environments), present-day convective mantle, ancient mantle and lower mantle, and magmas possibly sampling nitrogen recycled to mantle depths. Note that modern and ancient sediments do not reveal any obvious secular isotopic trends. For additional data and discussion on the N isotope composition of past sediments, the reader is referred to Thomazo and Papineau (2013 this issue).

(Rudnick and Gao 2003) are based on an early compilation and a limited data set. New investigations might thus lead to a significant re-evaluation of crustal nitrogen fluxes and isotopic signatures. From overall positive δ^{15}N values of organic matter, mostly between +3‰ and +7‰ (Fig. 1) and evidence that metamorphism-related devolatilization leads to a further ^{15}N increase, there is however no doubt that crustal nitrogen is enriched in ^{15}N relative to the atmosphere. From a mass balance approach, the N isotope composition of the Earth's surface (crust + sediment + atmosphere) is between +1‰ and +2‰ (approximately +1.8‰).

Near constant ratios between the ammonium and potassium contents of subduction-related material allow us to tie the flux of sedimentary ammonium arriving at arc trenches (~7.6 × 10^{11}g N/y; Busigny et al. 2011) to a non-volatile element, whose flux is more accurately determined. This amount represents an upper limit of the flux of surface nitrogen into the mantle, since metamorphism and devolatilization can lead to significant loss of nitrogen back to the surface, for example, via arc or back-arc magmatism. Sedimentary and metasedimentary rocks will either undergo pronounced devolatilization under a high (e.g. >15 °C/km) geothermal gradient or preserve volatiles under a low one (e.g. 8 °C/km). Devolatilization, which takes place when the local geothermal gradient intersects the stability curve of potassic minerals, leads to an increase in residual ^{15}N of metamorphic rocks (e.g. Haendel et al. 1986). Subducted nitrogen thus shows increasing positive δ^{15}N values with increasing metamorphic grade (Fig. 1). However, most present-day subduction zones have relatively low geothermal gradients, close to 8 °C/km, with presumably limited devolatilization. If this is the case, one would expect the present-day recycling rate of nitrogen to be elevated when compared to earlier times when the Earth was hotter. Available data for the (upper and lower) oceanic crust and the oceanic lithosphere suggest that these reservoirs have N contents about two orders of magnitude lower than those of modern oceanic sediments and sedimentary rocks (this reflects the fact that nitrogen is primarily cycled by biological activity). Yet the volume of both the oceanic crust and the oceanic lithosphere is an order of magnitude greater than the volume of oceanic sediment; thus, the flux of crustal nitrogen could represent half the sedimentary flux to subduction zones (~5.5 × 10^{11}g N/y; see Busigny et al. 2011 and references therein). This estimate is, however, underconstrained. The oceanic crust and lithosphere are generally poor in potassium (i.e. a few thousand ppm), potassic minerals are rare, and the speciation and the minerals hosting nitrogen are difficult to assess. Consequently, fluxes are estimated from the measured N contents only (that is, not from geochemical correlations with other tracers) and data are limited to low-geothermal-gradient contexts. However, as for sedimentary nitrogen, available δ^{15}N data for oceanic crust show largely positive values (Busigny et al. 2011).

The amount of nitrogen effectively subducted into the mantle can be estimated from the flux of nitrogen at trenches via both sediments and altered oceanic crust (13.2 × 10^{11}g N/y), minus the nitrogen lost in arc-related volcanic and metamorphic processes. Assuming that the flux returning to the atmosphere at arcs is 2.8 × 10^{11}g N/y (Hilton et al. 2002), the net recycling flux of nitrogen is 10.4 × 10^{11}g N/y. This is ~22% of the nitrogen entering subduction zones (~78% preserved in potassic minerals within both sediments and altered oceanic crust). Nitrogen from both sediments and altered oceanic crust would contribute to the arc budget (Mitchell et al. 2010). Direct evidence for deep recycling of nitrogen was found from the study of *metamorphic* diamonds formed in crustal rocks subducted to ultrahigh pressures (>35 GPa) (Cartigny et al. 2004 and references therein). The positive values measured in some lamproites (Jia et al. 2003), ocean island basalts (Marty and Dauphas 2003) and some deep diamonds (Palot et al. 2012) are also compatible with the presence of surface nitrogen that has been recycled into the deep mantle.

