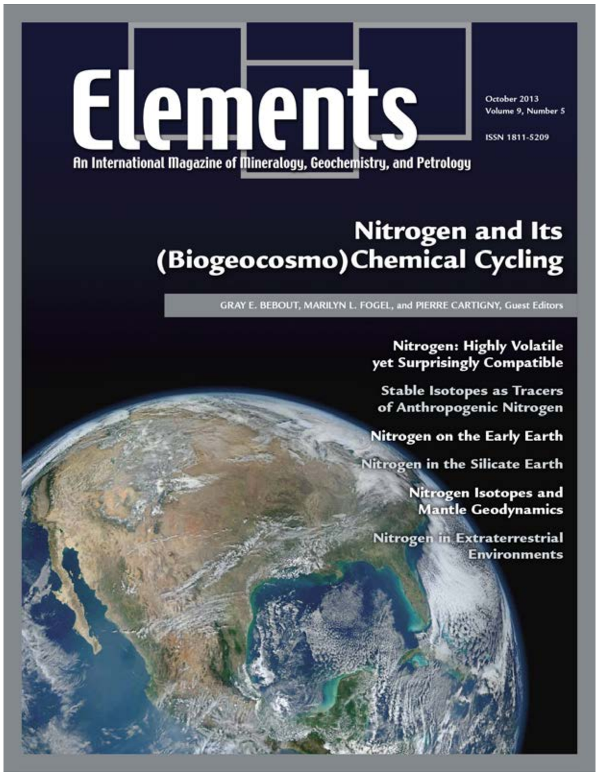
Elements
An International Magazine of Mineralogy, Geochemistry, and Petrology
October 2013
Volume 9, Number 5
ISSN 1811-5209
Nitrogen and Its (Biogeocosmo)Chemical Cycling
GRAY E. BEBOUT, MARILYN L. FOGEL, and PIERRE CARTIGNY, Guest Editors
Nitrogen: Highly Volatile yet Surprisingly Compatible
Stable Isotopes as Tracers of Anthropogenic Nitrogen
Nitrogen on the Early Earth
Nitrogen in the Silicate Earth
Nitrogen Isotopes and Mantle Geodynamics
Nitrogen in Extraterrestrial Environments

Nitrogen: Highly Volatile yet Surprisingly Compatible

Gray E. Bebout[1], Marilyn L. Fogel[2], and Pierre Cartigny[3]

1811-5209/13/0009-333$2.50 DOI: 10.2113/gselements.9.5.333

Aquamarine (beryl) and muscovite crystals; these minerals store organic-sourced nitrogen as molecular nitrogen and ammonium, respectively. ARKENSTONE SPECIMEN (4.9 × 4.0 × 3.2 CM) AND PHOTO (WWW.IROCKS.COM)

Nitrogen exhibits an intriguing combination of highly volatile behavior (particularly as N_2), appreciable reactivity, and surprising compatibility in the deep Earth. Nitrogen is incorporated into the biosphere and then, through diagenesis and low-grade metamorphism, is conveyed into the lithosphere and the deeper Earth. The investigation of N behavior in the biosphere, hydrosphere, and atmosphere has led to many important discoveries regarding biogeochemical pathways, including in areas such as trophic interactions and anthropogenic impacts on terrestrial and marine environments (e.g. nutrient pollution, eutrophication). Nitrogen can act as an excellent tracer of the transfer of sedimentary/organic materials into and within deep-Earth reservoirs and shows great potential as a tracer of life on early Earth and elsewhere in the Solar System.

KEYWORDS: nitrogen isotope, ammonium, biogeochemical cycling, biosphere, extraterrestrial life, metamorphism

INTRODUCTION

Nitrogen (N), one of the most abundant elements in our galaxy and the Solar System, makes up 78% of Earth's atmosphere by volume. It is depleted in the inner, rocky planets (including Earth) relative to the remainder of the Solar System and is in general concentrated into atmospheres on planets and moons. Nitrogen was discovered independently by Daniel Rutherford, Carl Wilhelm Scheele, and Antoine Lavoisier in the 1770s and was regarded by each as an extremely inert/unreactive gas (noncombustible and non-life-supporting). Lavoisier (1790) referred to nitrogen as *azote*, from the Greek word αζωτος meaning "lifeless," and this term became the French word for nitrogen. The English word *nitrogen* came from the French *nitrogène*, coined in 1790 by French chemist Jean-Antoine Chaptal from the Greek *nitron* (sodium carbonate) and the French *gène* (producing), referring to its occurrence in nitric acid, in turn formed from saltpeter then known as *nitre*. Nitrogen consists of two stable isotopes, ^{14}N and ^{15}N, with abundances of 99.636% and 0.364%, respectively. Stable isotope compositions of nitrogen are expressed as ratios of $^{15}N/^{14}N$ relative to a standard, the latter generally N_2 in Earth's atmosphere. The conventional notation for expressing nitrogen isotope compositions, in ‰ (delta notation), is: $\delta^{15}N$ (‰ versus atmospheric N_2) = $[(^{15}N/^{14}N_{sample} \div {}^{15}N/^{14}N_{AIR\text{-}N_2}) - 1] \times 1000$.

