Biogeochemical Cycling of Nitrogen on the Early Earth

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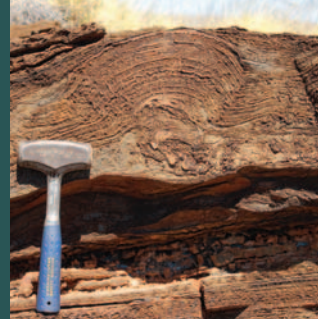
Variations in the nitrogen isotope composition of ancient organic matter and associated sediments provide clues for the early evolution of Earth's atmosphere–ocean–biosphere system. In particular, large isotopic variations have been linked to the protracted oxygenation of Earth's atmosphere during the Precambrian. Important problems being investigated include the nature of the variations observed at specific times in Earth's history and the degree of preservation of ancient nitrogen biogeochemical signatures during diagenesis and metamorphism. Interpreting these records in Archean sedimentary environments and their possible implications for the evolution of Earth's early atmosphere, ocean, and life is challenging.

KEYWORDS: Precambrian, biogeochemistry, nitrogen isotope, nitrogen cycle, early life

INTRODUCTION

Nitrogen is a major component of biomass and plays important roles in metabolic pathways. Nitrogen is a component of numerous macromolecules, including proteins and nucleic acids, and, together with phosphate and iron, can be a biolimiting nutrient in the environment. On the modern Earth, nitrogen is present in the atmospheric reservoir as di-nitrogen (N_2) and is by far the most abundant gas in the atmosphere. Nitrite (NO_2^-), nitrate (NO_3^-), ammonium (NH_4^+), and particulate and dissolved organic nitrogen are present as bioavailable forms of nitrogen in the oceanic reservoir (referred to as "fixed" nitrogen) and are linked by a complex web of biogeochemical processes (Sigman et al. 2009). In sedimentary rocks, nitrogen is mostly preserved as organic nitrogen and as fixed NH_4^+ substituting for K^+ in phyllosilicates (i.e. micas; Boyd and Philippot 1998; Busigny and Bebout 2013 this issue); together, these forms represent the available geological archive of past biogeochemical nitrogen cycling on Earth. In the late 1930s, Vernadski was the first to suggest the potential of nitrogen isotopes for recording past metabolic activity in deep time (Vernadski 1944). Indeed, physical, chemical, and biological processes discriminate the two stable isotopes of nitrogen (14 and 15 atomic mass units, respectively), leading to measurable differences in the $^{15}N/^{14}N$ ratios of sedimentary nitrogen.

The modern oceanic biogeochemical nitrogen cycle and its isotopic expression are well documented (Sigman et al. 2009; Hastings et al. 2013 this issue) and mostly reflect the fate and recycling of nitrogen compounds in the ocean. Changes in the nutrient supply and/or redox stratification of the water column can affect the relative importance and spatial distribution of dominant nitrogen metabolic pathways. For instance, the $\delta^{15}N$ value of +5 to +7‰ of modern sedimentary organic matter in oceanic sediments reflects the ^{15}N enrichment of fixed nitrogen during anaerobic ammonium oxidation (anammox) and denitrification in oxygen-minimum zones (Lam and Kuypers 2011). Periods of global change, such as the oceanic anoxic events of the Mesozoic and the protracted oxygenation of the Earth's atmosphere at the Archean–Proterozoic transition, are associated with variations in sedimentary $\delta^{15}N$ (Canfield et al. 2010). Consequently, nitrogen isotopes can provide a record of specific biosignatures and are sensitive to environmental redox changes during Earth history.

The detailed evolution of the nitrogen cycle over geologic timescales has remained an elusive target, owing partly to difficulties in interpreting the rock record in deep time. The main challenge is the ubiquitous metamorphism of Precambrian rocks (older than 0.542 billion years, Ga). As nitrogen isotopes are sensitive to thermal effects during postdepositional geological processes, primary signals inherited from ancient environments tend to be obscured. Studies of the Archean (4.0–2.5 Ga) and Proterozoic (2.5–0.542 Ga) thus require careful examination of rock samples before nitrogen isotopes can be used as reliable biosignatures of metabolic pathways and diagnostic paleoenvironmental proxies. In addition, nitrogen is found and preserved in measurable quantities in relatively few phases, which primarily include organic matter, phyllosilicates, feldspars, magnetite, and fluid inclusions. The nitrogen isotope ratios measured in such phases from ancient sedimentary rocks have to be evaluated for isotope fractionations imparted during metamorphism before reasonable interpretations of primary biosignatures can be made.