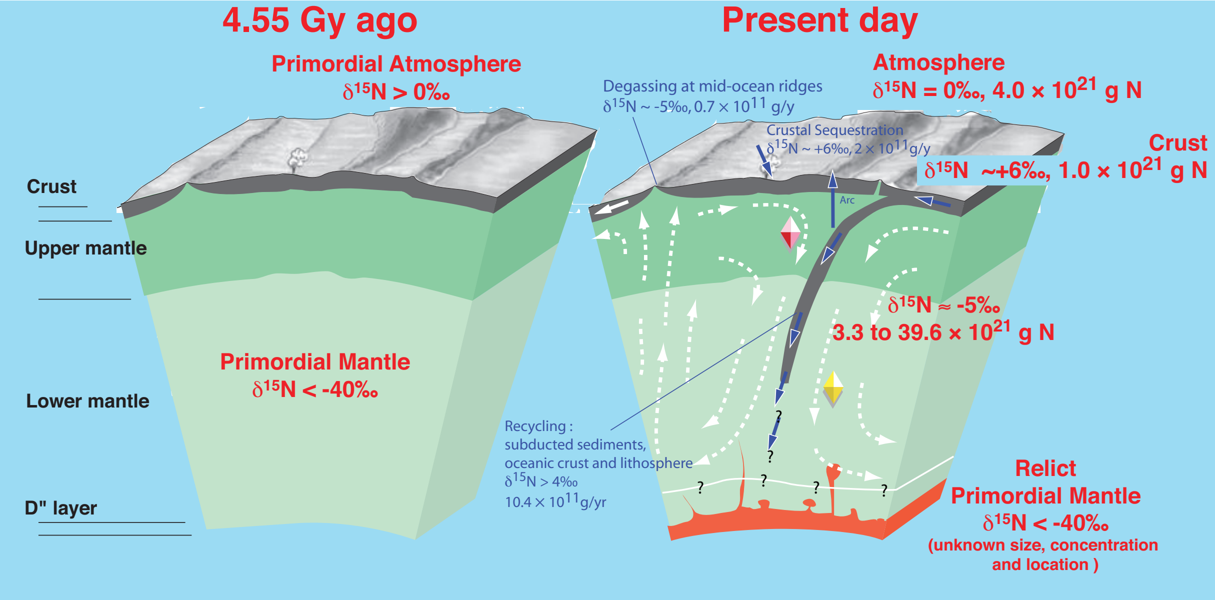

Figure 2 Illustration of the nitrogen isotope disequilibrium between internal and surface reservoirs of the Earth. The ^{15}N-depleted isotopic composition of nitrogen degassed from the mantle and the ^{15}N-enriched isotopic composition recycled into the mantle highlight a non–steady state cycle. Mantle nitrogen contents have been calculated for the upper mantle only and should thus be multiplied by a factor of 4 when extended to the whole mantle. The left-hand illustration shows the nitrogen isotope distribution among Earth reservoirs as predicted from the first study highlighting the *nitrogen isotope disequilibrium* between the Earth's surface and mantle (Javoy et al. 1984). Although few studies have actually supported this view, it has driven many subsequent studies.

NITROGEN ISOTOPE DISEQUILIBRIUM

From abundance and isotope mass balance considerations, the noble gases present in the atmosphere are thought to have been contributed to this reservoir very early in Earth history, as a result of vigorous convection of the mantle during magma ocean episodes and/or of shock degassing of accreting bodies. Following the same concept, the surface N reservoirs – i.e. the atmosphere and crust, including sediments – would have a bulk N isotope composition close to the mantle value. The amount of crustal nitrogen can be estimated from an isotope mass balance:

$$\delta^{15}N_{mantle} = (1 - C) \times \delta^{15}N_{atmosphere} + C \times \delta^{15}N_{crust}\ , \quad (1)$$

where C denotes the fraction of nitrogen stored in the crust. From equation 1, the nitrogen isotope composition of the mantle would be expected to lie somewhere between the atmospheric (0‰) and crustal nitrogen (about +6‰) values. Therefore, the negative $\delta^{15}N$ mantle value inferred from the analysis of mantle-derived samples is incompatible with equation 1 and highlights a nitrogen *isotope imbalance* – often referred to as *isotopic disequilibrium* – between the internal and external Earth reservoirs. This offers great potential for determining further constraints on atmosphere–crust–mantle interactions and, for example, on the origin and evolution of volatiles on Earth.