Despite its relatively inert and volatile behavior (particularly as N_2), nitrogen is an essential element for all living organisms and is central in the structure of amino acids, proteins, nucleic acids, and other substances vital to life. Living organisms have evolved an array of biochemical pathways for taking up and "processing" atmospheric N_2, along with nitrogen in all its other oxidation states (FIG. 1), in part conveying it into the lithosphere through sedimentation and diagenesis. The strong redox dependency of N results in its speciation into several important molecules other than N_2, including NH_4^+ (ammonium), NH_3 (ammonia), and NO_3^- (nitrate). This speciation increases its reactivity in both biotic and abiotic settings and produces significant stable isotope fractionation in the major Earth reservoirs (Busigny and Bebout 2013 this issue). Its association with life on Earth makes nitrogen a compelling element for consideration in our search for life elsewhere in the Solar System, leading to the mantra "Follow the nitrogen" (see Capone et al. 2006; Fogel and Steele 2013 this issue). In this paper, we highlight some directions for future research in the growing field of nitrogen (biogeocosmo)chemistry.

DISTRIBUTION ON EARTH

One common misperception is that nitrogen on Earth is dominantly in the atmosphere, and if we consider only the surface and near-surface environment, this is certainly true. Most work on nitrogen abundances and isotopic compositions has been done on surface/near-surface, low-temperature environments, even though the fraction of Earth's nitrogen in biomass, soils, and the oceans is very low (likely <1%; Chapin et al. 2002). Depending on the exact sizes of the nitrogen reservoirs in the mantle and crust, the atmospheric reservoir could constitute only about 25–30% of the Earth's nitrogen inventory (TABLE 1). Unfortunately, the sizes of the crust and mantle reservoirs are poorly constrained, relying on very small numbers of analyses of appropriate materials and/or mass-balance calculations and assumptions regarding incompatibility during partial melting (Busigny and Bebout 2013). It appears that N_2 in Earth's atmosphere has been at or near modern concentrations since the very early stages of degassing (Zhang and Zindler 1993; Tolstikhin and Marty 1998); however, some have suggested that the atmosphere on the earliest Earth was somewhat more concentrated

---

[1] Department of Earth and Environmental Sciences
Lehigh University, Bethlehem, PA 18015, USA
E-mail: geb0@lehigh.edu

[2] School of Natural Sciences,
University of California, Merced, CA 95343, USA
E-mail: mfogel@ucmerced.edu

[3] Laboratoire de Géochimie des Isotopes Stables
Institut de Physique du Globe de Paris, Sorbonne Paris Cité, Univ. Paris Diderot, UMR 7154 CNRS, 1 rue Jussieu, 75238 Paris, France
E-mail: cartigny@ipgp.fr

in N_2 (Boyd 2001; Goldblatt et al. 2009; see the potentially conflicting evidence presented by Marty et al. 2013). According to Goldblatt et al. (2009), N_2 levels in the early-Earth atmosphere could have been decreased by the onset of biological activity and incorporation of organic nitrogen into rapidly forming continental crust, an intriguing concept. Unfortunately, work on nitrogen inventories on the Moon, aimed at identifying indigenous/endogenic and exogenic components, has been greatly limited by the scarcity of lunar rock samples and analytical challenges associated with very low nitrogen concentrations in these rocks (see Marty et al. 2003).

RECENT RESEARCH ON NITROGEN ON EARTH AND IN THE SOLAR SYSTEM

Research papers published on nitrogen isotopes and associated nitrogen cycling for 2012 to mid-2013 (from a Web of Knowledge search with "nitrogen isotope" in the title) can be broken down into the following research categories:

- trophic interactions (terrestrial and marine combined), food webs [**43**]
- terrestrial ecosystems, watershed studies, limnology [**32**]
- anthropogenic effects (pollution of air, water) [**19**]
- atmosphere, aerosols, precipitation [**13**]
- ocean cycling – modern [**10**]
- methods for nitrogen isotope measurements [**6**]
- deep Earth (diamond/mantle, hydrothermal deposits, igneous/metamorphic rocks, volcanic gases) [**5**]
- forensic applications [**5**]
- experiments and theoretical studies [**3**]
- ancient-Earth atmosphere/ocean (oxygenation of the atmosphere, etc.) [**2**]
- extraterrestrial (meteorites, comets, lunar rocks, solar wind) [**0**]