The lack of oxygen in the atmosphere during the Archean and until the Great Oxidation Event, between about 2.50 and 2.06 Ga, has impacted the long-term evolution of the nitrogen biogeochemical cycle (Canfield et al. 2010). The anoxic Archean atmosphere prohibited the oxygenation of the oceans, except perhaps in localized oases

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of oxygen-producing cyanobacteria. The rise of nitrite-oxidizing bacteria in the Archean ocean was impeded by their need for molecular oxygen to convert NO_2^- to NO_3^-. Consequently, the growth of denitrifying bacteria and archaea, which breathe NO_3^- (denitrification *sensu stricto*), was stifled, leaving nitrogen fixation, anoxic ammonium oxidation to nitrite, anammox and ammonium assimilation as the dominant microbiologically mediated processes in the nitrogen cycle on the early Earth.

The fundamentally different oceanic redox chemistry during the Archean must also have affected key enzymatic systems of the nitrogen cycle because most of them require a range of metal cations to perform redox reactions. The abundance of banded iron formations in Archean supracrustal belts has given support to the hypothesis that oceans on the early Earth were generally anoxic and ferruginous. Such conditions would have favored an early evolution of Fe-bearing enzymes, such as nitrogenase for biological N_2 fixation, glutamate synthetase for NH_4^+ assimilation, and nitrite reductase for NO_2^- reduction into NH_4^+ (Glass et al. 2009). Since transition metals are required in all nitrogen metabolic pathways, the emergence of specific nitrogen-metabolizing microorganisms must have been modulated by the chemical evolution of the oceans (Anbar and Knoll 2002), which might therefore hold key information on the evolutionary history of the nitrogen biogeochemical cycle.

NITROGEN ISOTOPES DURING THE PRECAMBRIAN

Craton formation first began in the Precambrian. Shallow-water shelf deposits along craton margins, such as carbonate platforms and sandstones, are few until the end of the Archean around 2.5 Ga, when 2–3% of the Earth's surface area consisted of emerged continental crust (Flament et al. 2008). Archean and Paleoproterozoic terrains represent only about 10% of the present exposed continental crust. During the last few decades, nitrogen geochemistry studies have mostly focused on the Pilbara (Western Australia), the Kaapvaal and Zimbabwe (southern Africa), the Superior (Ontario and Québec), the North Atlantic (Nain) (Labrador, southern Greenland, and Scotland), the Dharwar and Aravalli (India), the West African (Ghana), and the Congo

(Gabon) cratons (FIG. 1). It has so far not been possible to obtain unmetamorphosed samples of Archean terrains because all have systematically experienced metamorphism above the subgreenschist facies (at temperatures of more than about 220°C). The degree to which secondary alteration (i.e. during diagenesis and metamorphism) may affect nitrogen isotope distribution in sediments and blur primary paleoenvironmental reconstructions is reviewed in BOX 1.

Reconstructions of the Archean to Paleoproterozoic nitrogen cycle have been attempted by studies of $\delta^{15}N$ in a range of rocks and minerals and are detailed in TABLE 1 and FIGURE 2A. In such studies, careful consideration of the metamorphic history of the metasedimentary rocks is necessary to evaluate paleoenvironmental conditions. After all, the nitrogen isotope record is the only direct means of reconstructing the nitrogen cycle on the early Earth. The record is established through the analysis of metamorphosed whole-rock samples (Pinti et al. 2001; Jia and Kerrich 2004; Nishizawa et al. 2005; Garvin et al. 2009; Godfrey and Falkowski 2009; Papineau et al. 2009; Thomazo et al. 2011), sedimentary organic matter (Beaumont and Robert 1999; Godfrey and Falkowski 2009), graphite (Van Zuilen et al. 2005), structural NH_4^+ contained in metamorphic minerals such as biotite (Jia and Kerrich 2004; Papineau et al. 2005), impurities in Fe-bearing phases (Pinti et al. 2001), and fluid inclusions (Sano and Pillinger 1990; Nishizawa et al. 2007).