Several applications are straightforward. For example, if several distinct mantle reservoirs exist, the analysis of N isotopes in mantle samples for which independent controls on the chemistry and depth of origin are available could be used to constrain the convection modes of the Earth (Fig. 2), to detect the occurrence of subducted nitrogen in the mantle source (as it should display positive $\delta^{15}N$ values) and to constrain the source of some diamonds, ocean-island basalts and lamproites (Jia et al. 2003; Marty and Dauphas 2003; Palot et al. 2012).

Nitrogen degassed at mid-ocean ridges (negative $\delta^{15}N$) and N recycled at subduction zones (positive $\delta^{15}N$) have different isotopic compositions (Fig. 1). In addition, the flux of nitrogen returning to the mantle appears much larger than the flux of nitrogen outgassed from the mantle (Marty 1995; Busigny et al. 2011 and references therein). A non–steady state cycle for nitrogen predicts secular evolution of both the nitrogen contents of the terrestrial reservoirs and their isotopic compositions. Both the secular cooling of the Earth, which might have allowed increasing recycling of surface nitrogen, and the evolution of the biosphere, which controls the first-order transfer of N from the atmosphere and hydrosphere to rocks and minerals, might have modulated the contents and the isotopic compositions of the major terrestrial reservoirs. For the early Earth, additional processes should also be considered. For example, rapid escape of light gases (hydrogen, helium) could have exerted an aerodynamic drag on heavier gases, and interaction of hard, solar UV light might have resulted in significant loss and isotopic fractionation of atmospheric nitrogen (e.g. Lichtenegger et al. 2010). Thus a complete understanding of the nitrogen cycle requires the investigation of secular variations of the major N reservoirs. Ancient rocks of sedimentary origin allow the investigation of past environments, provided that corrections can be made for the effects of aging and metamorphism.

THE ARCHAEAN AND THE ELUSIVE SECULAR TRENDS OF ATMOSPHERIC AND MANTLE NITROGEN

The Archaean–Proterozoic transition ~2.4 billion years ago, which corresponds to the rise of atmospheric oxygen, was one of the largest-scale events that affected the terrestrial environment. Since that time, plate tectonics with modern-style subduction has likely been operative, and a high rate of biological oceanic N fixation has allowed the efficient transfer of nitrogen into potassic minerals. It is unclear, however, whether subduction zones were cold enough to have allowed massive transfer of nitrogen into the mantle; few data suggest that this was the case, at least 1.8 Gy ago (Cartigny et al. 2004). For earlier geological periods, such as the Archaean and Hadean, the characterisation of terrestrial reservoirs is difficult and the fluxes are highly model dependent. The Earth was warmer, as evidenced by the predominance of tonalite-trondhjemite-granodiorite magmatism; these rocks are the most abundant rocks in Archaean and, presumably, Hadean crust.

Lower nitrogen recycling fluxes to the mantle in the past can be inferred from present-day nitrogen recycling fluxes (Busigny et al. 2011). The present-day net recycling flux of nitrogen is high (a recycling flux of 10.4×10^{11} g N/y minus a degassing flux of 0.7×10^{11} g N/y $\approx 9.7 \times 10^{11}$ g N/y) compared to the reservoir inventories. For instance, the present-day amount of atmospheric nitrogen would be recycled back into the mantle in ~4 Gy with such a recycling rate. Thus, either the above flux estimate is overestimated by about an order of magnitude, which is unlikely given the mass balance of nitrogen at arcs, or the modern cycle is not representative of the ancient one, implying lower N-recycling flux to the mantle in the past. Secular change in the N-recycling flux into the mantle might relate to a change in the geothermal gradient of subduction zones and/or to limited N fixation in the Archaean.