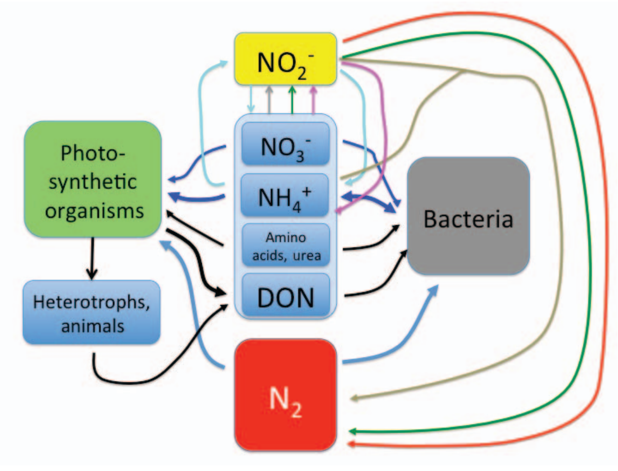

FIGURE 1 Photosynthetic organisms compete with bacteria (and vice versa) for inorganic N-containing nutrients (blue lines). Simple organic compounds, like urea and amino acids, are often taken up by plants and phytoplankton, a process that is more common than once thought (black lines). Nitrogen fixation is important for both groups of organisms, much more so than was previously considered (pale blue lines) (Zehr and Ward 2002).

Nitrite (NO_2^-) is a key molecule in many microbial reactions between NH_4 and NO_3^-: nitrification and denitrification (turquoise lines), as well as the more recently discovered pathways of anammox (light brown lines), NO dismutation (red lines), and denitrification (green lines). Dissimilatory nitrate reduction (purple lines) occurs in many deep-sea, hydrothermal areas (Kraft et al. 2011). DON = dissolved inorganic nitrogen

From this quick survey, one sees that most of the recent work on nitrogen isotopes is centered on modern ecosystems, trophic interactions and transfers, and anthropogenic effects. Far fewer studies focus on higher-temperature systems, ancient-Earth atmospheric evolution, and extraterrestrial materials.

EARTH'S SURFACE AND NEAR SURFACE

> "By the end of the nineteenth century, humans had discovered nitrogen and the essential components of the nitrogen cycle. In other words, they then knew that some microorganisms convert N_2 to NH_4, other microorganisms convert NH_4 to NO_3, and yet a third class of microorganisms convert NO_3 back to N_2, thus completing the cycle."
>
> –Galloway (2003)

Although high-temperature fractionations can produce significant shifts in nitrogen isotope composition in melt–fluid–rock settings (Busigny and Bebout 2013), it is the low-temperature nitrification/denitrification reactions that produce the largest stable isotope fractionations. With more than 30‰ natural variability observed in sedimentary and biological systems, this nitrogen is then conveyed into continental crust and into the mantle, in the latter case via subduction (Holloway and Dahlgren 2002; Cartigny and Marty 2013 this issue). FIGURE 1 shows a framework of key biological reactions in this cycle, involving N fixation, assimilation, nitrification, decomposition, ammonification, and denitrification. In the past decade, microbiologists have identified several new pathways that show the depth and complexity of the ways that organisms process this important, and often limiting, nutrient (Zehr and Ward 2002; Canfield et al. 2010; Fogel 2010; Kraft et al. 2011). The isotopic compositions of the different nitrogen phases are key tools for understanding surface processes and the microbes that carry out the specialized reactions.

Recent research on surface nitrogen biogeochemistry has emphasized the ways in which anthropogenic nitrogen is being processed through the atmosphere, groundwater, stream networks, and the oceans. As discussed in Hastings et al. (2013 this issue), humans have doubled the amount of reactive nitrogen in the Earth system over a very short time period (the last 200 years)—this complicates comparisons of modern nitrogen cycling with records of nitrogen biogeochemistry on the ancient Earth (Thomazo and Papineau 2013 this issue; Cartigny and Marty 2013). It is unclear how this anthropogenic loading of nitrogen will alter the biogeochemical pathways in the oceans and be recorded in sediments and the future sedimentary rock record.