SECULAR VARIATIONS IN THE ARCHEAN TO PALEOPROTEROZOIC SEDIMENTARY NITROGEN ISOTOPE RECORD

The Evolution of the Nitrogen Cycle from $\delta^{15}N$

We present an extensive $\delta^{15}N$ database spanning time from 3.8 Ga in the Archean to 1.4 Ga in the early Mesoproterozoic (1.6 to 1.0 Ga), and we use statistical methods (see online supplementary information at www.elementsmagazine.org/supplements) applied to geochemical time series in our analysis of the database. The data set presented in FIGURE 2A (table and references in online supplementary material) is based on a compilation of 874 published $\delta^{15}N$ values
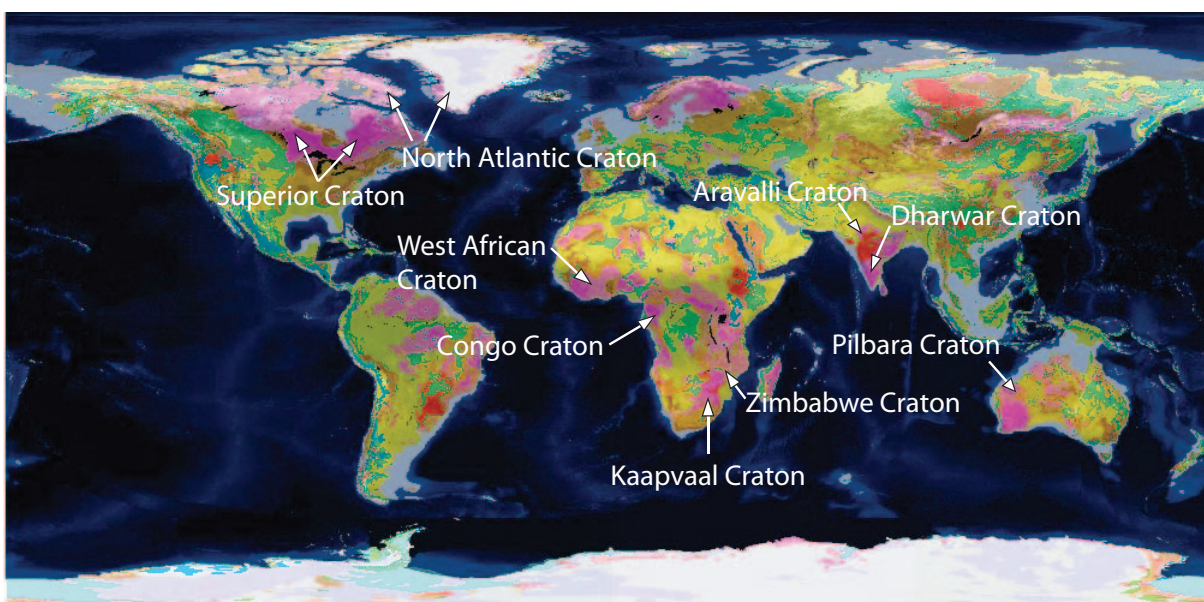

FIGURE 1   Geological map of the world showing the locations of the Archean and Proterozoic cratons most studied for their nitrogen geochemical signatures. Archean and Proterozoic cratons (shown in purple) represent the oldest pieces of the continental crust. The orange, yellow, green, and blue colors represent Phanerozoic terrains. SOURCE: HTTP://PORTAL.ONEGEOLOGY.ORG

measured on various Precambrian sedimentary lithologies and materials, including kerogen, phyllosilicates, shales, carbonates, cherts, banded iron formations (BIFs), and N_2-bearing fluid inclusions. Various levels of secondary alteration have been reported for the sample set and these have been carefully considered. All samples are included in the statistical analysis of $\delta^{15}N$ values from the Precambrian record, allowing us to test the robustness of single, short-term isotopic excursions suggested in previous studies and to identify possible long-term secular variations (again, the reader is referred to Box 1 for considerations of the degree of $\delta^{15}N$ preservation regarding secondary processes). The "SiZer" statistical approach referred to in Figure 2B is used to detect significant trends in $\delta^{15}N$ variations. This method is based on the construction of curves fitting time series using different levels of smoothing (h); the h values represent different binnings of age ranges. The first derivatives of each curve (i.e. the slopes) are simultaneously computed with their 95% confidence intervals, allowing the signs of the derivatives to be statistically tested. The results of multiple tests are then reported under the form of SiZer maps (Fig. 2B) with different colors; these maps are a graphical representation of increasing (positive slope) and decreasing (negative slope) $\delta^{15}N$ values for variable lengths of time periods. Clearly, this first-order statistical analysis is based on currently available data sets and will evolve with future additional data.