Nitrogen *isotope imbalance* predicts secular evolution of the terrestrial reservoirs. The isotopic composition of early atmospheric nitrogen should have been enriched in $\delta^{15}N$ by at least ~ +2‰ (i.e. by re-injecting crustal nitrogen into the atmosphere; see above), or by more than +2‰ depending on the amounts of crustal/sedimentary nitrogen subducted into the mantle. In the most extreme model, the atmospheric nitrogen isotope composition would have decreased over time by ca. 40‰ (Javoy 1998; Jia and Kerrich 2004), and the recycling of crustal nitrogen with positive $\delta^{15}N$ and concomitant outgassing of negative $\delta^{15}N$ from the mantle would have led to secular evolution of the Earth's reservoirs to their present-day isotopic compositions.

A secular evolution of atmospheric nitrogen isotope composition can be deciphered from the study of crustal rocks, the idea being that within several per mil these rocks likely record the N isotope composition of the Earth's atmosphere (that is, most sediments are only enriched in ^{15}N by 5‰ compared to the atmosphere). Yet, the study of fluid inclusions and crustal/sedimentary (Archaean and Proterozoic) rocks has led, so far, to opposite conclusions. On the one hand, studies of several Archaean crustal rocks (giant quartz veins) and 2.7 Ga kerogens suggest significant $\delta^{15}N$ evolution of atmospheric nitrogen, from greater than +40‰ to the present value of 0‰ (Jia and Kerrich 2004). Mass balance considerations also support massive exchange between the Earth's surface and the mantle, with an inferred decrease in atmospheric N pressure by a factor of ~2–3 (Goldblatt et al. 2009). An important implication is that a high atmospheric N pressure would contribute indirectly (by broadening the absorption lines of greenhouse gases) to the warming of the Earth's surface, despite the faint-young-Sun paradox (Goldblatt et al. 2009). On the other hand, an increasing amount of data suggests rather constant $\delta^{15}N$ values (Sano and Pillinger 1990; Thomazo and Papineau 2013) with little change in atmospheric nitrogen levels (Busigny et al. 2011; Marty et al. 2013). In this case, the very positive N isotope composition of some metasediments and hydrothermal micas might rather reflect isotopic fractionation related to fluid circulation and metamorphism and/or to specific ecosystems. Here also, future studies are needed to clarify this issue.

Owing to sample scarcity, the value of $\delta^{15}N$ in the ancient mantle is even more difficult to constrain and the evidence is not yet in for satisfactorily interpreting ancient secular variations. Studies of *old* diamonds, that is, diamonds with silicate and sulfide inclusions pointing to Archaean ages, have highlighted a large range of $\delta^{15}N$ values, from –40 to +18‰. This range is commonly interpreted to reflect the interplay between source heterogeneity (for the most ^{15}N-depleted isotope compositions) and isotope fractionation in melt/fluids percolating through the mantle (Cartigny 2005). Most diamond populations, however, define a narrower range, typically between –12‰ and +5‰, with a mode around –5 ± 3‰ (Cartigny 2005; Fig. 1), which indicates no obvious secular change in mantle $\delta^{15}N$ over the last ~3 Gy. The only support for secular change in mantle $\delta^{15}N$ values comes from the very negative $\delta^{15}N$ values (down to –40‰) measured in a few diamonds. It is unlikely that these reflect isotope fractionation in melt/fluids; rather, they have been interpreted to be the result of a primordial heterogeneity of mantle nitrogen (e.g. Palot et al. 2012). If the data are interpreted to highlight the existence of two mantle reservoirs (Fig. 2), there is a suggestion but no direct evidence/record of a secular change in mantle $\delta^{15}N$ values. The absence of a direct and undisputable secular record for mantle $\delta^{15}N$ could reflect limited N recycling as a consequence of high N contents in the mantle (long residence time of nitrogen in the mantle). This view is however difficult to reconcile with positive $\delta^{15}N$ values from ocean island basalts, some carbonatites, lamproites and some diamonds from the transition zone (located between the upper and lower mantle) (Jia et al. 2003; Marty and Dauphas 2003; Palot et al. 2012), suggesting reservoir(s) buffered by subducted nitrogen. Marty and Dauphas (2003) suggested that the depth of recycling changed through time, from the shallow (upper) mantle to deeper part(s) of the mantle. However, this hypothesis is contradicted by $\delta^{15}N$ values measured in deep diamonds (300 to >800 km depths) (Palot et al. 2012). Alternatively the deep mantle may be heterogeneous for nitrogen isotopes. Still another alternative is that the reducing conditions prevailing at the surface of the early Earth allowed massive abiotic nitrogen fixation. This is experimentally supported by the formation of ammonium under hydrothermal conditions in the presence of iron (Brandes et al. 1998), but this possibility relies on little other experimental work and no direct quantitative observation in nature.