NITROGEN IN MINERALS AND ROCKS

Holloway and Dahlgren (2002) summarized the history of analyses of nitrogen in minerals and rocks and the methods by which nitrogen concentrations and isotopic compositions have been determined. Early reports of nitrogen in rock systems and volcanic gases date back to Rayleigh (1939) and Hutchinson (1944). Analyses of mineral and rock concentrations and $\delta^{15}N$ originated with studies by Hoering (1955), who also presented the earliest analyses of biological (e.g. rats and plants) and nonbiological Earth materials (e.g. petroleum, coal, igneous rocks). Work by Mayne (1957), Scalan (1958), and Stevenson (1962) followed these pioneering studies, and applications of nitrogen isotopes expanded considerably in the 1970s and 1980s, notably by the former East German group in Leipzig (e.g. Haendel et al. 1986). The methods for analyzing small amounts of nitrogen, in general requiring laborious extraction methods and high-sensitivity mass spectrometry, have restricted the number of applications of nitrogen isotopes in silicate rock systems. The isotope analyses have been achieved largely by static or dual-inlet, dynamic gas-source mass spectrometry, more recently employing carrier gas and SIMS methods (see Analytical Box in Cartigny and Marty 2013).

GREAT STABILITY OF NITROGEN IN SILICATE MINERALS TO HIGH TEMPERATURES AND PRESSURES

The chemical reactivity of nitrogen results in its incorporation into numerous mineral phases, often as NH_4^+, resulting in the potential for long-term storage in the solid Earth (Busigny and Bebout 2013). Incorporation into clay minerals of nitrogen released from organic matter during diagenesis (as NH_4^+) initiates the key pathway for nitrogen in the biosphere to enter the deep Earth (Boyd 2001; Fig. 2). The close association of nitrogen with potassium (K) in various minerals reflects the tendency for NH_4^+ to substitute for K^+ in many minerals, including the silicates (Honma and Itihara 1981). Palya et al. (2011) demonstrated the extraordinary retention of nitrogen, with what appeared to be sedimentary/organic elemental C/N ratios, in rocks that had experienced multiple partial melting reactions (up to 850 °C at 2–4 kilobars pressure, the latter corresponding to depths of ~5–15 km). In these rocks, cordierite in the partial melting residues contains appreciable amounts of N_2 in its channels. Although these observations point to the feasibility of long-term nitrogen storage to even greater depths in the continental crust (see Boyd 2001; Goldblatt et al. 2009), the paucity of data for appropriate rocks makes it difficult to estimate the size of the continental crust nitrogen reservoir (Rudnick and Gao 2003; Goldblatt et al. 2009; Palya et al. 2011; Table 1). The significance of nitride for nitrogen storage in the mantle remains underexplored, as is the possibility that significant amounts of nitrogen are stored in the crust in microporous mineral phases such as cordierite and beryl (see Lazzeri et al. 2011 and discussion by Busigny and Bebout 2013).

DEEP-EARTH NITROGEN CYCLING

Boyd (2001) provided a holistic synthesis of whole-Earth nitrogen cycling (Fig. 2), with emphasis on the biosphere and incorporation of biologically fixed nitrogen into the silicate Earth. He also included the concept of biologically mediated uptake of nitrogen from the atmosphere into the crust over geological time (a concept expanded upon by Goldblatt et al. 2009). A large fraction of Earth's nitrogen probably resides in the mantle (Busigny and Bebout 2013), with subduction as the only significant mechanism for conveying surface nitrogen, presumably largely in sediment and variably altered oceanic crust, to mantle depths. In their review of the fate of nitrogen in the mantle, Cartigny and Marty (2013) suggest that the recycling of nitrogen into the mantle exceeds outgassing flux: the Earth's mantle presently stores more nitrogen than it looses. Based on a study of high-pressure and ultrahigh-pressure metamorphic rocks (Bebout et al. 2013) and studies of nitrogen return at individual volcanic arcs (Mitchell et al. 2010), >50% of the initially subducted nitrogen (in sediments and altered oceanic crust) could be transported to depths in the mantle beyond those experienced by subducting slabs beneath volcanic arcs (~100 km; see discussions by Li and Bebout 2005; Elkins et al. 2006; Mitchell et al. 2010). This could imply that the mantle is currently accumulating nitrogen; however, the fact that mantle-derived igneous rocks and diamonds have fairly uniform $\delta^{15}N$ values near –5‰ could reflect a relatively small input to the mantle of nitrogen with elevated $\delta^{15}N$ inherited from shallow processes. Another possibility is that sedimentary/organic nitrogen with positive $\delta^{15}N$ is preferentially delivered into volcanic arcs (Elkins et al. 2006), leaving the low-$\delta^{15}N$ nitrogen in subducting oceanic lithosphere to contribute to the mantle nitrogen inventory (Li et al. 2007; see a contrasting view by Busigny et al. 2011, who proposed that oceanic crust has a positive bulk $\delta^{15}N$ value).