The Eo- and Paleoarchean Nitrogen Cycle (4.0–3.2 Ga)

The available nitrogen isotope data set from Paleoarchean (3.6–3.2 Ga) metamorphosed sedimentary rocks and organic matter (Fig. 2A) shows $\delta^{15}N$ values centered around +3‰ and ranging between –6.2 and +27.5‰. Considering that Eo- and Paleoarchean environments were anoxic and that NH_4^+ must have been the dominant bioavailable form of nitrogen in the ocean, most workers have interpreted this record to indicate that the nitrogen cycle at that time was dominated by nitrogen-fixing and/or ammonium-assimilating microorganisms (see water column I in Fig. 3; Table 1). Notably, N_2-bearing fluid inclusions rich in the seawater component and preserved in the 3.5 Ga North Pole hydrothermal deposits in the Pilbara craton (Western Australia) have $\delta^{15}N$ values between –0.7 and –2‰ (Nishizawa et al. 2007). These N_2-bearing fluid inclusions data suggest that the $\delta^{15}N$ value of the Paleoarchean

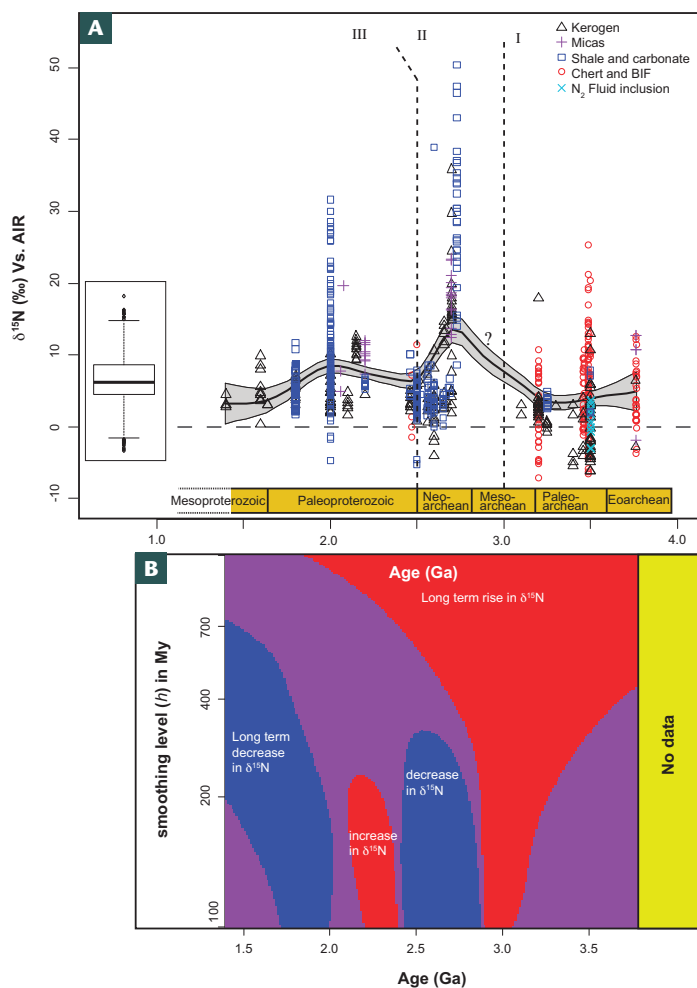**Figure 2** (**A**) Compilation of Precambrian sedimentary nitrogen isotope compositions measured in kerogen, phyllosilicates, fluid inclusions (as N_2), and bulk rocks for shales, carbonates, cherts, and banded iron formations (BIFs) (values and references are available online in supplementary material). The smoothed curve in gray represents the 95% confidence interval calculated for sedimentary $\delta^{15}N$ time series and is generated using a kernel regression with a bandwidth (h) of 200 My. I, II and III refer to possible evolutionary states of the redox stratification of the ocean depicted in Figure 3. The inset diagram shows the results of a statistical analysis of the modern sedimentary nitrogen isotope composition based on 1140 δ15N values; the results are represented as a box-and-whisker diagram with the ends of the whiskers at the 1.5 interquartile range of the lower and the upper quartiles. (**B**) "SiZer" map (see text) depicting the significance, at different smoothing levels from 0.1 to 1.0 Gy, of the increase (red) and decrease (blue) in $\delta^{15}N$. No significant variation in $\delta^{15}N$ is shown in purple.