NITROGEN ISOTOPE HETEROGENEITY OF EARTH

Using the above estimates, the residence time of nitrogen in terrestrial reservoirs can be constrained. First, nitrogen's residence time at the Earth's surface, computed by dividing the surface inventory (5.0 × 10^{21}g N) by the N flux from the mantle approximated by its mid-ocean ridge flux, is ~7 × 10^{10} y, much greater than the age of the Earth, thus supporting limited recycling and early degassing. Second, this residence time is intermediate between the residence times of C and the noble gases (e.g. 5 × 10^{12} y for ^{36}Ar), and we know that the noble gases are also in *isotopic disequilibrium* since their return flux is weak enough to have allowed preservation of primordial components at depth.

Estimating the residence time of mantle nitrogen requires a precise knowledge of the mantle's N content and nitrogen's behaviour (i.e. its bulk partition coefficient) during melting. Nitrogen's behaviour depends on its speciation under melting conditions (for example, as ammonium ions substituting for potassium or as N^{3-} ions substituting for oxygen). This knowledge will require experimental work and a consensus about oxygen fugacity in the mantle; both are currently lacking. For example, if the deep mantle is metal saturated at depths greater than 240 km (Frost and McCammon 2008), then nitrogen would exist as nitride (N^{3-} groups) and/or be dissolved in the metal phase. In this case, N would be compatible during partial melting. Under higher oxygen fugacities, nitrosyl (with N–O groups), ammonium and N_2 are more likely (e.g. Roskosz et al. 2006; Busigny and Bebout 2013) and nitrogen may behave as an incompatible element (again, following potassium). Estimates of mantle nitrogen concentration thus range over two orders of magnitude, from 0.26 to 36 ppm (Marty 1995; Javoy 1998; Marty and Dauphas 2003). The mass of nitrogen in the upper mantle would accordingly vary between 0.3 and 39.6 × 10^{21} g N. The latter values are deduced from the two extreme mantle N contents quoted above and extended to the upper mantle. These values would thus be 4 times higher for the whole (i.e. upper + lower) mantle. A further difficulty in determining mantle nitrogen contents is accessing mantle samples. As for carbon (since carbonates are decarbonated during ascent) and hydrogen (which diffuses out of or into grains during ascent), the study of mantle xenoliths is seen as unsuitable owing to late-stage re-equilibration/diffusion processes (Yokochi et al. 2009). As mentioned above, the quantities of N stored in the lower (or primordial) mantle and the core are even more uncertain.

Assuming a bulk partition coefficient for nitrogen acting incompatibly during melting, a minimum residence time of ~1.7 to 7 Gy can be derived, which is similar to that of carbon. This residence time for nitrogen is obtained using the following assumptions: the amount of basalt extracted per year is 21 km^3/y, the average melting rate is 10%, and the size of the reservoir, taken from the upper to whole mantle size, respectively. The upper value of this range suggests that a primordial nitrogen reservoir might exist. If a secular evolution of nitrogen isotope composition occurred in the mantle owing to non–steady state conditions, primordial nitrogen should have been more depleted in ^{15}N than today's mantle because the recycling of surface nitrogen with positive $\delta^{15}N$ should have caused the mantle to evolve towards increasing $\delta^{15}N$ values. The most depleted values found in a few diamonds (as low as –40‰; Palot et al. 2012) may therefore reflect relict primordial nitrogen. However, both the size and location (deep layer, blobs of primordial material in a convective mantle, core–mantle interactions) of this reservoir are unknown.