EARLY-EARTH RECORDS OF ATMOSPHERIC OXYGENATION

Studies employing nitrogen isotopes to evaluate ancient-Earth atmospheric evolution have proliferated. Some of these correlate the behavior of nitrogen with that of other elements of biological interest (e.g. Fe, Mo, S, C isotopes; Thomazo and Papineau 2013). A more robust interpretation of nitrogen records in rocks billions of years old will require additional information regarding the preservation of ancient $\delta^{15}N$ records through diagenesis and low-grade metamorphism and will have to evaluate issues of contamination and syngenicity (i.e. whether a textural, chemical, mineral, or biological feature formed at the same time as the encapsulating material). Interestingly, however, many metamorphosed sedimentary rocks, even those subjected to high-grade metamorphism and partial melting, appear to preserve carbon and nitrogen concentrations (and thus C/N) and isotopic compositions resembling those of their protoliths (Palya et al. 2011). Further work on early-Earth nitrogen biogeochemical cycling should also take into account the varying sedimentological settings of the relatively small number of Archean metasedimentary suites, as significant variability is observed on the modern Earth among different settings (e.g. related to varying redox conditions; see Quan et al. 2013).

STUDY OF EXTRATERRESTRIAL NITROGEN

In this issue, Fogel and Steele (2013) provide an overview of the work on nitrogen in extraterrestrial materials that could elucidate the evolution of the Solar System and planets and potentially help focus efforts in the search for extraterrestrial life. Future work will be stimulated by the recent

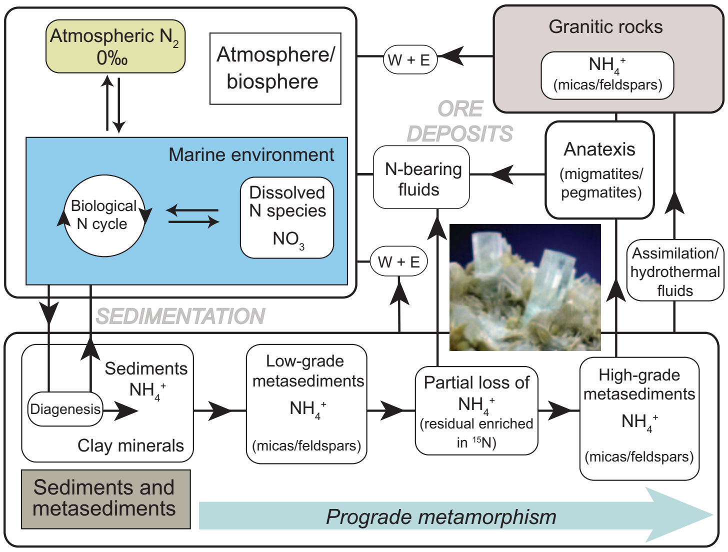

Figure 2 Diagram illustrating the surface–deep-Earth cycling of nitrogen through deposition, diagenesis, metamorphism, and melting of sediment (modified after Boyd 2001; see also Holloway and Dahlgren 2002). W + E = weathering and erosion. Inset photograph shows a beryl–muscovite intergrowth. Beryl and muscovite store organic-sourced nitrogen as N_2 and ammonium, respectively (Lazzeri et al. 2011; Busigny and Bebout 2013). Photo courtesy of Desert Winds Gems and Minerals (www.desertwindsgemsandminerals.com)

TABLE 1 ESTIMATES OF THE MODERN-EARTH NITROGEN BUDGET, SHOWING THE VARIOUS RESERVOIRS, THEIR SIZES, AND THEIR PERCENT OF NITROGEN[1]

	Reservoir size (10^{21} g)	% in reservoir
Goldblatt et al. (2009)		
Atmosphere	4	27.0
Continental crust	2.1	14.2
Oceanic crust	0.32	2.2
Mantle	8.4	56.7
TOTALS	**14.82**	**100**
Galloway (2003) – surface/near surface only		
Atmosphere	3.95	79.5
Sedimentary rocks	1	20.1
Ocean N_2	0.02	0.4
Ocean NO_3^-	0.00057	0.01147
Soil organics	0.00019	0.00382
Land biota	0.00001	0.00020
Marine biota	0.0000005	0.00001
TOTALS	**4.97**	**100**

	Reservoir size (10^{21} g)	% in reservoir
Palya et al. (2011)[2]		
Atmosphere	3.9	30.1
Continental crust	1.1	8.5
Oceanic crust	no estimate	
Upper mantle	0.17	1.3
Lower mantle	7.8	60.1
Deep ocean	0.0006	0.00463
Surface ocean	0.00006	0.00046
Soils	0.0001	0.00077
Biomass	0.0000043	0.00003
Marine biota	0.0000003	0.000002
Terrestrial vegetation	0.000004	0.00003
TOTALS	**12.97**	**100**

1 From Chapin et al. (2002); Galloway (2003); Kerrich et al. (2006); Goldblatt et al. (2009); Palya et al. (2011)

2 The compilation of Palya et al. (2011) incorporates estimates from Kerrich et al. (2006) and Chapin et al. (2002).

discovery that the solar wind is very depleted in ^{15}N ($\delta^{15}N \approx -400‰$; Marty et al. 2011). This observation indicates a similar depletion in ^{15}N in the modern Sun and the protosolar nebula and sheds new light on the very wide range of $\delta^{15}N$ values in meteorites (for example, in iron meteorites and among the different classes of meteorites). The emerging picture for the evolution of nitrogen in the Solar System involves a ^{15}N-depleted protosolar nebula, likely dominated by silicates, and a ^{15}N-enriched end-member represented by organic matter and most comets.