Geological terrain	Sample age (Ga)	Metamorphic grade	$\delta^{15}N$ (source)	Interpretations	References
Isua Supracrustal Belt (Nain)	ca. 3.77	Amphibolite facies	+5.4 to +20.0‰ (WR BIF, magnetite in BIF, and WR metapelite)	Metamorphically altered pristine nitrogen possibly from chemosynthetic microorganisms	Pinti et al. (2001)
Isua Supracrustal Belt (Nain)	ca. 3.77	Amphibolite facies	–1.85 to +27.47‰ (biotite from metapelite)	Metamorphic nitrogen for highest values and BNF for lowest values	Papineau et al. (2005)
Isua Supracrustal Belt (Nain)	ca. 3.77	Amphibolite facies	–3.66 to +7.29‰ (graphite)	Modern atmospheric nitrogen or BNF for lowest values and D or metamorphism for highest values	Van Zuilen et al. (2005)
Isua Supracrustal Belt (Nain)	ca. 3.77	Amphibolite facies	–3.1 to +11.4‰ (WR BIF)	Derived from kerogenous material	Nishizawa et al. (2005)
Warrawoona Group (Pilbara)	3.4–3.5	Prehnite–pumpellyite facies	–11.0 to +12.1‰ (WR chert, chert separate)	Ammonium assimilation for lowest values, paleoatmospheric nitrogen for near-zero values, and metamorphic nitrogen for highest values	Pinti et al. (2001)
Warrawoona and Gorge Greek groups (Pilbara), Onverwacht (Kaapvaal)	3.4–3.5	Prehnite–pumpellyite to amphibolite facies	–6.2 to +13.0‰ (organic matter in chert)	Biological consumption of N_2 and/or NH_4^+ for lowest values	Beaumont and Robert (1999)
Barberton Greenstone Belt (Kaapvaal)	ca. 3.2	Greenschist facies	–3 to +12‰ (chert)	Atmospheric signature with some metamorphic overprint	Sano and Pillinger (1990)
Harare Greenstone Belt (Zimbabwe), Penhalonga Formation (Kaapvaal), Abitibi terrain (Superior)	ca. 2.7	Greenschist facies	+14.8 to +23.4‰ (mica and carbonaceous shale)	Change in atmospheric $\delta^{15}N$ composition through delivery of CI chondrite meteorites and comets with isotopically heavy nitrogen	Jia and Kerrich (2004)
Michipicoten Formation, Steeprock Group (Superior), Fortescue Group (Pilbara)	ca. 2.7	Greenschist facies	–4.1 to +35.8‰ (organic matter in black chert)	Biological consumption of N_2 and/or NH_4^+ for lowest values and D for highest; increased redox states	Beaumont and Robert (1999)
Tumbiana Formation (Pilbara)	2.727	Greenschist facies	+8.6 to +50.4‰ (stromatolitic dolomite, mudstone, siltstone)	BNF and ammonia oxidation for lowest values and D for highest; increased redox states	Thomazo et al. (2011)
Campellrand and Malmani formations (Kaapvaal)	ca. 2.67–2.50	Greenschist facies	–1.5 to +7.5‰ (kerogen, WR chert, carbonate, BIF)	BNF for lowest values followed by D for highest; increased redox states	Godfrey and Falkowski (2009)
Mt. McRay Formation (Pilbara)	2.50	Greenschist facies	+1.0 to +7.5‰ (WR shale, BIF, and carbonate)	BNF for lowest followed by D for highest; increased redox states	Garvin et al. (2009)

WR = whole rock, BIF = banded iron formation, BNF = biological nitrogen fixation, D = denitrification

atmosphere was similar to the value of the present-day atmosphere (i.e. 0‰). Kerogens in Paleoarchean cherts from the Kaapvaal and Pilbara cratons have low $\delta^{15}N$ values, as low as –6.2‰, which have been interpreted as the result of biological nitrogen fixation and/or NH_4^+ assimilation at the time of formation (TABLE 1; Beaumont and Robert 1999). These latter values are similar to the range of values reported from Eoarchean metasediments from the Isua Supracrustal Belt and which collectively vary between –3.7 and +27.5‰ (TABLE 1). However, high $\delta^{15}N$ values from Isua that were measured in biotite and whole-rock samples have been differently interpreted as postdepositional metamorphic fluid alterations of primary compositions (Pinti et al. 2001; Papineau et al. 2005; Van Zuilen et al. 2005). Unless other constraints can be used, $\delta^{15}N$ values from highly metamorphosed sedimentary rocks can only be interpreted as maxima of their premetamorphic values (as explained in BOX 1). The lighter $\delta^{15}N$ values from Isua have thus been interpreted by some workers as possible indications of an Eoarchean biological nitrogen cycle (Nishizawa et al. 2005) dominated by chemosynthetic microorganisms (Pinti et al. 2001) and/or biological nitrogen-fixing microorganisms (Papineau et al. 2005). Importantly, however, these light nitrogen isotope compositions do not necessarily reflect biological processes but could conceivably indicate atmospheric or fluid-based contaminants (Van Zuilen et al. 2005). Therefore, the large range of $\delta^{15}N$ values from Isua is challenging to interpret as a primary biosignature because these rocks have experienced a protracted metamorphic history.