POSSIBLE ORIGINS OF THE NITROGEN ISOTOPE DISEQUILIBRIUM

Several models have been proposed to account for the present isotopic distribution of nitrogen among reservoirs of the Earth. These include isotope fractionation of atmospheric N during hydrodynamic escape, N isotope fractionation during mantle–core segregation, the late accretion of ^{15}N-rich volatiles to form the atmosphere and oceans of the Earth, the recycling of light (^{15}N-depleted) nitrogen metabolized during ancient times (but see

Figure 1 in Thomazo and Papineau 2013), and preservation of a primordial light-N component in the deep Earth. As discussed below, these models are not mutually exclusive and each presents weaknesses and shortcomings.

Studies of iron meteorites have demonstrated that N can be concentrated in Fe–Ni minerals and nitrides. Under reducing conditions, nitrogen behaves as a siderophile element (Bouhifd et al. 2010) and might have been sequestered into the Earth's core. Assuming that atmospheric N accumulated mainly during Earth's accretion and early degassing when the core had not yet differentiated, subsequent core segregation would have created a residual mantle reservoir with a N isotope composition different from that of the initial atmosphere. Experimental data are lacking, but, given that equilibrium isotope fractionation typically causes the lighter isotope to be enriched in the most reduced phases (i.e. nitrides) (Busigny and Bebout 2013), a ^{15}N-enriched mantle would be predicted (that is, the opposite to what is observed) and this possibility is therefore currently seen as unlikely.

During hydrodynamic escape, the rise of light gases (hydrogen, helium) towards space exerts an aerodynamic drag on heavier gases, resulting in the preferential escape to space of the light elements and of the light isotopes relative to the heavy ones (e.g. Lichtenegger et al. 2010). According to this model, the nitrogen isotope composition of the Earth's surface reservoirs, which are richer in ^{15}N than the mantle, could originate from mantle degassing followed by hydrodynamic escape. At the end of this early phase, atmospheric N would have had a positive δ^{15}N value, contrasting with the negative δ^{15}N value of the mantle. This suggestion is possible, but difficult to quantify. However, the hydrodynamic escape model cannot explain the abundance and isotopic composition of atmospheric xenon, which is more depleted and isotopically fractionated than krypton or argon, while the opposite is expected on the basis of respective atomic weights. This model would predict a strong isotopic contrast between the atmosphere and mantle isotope compositions for both argon and krypton compared to xenon, whereas the mantle and atmosphere in fact display very similar stable isotope compositions. The suggestion that significant recycling of argon, krypton and xenon occurs, leading to similar present-day stable isotope compositions for the mantle and atmosphere, would be at odds with the comparatively limited recycling of nitrogen, as outlined above. Explaining the distribution of volatiles among terrestrial reservoirs might therefore require additional processes. One such process could possibly be related to UV photochemistry or solar wind–atmosphere interactions, as was suggested for Mars (Marty 2012).

Heterogeneous accretion of the Earth could be a solution for the nitrogen isotope imbalance (Javoy 1998). The Earth would have been initially formed from material with δ^{15}N values as low as –40‰ (i.e. the lowest value for δ^{15}N measured on Earth). This material would most likely resemble either enstatite chondrites or remnants of the proto–solar nebula, with a subsequent contribution of a "late veneer" with high positive δ^{15}N values; the "late veneer" would most likely be composed of chondritic material(s), commonly with a minor contribution of cometary materials (e.g. Javoy 1998; Jia and Kerrich 2004; Marty 2012) (Fig. 3). Over time, the degassing of mantle N with negative δ^{15}N would have progressively decreased the δ^{15}N values of surface reservoirs, while the recycling of surface N via subduction zones would have increased the upper mantle δ^{15}N value. All these possibilities remain to be confirmed and quantified.