Goals for work on nitrogen on Mars include evaluating the modern and ancient inventories of nitrogen, in both surface/near-surface and deep planetary reservoirs (Jakosky and Phillips 2001; Fogel and Steele 2013), and determining the degree and timing of the volatilization of nitrogen into space and its associated isotope fractionation. There has been considerable interest in nitrogen as a potentially key element in developing strategies for the search for signs of life on Mars. Related work has included biogeochemical studies of modern environments on Earth that are similar to modern Mars environments (e.g. gypsum sand dunes); the study of ancient-Earth nitrogen biogeochemical cycling, which could have resembled that on Mars given the likelihood that surface conditions on Mars were similar to those on Earth during the Archean (Thomazo and Papineau 2013); and work on hydrothermal and microbial activity associated with impact craters on Earth (Osinski et al. 2013). A number of minerals common on Earth are likely to be present and possibly abundant on the surface of Mars, most notably phyllosilicates (Bish et al. 2003)—which are known on Earth to incorporate significant amounts of organically derived nitrogen as NH_4^+— but also mineral phases such as zeolites and even sulfates such as jarosite, capable of incorporating nitrogen as N_2 and NH_4^+, respectively. A large part of Mars's surface is home to hydrothermally altered (palagonitized) basaltic rocks; on Earth, basalts palagonitized on the seafloor are enriched in

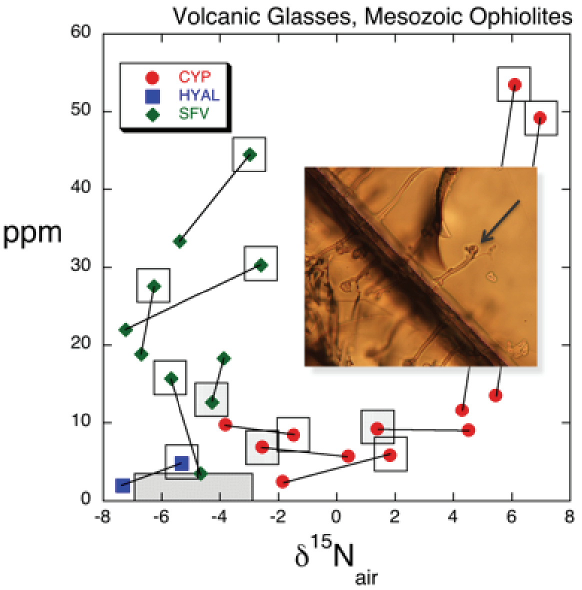

FIGURE 3 Nitrogen concentrations and isotopic compositions of volcanic glasses showing more alteration (in square boxes) and less alteration (no boxes, connected by lines to more altered glass from the same sample), as judged microscopically from varying amounts of palagonite developed on edges of grains. Samples are from Cyprus (CYP) and the Stonyford Volcanics, California (SFV). HYAL = glass from hyaloclastites from Cyprus. Data from Lazzeri et al. (2011). Note that, in most cases, the more altered glass has a higher nitrogen concentration and higher $\delta^{15}N$ value (gray squares indicate lower $\delta^{15}N$ values). Note also that the SFV glasses retain near "mantle values" of $\delta^{15}N$ (–5 ± 2‰; gray-shaded box in lower left of figure; see Cartigny and Marty 2013) despite nitrogen enrichment, possibly reflecting incorporation of nitrogen degassing from the crystallizing and cooling volcanic rocks. The inset photomicrograph is of putative microbial ichnofossils near a palagonitized fracture (the latter oriented from upper left to lower right) in glass from the Stonyford Volcanics (horizontal dimension is 200 μm; example of putative microbial feature is indicated by arrow). PHOTOGRAPH COURTESY OF M. R. M. IZAWA AND N. R. BANERJEE

nitrogen that is interpreted to be of sedimentary/organic origin, based on stable isotope compositions (Busigny et al. 2005; Li et al. 2007; and analyses of palagonitized volcanic-glass separates by Bebout et al. 2012; Fig. 3).