The Meso- and Neoarchean Nitrogen Cycle (3.2–2.5 Ga)

During the Meso- and Neoarchean, the average $\delta^{15}N$ value increases to +15‰ and the range of $\delta^{15}N$ variations also increases drastically in some paleoenvironments, reaching values up to +50.4‰. However, the detailed structure of the $\delta^{15}N$ secular variation between 3.1 Ga (average $\delta^{15}N$ value of +2.3‰) and the positive excursion recorded at 2.7 Ga (average $\delta^{15}N$ value of +29.5‰; Thomazo et al. 2011) is unknown because of a gap in the record (FIG. 2A). The key observation by Beaumont and Robert (1999) that organic matter in Archean sedimentary rocks commonly has negative $\delta^{15}N$ values has thus been supplemented by observations of highly ^{15}N-enriched samples in the Neoarchean around 2.7 Ga (TABLE 1; FIG. 2A) and a long-term increase in $\delta^{15}N$ (FIG. 2B). ^{15}N-enriched values in slightly metamorphosed Neoarchean sedimentary rocks around 2.7 Ga have been mostly interpreted as the record of the initiation of the oxidative part of the nitrogen cycle (i.e. the rise of nitrification and denitrification metabolisms; see water column II in FIG. 3) (Garvin et al. 2009; Godfrey and Falkowski 2009; Thomazo et al. 2011).

Jia and Kerrich (2004), however, have interpreted the large range of highly positive $\delta^{15}N$ values in the Neoarchean to reflect a significant increase in atmospheric $\delta^{15}N$ composition resulting from the delivery of CI chondrite meteorites and comets with heavy nitrogen at the end of Earth accretion at about 4.5 Ga. While this hypothesis remains to be tested, evidence based on nitrogen isotope analyses of N_2-bearing fluid inclusions in Precambrian cherts indicates
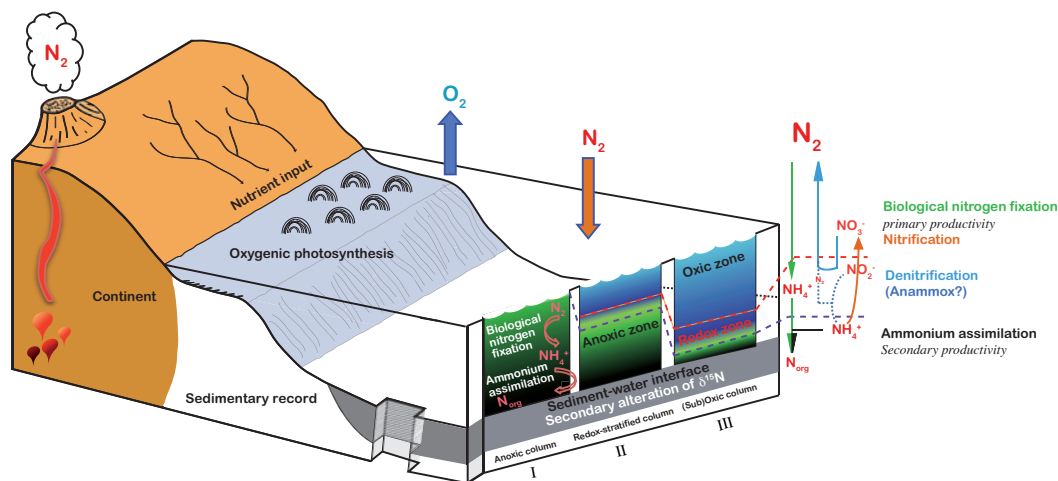
no significant variation of the atmospheric $^{15}N/^{14}N$ ratio since ~3.5 Ga (Nishizawa et al. 2007). Moreover, because N_2 in the atmosphere has a residence time of 1 Gy, the nitrogen isotope composition of the atmosphere probably has not varied much since the Hadean as it has likely been controlled by the recycling of sedimentary nitrogen into the mantle (Marty and Dauphas 2003; compare Jia and Kerrich 2004).