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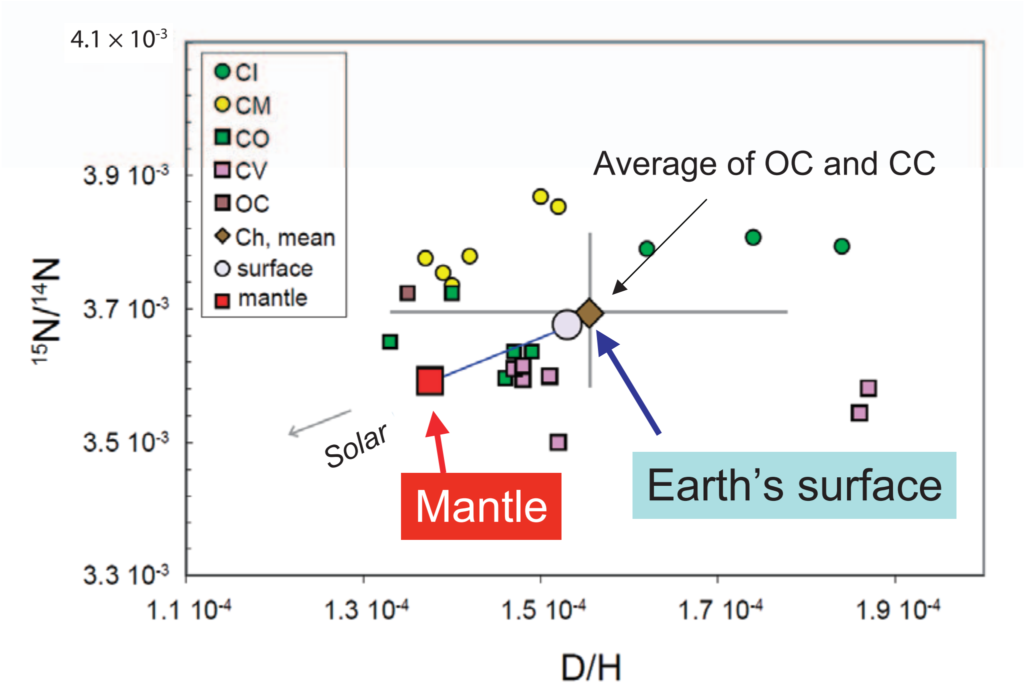
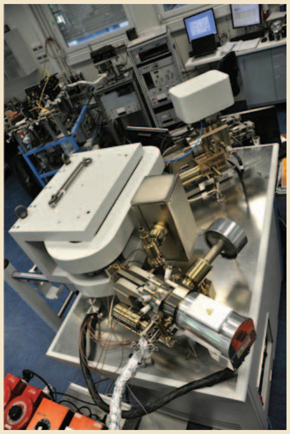


Figure 3 Variations in D/H and ^{15}N/^{14}N ratios for solar, Earth's mantle and surface, and meteorites, illustrating that the Earth's nitrogen budget (surface and mantle) lies between solar-like and meteorite-like endmembers. *CI, CM, CO* and *CV* refer to the different carbonaceous chondrite groups, while *OC* refers to ordinary chondrites. *Ch, mean* refers to the average values of all meteorite data. As their name implies, carbonaceous chondrites are rich in carbon and other volatile elements compared to ordinary chondrites. The figure also illustrates the difference between the Earth's mantle and surface (modified from Marty 2012).

ANALYTICAL BOX

Almost every N isotope composition – for whatever the material analyzed or the geological context – has been determined using conventional gas-source ion-ratio mass spectrometry on the N_2 molecule. As such, all these measurements share the same chemistry-related analytical difficulties, as analyses of any trace amount of an H- or C-bearing compound (CH_4, CO_x, H_2, H_2O) can result in significant isobaric interferences (production on m/z = 29 of $^{14}N_2–H^+$, $^{13}C–^{16}O^+$ or $C_2H_5^+$) not separable by most low-resolution ion-ratio mass spectrometers (IRMS). For example, Beaumont et al. (1994) reported an increase of 7‰ of $\delta^{15}N$ for every 1% of CO present in a sample of N_2, casting some doubt on the early very positive $\delta^{15}N$ values reported for samples with high C/N ratios (e.g. highly metamorphosed rocks, diamonds). Nitrogen being a reactive element, additional difficulties have recently been recognised, including Mo–N interactions occurring during step-heating (combustion or pyrolysis) extractions using a Mo crucible. These interactions can be associated with $\delta^{15}N$ shifts in excess of 10‰ even at temperatures up to 1800 °C (Yokochi and Marty 2006). These difficulties highlight the need for appropriate standard reference materials, including low-N organic matter, silicates, and diamonds, and for intercalibration of every technique to the same extraction method, in particular, the sealed-tube method (the so-called Dumas combustion), considered the most reliable technique and for which subnanomole-size procedural blanks can now be achieved (e.g. Kendall and Grim 1990; Boyd et al. 1993).