TOWARD MORE QUANTITATIVE APPLICATIONS

The study of microbes continues to reveal innovative pathways for cycling nitrogen and remains an active area of research. The terrestrial environment, now overwhelmingly impacted by human activities with respect to nitrogen cycling, is changing rapidly, and understanding these changes is critical for predicting future climate patterns. For the solid Earth, more quantitative applications of nitrogen isotopes to high-temperature fluid–rock problems require further constraints on relevant isotope fractionation factors in both experimental measurements and theoretical calculations (Busigny and Bebout 2013). Particularly for the mantle, because of its immense volume, minor uncertainty in the average nitrogen concentration produces huge differences in the calculated distribution of nitrogen on Earth. Better constraints on the concentration and isotopic composition of nitrogen in continental crust are necessary for evaluating the significance of contemporaneous crust formation and evolution of the biosphere.

ACKNOWLEDGMENTS

We acknowledge the contributions of Stuart R. Boyd (deceased), to this field in general and in helping with the initial conceptualization of a journal issue or book on this topic. We thank Pierrette Tremblay and Tim Drever for their assistance at all stages of this publication project and we thank David Velinsky and JoAnn Holloway for their constructive reviews of this manuscript. Funding from the National Science Foundation (most recently, EAR-0711355, to GEB) supported the nitrogen isotope work conducted at Lehigh University.

We dedicate this issue to Thomas C. Hoering, the father of nitrogen geochemistry. Hoering made some of the first nitrogen isotope measurements, taught several generations of scientists, and left his mark on everything "nitrogen" from igneous rocks to microbes.

REFERENCES

Bebout GE and 6 coauthors (2012) Nitrogen concentrations and isotopic compositions of altered terrestrial glassy basaltic rocks, and implications for astrobiology. Proceedings of the 2012 Astrobiology Conference (AbSciCon), Atlanta, Georgia, April 16–20

Bebout GE, Agard P, Kobayashi K, Moriguti T, Nakamura E (2013) Devolatilization history and trace element mobility in deeply subducted sedimentary rocks: Evidence from Western Alps HP/UHP suites. Chemical Geology 342: 1-20

Bish DL, Carey JW, Vaniman DT, Chipera SJ (2003) Stability of hydrous minerals on the martian surface. Icarus 164: 96-103

Boyd SR (2001) Nitrogen in future biosphere studies. Chemical Geology 176: 1-30

Busigny V, Bebout GE (2013) Nitrogen in the silicate Earth: Speciation and isotopic behavior during mineral–fluid interactions. Elements 9: 353-358

Busigny V, Ader M, Cartigny P (2005) Quantification and isotopic analysis of nitrogen in rocks at the ppm level using sealed tube combustion technique: A prelude to the study of altered oceanic crust. Chemical Geology 223: 249-258

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

Canfield DE, Glazer AN, Falkowski PG (2010) The evolution and future of Earth's nitrogen cycle. Science 330: 192-196

Capone DG, Popa R, Flood B, Nealson KH (2006) Follow the nitrogen. Science 312: 708-709

Cartigny P, Marty B (2013) Nitrogen isotopes and mantle geodynamics: The emergence of life and the atmosphere–crust–mantle connection. Elements 9: 359-366

Chapin FS III, Matson PA, Mooney HA (2002) Principles of Terrestrial Ecosystem Ecology. Springer, New York, 450 pp

Elkins LJ, Fischer TP, Hilton DR, Sharp ZD, McKnight S, Walker J (2006) Tracing nitrogen in volcanic and geothermal volatiles from the Nicaraguan volcanic front. Geochimica et Cosmochimica Acta 70: 5215-5235

Fogel ML (2010) Variations of abundances of nitrogen isotopes in nature. In: The Encyclopedia of Mass Spectrometry Volume 5, Elsevier, Amsterdam, pp 842-852

Fogel ML, Steele A (2013) Nitrogen in extraterrestrial environments: Clues to the possible presence of life. Elements 9: 367-372

Galloway JN (2003) The global nitrogen cycle. Treatise on Geochemistry, Elsevier, Chapter 8.12

Goldblatt C, Claire MW, Lenton TM, Matthews AJ, Watson AJ, Zahnle KJ (2009) Nitrogen-enhanced greenhouse warming on early Earth. Nature Geoscience 2: 891-896

Haendel D, Mühle K, Nitzsche H-M, Stiehl G, Wand U (1986) Isotopic variations of the fixed nitrogen in metamorphic rocks. Geochimica et Cosmochimica Acta 50: 749-758

Hastings MG, Casciotti KL, Elliott EM (2013) Stable isotopes as tracers of anthropogenic nitrogen sources, deposition, and impacts. Elements 9: 339-344

Hoering TC (1955) Variations of nitrogen-15 abundance in naturally occurring substances. Science 122: 1233-1234

Holloway JM, Dahlgren RA (2002) Nitrogen in rock: Occurrences and biogeochemical implications. Global Biogeochemical Cycles 16: doi:10.1029/2002GB001862