The Paleoproterozoic Nitrogen Cycle (2.5–1.6 Ga)

The rise of atmospheric oxygen during the Paleoproterozoic between about 2.50 and 2.06 Ga must have impacted the nitrogen biogeochemical evolution of early Earth environments. In fact, during the Paleoproterozoic at around 2.0 Ga, both oxygenated and redox-stratified water masses existed during deposition of the Aravalli Supergroup (India), where $\delta^{15}N$ values reach +31.6‰ (Papineau et al. 2009). After 2.0 Ga, $\delta^{15}N$ values are between 0 and +10‰, with a statistical average close to +5‰ and a smaller variability. These data are comparable to the modern nitrogen signal (inset, FIG. 2A) and have been interpreted to reflect the expansion of the redox transition zone (see water column III in FIG. 3). In this paleoenvironment, ammonium (NH_4^+) would be present in the deep anoxic ocean, NO_2^- would accumulate at the oxic–anoxic interface during nitrification and denitrification cycles, and NO_3^- would accumulate in the oxygenated surface water in response to increasing atmospheric and oceanic oxygen concentrations. Geochemical data are thus consistent with the view that (1) abundant free oxygen had stabilized NO_3^- in the oceans and (2) a complete nitrogen biogeochemical cycle was established by about 2.0 Ga.

INSIGHTS FROM MOLECULAR BIOLOGY

Because of the incomplete geological record of the earliest Earth, it is unclear when, exactly, life started to evolve. However, the availability of nitrogen compounds for the synthesis of biomolecules on the early Earth was an important factor in the evolution of the first nitrogen metabolisms. The ability to assimilate NH_4^+ directly from solution and incorporate it into amino acids and nucleotide bases is indeed likely to have been an ancient metabolic pathway (Glass et al. 2009). Two enzymes catalyze this process (glutamine synthetase and glutamate synthase), which results in the synthesis of glutamine and glutamate, the precursors of all nitrogenous compounds in the cell. These two key enzymes of the nitrogen cycle require Fe

for catalysis and are thought to be ancient—perhaps they were already present in the last universal common ancestor (Raymond 2005).

Similarly, biological nitrogen fixation also likely evolved early in the history of life. Nitrogen-fixing enzymes need Fe, although it can be substituted by or combined with Mo or V when these are available (the Fe-Fe nitrogenase enzyme is less efficient, but it is likely that this form was dominant in the anoxic and ferruginous Archean oceans [Glass et al. 2009]). While lateral gene transfer might have occurred for some nitrogen-fixing genes in some microorganisms, nitrogen-fixing microorganisms include a large range of both archaea and bacteria, which suggests that nitrogen fixation was operative very early in the history of life, and possibly at the time of prebiotic chemistry. The relationship between metal-cation availability in the water column and the enzymatic requirement for metal cations in some of the most ancient nitrogen metabolisms suggests that there was a nitrogen-based bioinorganic bridge during the earliest Archean.

PREBIOTIC AND NONBIOLOGICAL EARLY-EARTH NITROGEN CYCLING

Several nonbiological geochemical processes fix nitrogen into bioavailable forms or change its redox state (FIG. 4), and these processes have been demonstrated experimentally. Mechanisms such as lightning, mineral catalysis during hydrothermal circulation, and photolysis were operative on the early Earth and could have resulted in the abiotic fixation of nitrogen into bioavailable forms (FIG. 4). Subaerial komatiitic volcanism could have provided additional fixed N oxides to the early-Earth environment (Mather et al. 2004). Experiments with lightning have also shown that nitrogen compounds can be synthesized from precursor N_2 gas, and, depending on the partial pressure of H_2, these compounds can be either reduced or oxidized (Navarro-Gonzales et al. 2001). Other experiments have shown that reduced and sulfidic hydrothermal vent fluids can reduce N_2 to NH_4^+ (Schoonen and Xu 2001). Various Fe- and Ni-bearing minerals can also catalyze the reduction of N_2 or oxidized nitrogen species to NH_3 under hydrothermal conditions in simulated prebiotic environments (Smirnov et al. 2008), and Ti oxide catalysts can reduce nitrogen compounds under photochemical influence (Bickley and Vishwanathan 1979). The types of reactions noted here could have provided a prebiotic source of NH_3 before N_2 fixation had evolved in Hadean environments.