Nitrogen occurs in a very wide range of oxidation states (from +5 in nitrate to –3 in nitride) and therefore of molecules (nitrate, N_2O and N_2 gas, ammonium, nitride, etc.), with a very large range of concentrations as ammonium in, for example, the potassic minerals (e.g. muscovite, biotite, K-feldspar). Corresponding sample sizes, resulting from extractions, can vary between being too large (the geochemist's dream) and very small, even picomoles in size (the geochemist's challenge). The desire to determine the N isotope compositions of very small samples of N_2 has led to a very large number (if not the largest) of dedicated, compound-specific, analytical protocols and instrumentations. Large sample sizes, including those produced for nitrogen in organic matter, can be analyzed using nearly fully automated instrumentation such as elemental analyzers (EA; avoiding the need for vacuum extraction lines), which have produced a wealth of data with very good precision (<0.1‰) from many ecological/geological contexts. Still, one technique commonly employed involves combusting samples in sealed quartz tubes and purifying the resulting N_2 gas using high-vacuum extraction lines. Among the other available analytical methods, it is worth mentioning the microbial denitrification method (Sigman et al. 2001) as it allows nitrate to be accurately and rapidly converted to N_2. The use of gas chromatography, coupled with dedicated combustion/reduction furnaces, now even permits the study of the N isotope compositions of specific compounds or gas mixtures (see Meier-Augenstein and de Groot 2004 for a review).


Very low concentrations of nitrogen can be measured using static mass spectrometry originally developed for noble gas analysis. Noble gas–nitrogen isotope lab at CRPG Nancy, France

The study of N in silicate minerals is limited owing to difficulties in releasing very small amounts of N from silicate matrices. Early work on crustal N was initiated by several groups in the 1970s, but with notable contributions by the Leipzig group in the former East Germany (e.g. Haendel et al. 1986 and references therein), while studies on mantle-related samples were undertaken in the early 1980s (Javoy et al. 1984). Standard dual-inlet IRMS requiring micromoles of N_2 gas for reliable analyses and the very small amounts of N (typically sub-ppm levels) in typical mantle silicates presented large obstacles. Furthermore, standard stable isotope techniques did not allow monitoring of potential atmospheric and organic contamination, using Ar isotopes, for example.

Nitrogen in samples of most mantle-derived materials, such as mid-ocean ridge basalts, ocean-island basalts, silicates, and most diamonds, is too scarce, at the sub-ppm level, to be analyzed using standard stable isotope techniques.

In the early 1980s, the development of static mass spectrometry (in which the gas is left under static vacuum in the ion source during analysis), first developed for noble gas analysis and then adapted for the analysis of N isotopes, offered the ability to increase the sensitivity of N isotope analysis by up to ~5 orders of magnitude. Samples as small as 10^{-11} mol N (0.1 ng N) can now be routinely analyzed with sub-permil precision (Hashizume et al. 2004). The simultaneous analysis of N and noble gas isotopes (e.g. of He and Ar) allows to constrain the origin(s) (e.g. in mantle plumes, depleted mantle, or crust) of the N that is analyzed and provides an efficient diagnostic for atmospheric/surface contamination.

Although most available data have been obtained using static mass spectrometry, the development of He carrier gas continuous flow now allows analyses by conventional dynamic IRMS of sample sizes down to a few tens of nanomoles (Bebout et al. 2007) – relevant, therefore, to sedimentary, crustal, and hydrothermal settings. Also, ion probes (for N-rich minerals such as nitrides and diamonds) or elemental analyzers (for N-rich minerals such as micas) remain effective options for future studies of appropriate materials.

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