Honma H, Itihara Y (1981) Distribution of ammonium in minerals of metamorphic and granitic rocks. Geochimica et Cosmochimica Acta 45: 983-988

Hutchinson GE (1944) Nitrogen in the biogeochemistry of the atmosphere. American Scientist 32: 178-195

Jakosky BM, Phillips RJ (2001) Mars' volatile and climate history. Nature 412: 237-244

Kerrich R, Jia Y, Manikyamba C, Naqvi SM (2006) Secular variations of N isotopes in terrestrial reservoirs and ore deposits. Geological Society of America Memoir 198: 81-104

Kraft B, Strous M, Tegetmeyer HE (2011) Microbial nitrate respiration – Genes, enzymes and environmental distribution. Journal of Biotechnology 155: 104-117

Lavoisier A (1790) Elements of Chemistry, trans. Robert Kerr (Edinburgh, 1790; New York: Dover, 1965), 52 pp

Lazzeri KE, Bebout GE, Geiger CA, Idleman BD, Li L (2011) Storage of nitrogen in cyclosilicates beryl and cordierite: Nitrogen cycling, isotope fractionation, and fluid-rock interactions. American Geophysical Union 2011 Fall Meeting Abstract V11A-2494

Li L, Bebout GE (2005) Carbon and nitrogen geochemistry of sediments in the Central American convergent margin: Insights regarding paleoproductivity and carbon and nitrogen subduction fluxes. Journal of Geophysical Research 110: B11202, doi:10.1029/2004JB003276

Li L, Bebout GE, Idleman BD (2007) Nitrogen concentration and δ^{15}N of altered oceanic crust obtained on ODP Legs 129 and 185: Insights into alteration-related nitrogen enrichment and the nitrogen subduction budget. Geochimica et Cosmochimica Acta 71: 2344-2360

Marty B, Hashizume K, Chaussidon M, Wieler R (2003) Nitrogen isotopes on the Moon: Archives of the solar and planetary contributions to the inner Solar System. Space Science Reviews 106: 175-196

Marty B, Chaussidon M, Wiens RC, Jurewicz AJG, Burnett DS (2011) A ^{15}N-poor isotopic composition for the Solar System as shown by Genesis solar wind samples. Science 332: 1533-1536

Marty B, Zimmermann L, Pujol M, Burgess R, Philippot P (2013) Nitrogen isotopic composition and density of the Archean atmosphere. Science 342: 101-104

Mayne KI (1957) Natural variations in the nitrogen isotope abundance ratio in igneous rocks. Geochimica et Cosmochimica Acta 12: 185-189

Mitchell EC and 7 coauthors (2010) Nitrogen sources and recycling at subduction zones: insights from the Izu–Bonin–Mariana arc. Geochemistry Geophysics Geosystems 11 (2): http://dx.doi.org/10.1029/2009GC002783

Osinski GR and 12 coauthors (2013) Impact-generated hydrothermal systems on Earth and Mars. Icarus 224: 347-363

Palya AP, Buick IS, Bebout GE (2011) Storage and mobility of nitrogen in the continental crust: Evidence from partially melted metasedimentary rocks, Mt. Stafford, Australia. Chemical Geology 281: 211-226

Quan TM, Wright JD, Falkowski PG (2013) Co-variation of nitrogen isotopes and redox states through glacial-interglacial cycles in the Black Sea. Geochimica et Cosmochimica Acta 112: 305-320

Rayleigh L (1939) Nitrogen, argon, and neon in the earth's crust with application to cosmology. Philosophical Transactions of the Royal Society of London A 170: 451-464

Rudnick RL, Gao A (2003) Composition of the continental crust. In: Holland HD, Turekian KK (eds) Treatise on Geochemistry 3. Elsevier, Amsterdam, pp 1-64

Scalan RS (1958) The isotopic composition, concentration, and chemical state of the nitrogen in igneous rocks. PhD dissertation, University of Arkansas

Stevenson FJ (1962) Chemical state of the nitrogen in rocks. Geochimica et Cosmochimica Acta 26: 797-809

Thomazo C, Papineau D (2013) Biogeochemical cycling of nitrogen on the early Earth. Elements 9: 345-351

Tolstikhin IN, Marty B (1998) The evolution of terrestrial volatiles: a view from helium, neon, argon and nitrogen isotope modelling. Chemical Geology 147: 27-52

Zehr JP, Ward BB (2002) Nitrogen cycling in the ocean: New perspectives on process and paradigms. Applied Environmental Microbiology 68: 1015-1024

Zhang Y, Zindler A (1993) Distribution and evolution of carbon and nitrogen in Earth. Earth and Planetary Science Letters 117: 331-345 ▪