Extraterrestrial input could have provided additional fixed nitrogen to the prebiotic Earth. Carbonaceous chondrite meteorites are usually rich in amino acids and sometimes
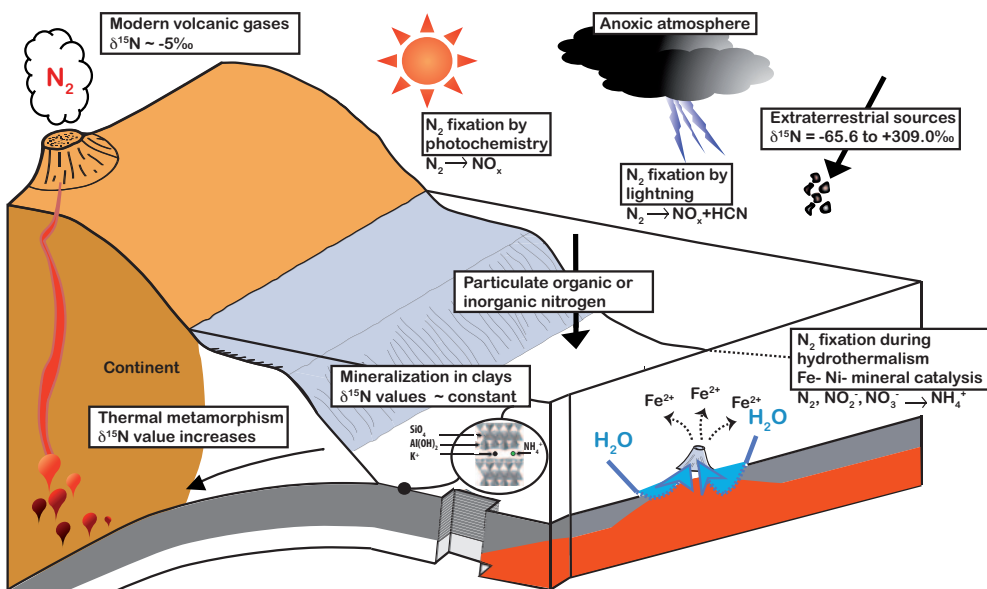
FIGURE 4 Cartoon of the nitrogen cycle on the prebiotic Earth, with an anoxic atmosphere–ocean system and ferruginous oceans

in ammonia (Pizzarello et al. 2011), and these sources of extraterrestrial nitrogen could have periodically delivered fixed nitrogen to the early Earth, although the net fluxes are difficult to quantify. Meteorites of all types have a large range of nitrogen isotope compositions, with $\delta^{15}N$ values between −65.6 and +309.0‰ in acid-insoluble residues (Alexander et al. 2007). The N/C_{atomic} ratio of these residues is typically greater than 1 (it varies between 0.1 and 6.5), and therefore the extraterrestrial contribution of nitrogen is of the same order of magnitude as that of carbon. In brief, during the initiation of the Hadean–Archean biogeochemical nitrogen cycle, several inorganic processes and nonbiological sources of fixed nitrogen led to the presence of yet-to-be-quantified fixed nitrogen in early oceans, which might have favored the emergence of life.

FUTURE DIRECTIONS

In the last decade, our knowledge of the evolution of the biogeochemical nitrogen cycle during the Archean–Paleoproterozoic period has greatly improved thanks to analytical developments that have allowed precise isotopic measurements of low nitrogen contents in rock and mineral samples. The general picture that has emerged is that biogeochemically induced nitrogen fractionations were recorded early in some of the oldest metasedimentary rocks during the Paleoarchean and in the increasingly oxidizing global environments of the Neoarchean–Paleoproterozoic ocean–atmosphere system.

Some of the fundamental questions to be investigated are: Which nitrogen metabolisms operated during the Eoarchean? How did the atmospheric $\delta^{15}N$ value evolve during the Archean, if at all? What is the nature of the Neoarchean and Paleoproterozoic global secular variations in sedimentary $\delta^{15}N$ values? What are the main sedimentary controls on nitrogen isotope compositions? Most of these questions can probably be answered by more thorough sampling strategies applied to Archean sedimentary rocks (shown in pink in Fig. 1) for future biogeochemical analysis.

Finally, because our interpretations of the past $\delta^{15}N$ sedimentary record can only be based on a detailed knowledge of isotopic effects from metabolic pathways and similar observations from modern analogs, such as redox-stratified lakes and basins (Fig. 5), the scientific community will need to continue merging the disciplines of limnology, paleoceanography, geobiology, and global biogeochemical

FIGURE 5 A possible analog of the stratified Archean ocean: the Lake Pavin meromictic crater (Puy de Dôme, France); the scale is shown by the roads near the lake. PHOTO COURTESY OF DIDIER JEZEQUEL

cycles to better decipher the evolutionary history of the ancient nitrogen cycle and the early evolution of life on our planet.

ACKNOWLEDGMENTS

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