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Nitrogen and Its (Biogeocosmo) Chemical Cycling

Guest Editors: Gray E. Bebout, Marilyn L. Fogel, and Pierre Cartigny

Nitrogen: Highly Volatile yet Surprisingly Compatible
Gray E. Bebout, Marilyn L. Fogel, and Pierre Cartigny

Stable Isotopes as Tracers of Anthropogenic Nitrogen Sources, Deposition, and Impacts
Meredith G. Hastings, Karen L. Casciotti, and Emily M. Elliott

Biogeochemical Cycling of Nitrogen on the Early Earth
Christophe Thomazo and Dominic Papineau

Nitrogen in the Silicate Earth: Speciation and Isotopic Behavior during Mineral–Fluid Interactions
Vincent Busigny and Gray E. Bebout

Nitrogen Isotopes and Mantle Geodynamics: The Emergence of Life and the Atmosphere–Crust–Mantle Connection
Pierre Cartigny and Bernard Marty

Nitrogen in Extraterrestrial Environments: Clues to the Possible Presence of Life
Marilyn L. Fogel and Andrew Steele

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This is my final editorial for Elements: it seems a good moment to look back on my experiences with the magazine. My first awareness of it came when Rod Ewing gave a presentation to the Geochemical Society Board of Directors (I was vice president at the time) at the Kurashiki Goldschmidt in 2003. I must admit I was not enthusiastic. The GS had just put a major effort (thanks largely to Carla Koresky and Johnson Haas) into upgrading the Geochemical News, which I was reluctant to abandon, and I wondered who among us would have the time and experience necessary to launch a completely new magazine. The idea was attractive, but were there enough good topics and people willing to be guest editors for the long haul?

A year later I attended another meeting, this time of the presidents (or their representatives) of what became the five original sponsoring societies of Elements. Again Rod presented the concept, but this time Pierrette Tremblay was in attendance and, thanks largely to Pierrette, there was a detailed business plan, with projections for all the likely costs and the subscriptions we would need to cover them until (we hoped) advertising revenues would pick up. Rod convinced us all that his idea was viable. Elements was Rod Ewing’s baby, and it is thanks to his persistence that it came into being.

I have been asked several times at meetings: “Who is your publisher? Is it Elsevier?” The answer is that Elements is self-published by the participating societies. MSA is the publisher of record acting on behalf of the participating societies, and handles mailings, subscriptions, finances, and contracts on their behalf. I have the impression that the membership of our societies actually reads and enjoys the magazine.

The big impending change, though, is the retirement of Pierrette Tremblay as managing editor. She, more than anyone else, is responsible for the success of the magazine, from the quality of its appearance to the fact that it actually comes out on time six times a year. It is hard to imagine finding someone who will do all she does now (and has a copyediting partner!). But then, I was originally skeptical about the whole concept of Elements. Now that Pierrette has moved on and I have returned to the required reporting, but essentially everything else is handled by Pierrette Tremblay. She keeps the editors on track, does the layout work in collaboration with the graphic artist, lines up advertisers, contacts printers and does numerous other tasks that come along. Copyediting and proofreading are largely the work of her husband, Thomas Clark, whose mostly volunteer efforts have contributed enormously to the magazine. Another question I get asked at conferences is: “Who do you think is going to go through the membership lists of all (now) 17 societies, identify the duplicates, work up a new mailing list, and proportionately charge each society accordingly?” While the simple task of eliminating duplicate mailings is done, and all societies share in that cost savings, producing a subscription list for rebilling would end up costing more than any imagined savings.

The magazine is now at something of a turning point. Our fiftieth issue came out earlier this year, and the five original sponsoring societies have grown to seventeen. The increased subscription base plus advertising revenues make our finances secure. Rather than running out of topics, we have been receiving so many proposals that we have had to change the way we manage acceptances and scheduling. In the past, we evaluated proposals as they came in, and after they were accepted (usually after iterations with the proposer) they were put in the queue to be scheduled for publication. We had been receiving so many good proposals that the queue had become unreasonably long: guest editors are not happy if you tell them that their issue will be scheduled three years from now. We now schedule one year at a time, which I think will have several advantages. The magazine has become appreciated in the mineralogical and geochemical community. Well-known figures are eager to be guest editors and to write articles when asked—and to become principal editors. I have the impression that the membership of our societies actually reads and enjoys the magazine.

The big impending change, though, is the retirement of Pierrette Tremblay as managing editor. She, more than anyone else, is responsible for the success of the magazine, from the quality of its appearance to the fact that it actually comes out on time six times a year. It is hard to imagine finding someone who will do all she does now (and has a copyediting partner!). But then, I was originally skeptical about the whole concept of Elements. Now that Pierrette has done all the hard work of establishing the magazine, I am confident that Elements will continue to be a success in the future. I hope future principal editors find the experience as rewarding as I have.

James I. Drever*
(drever@uwyo.edu)

* Principal editor in charge of this issue

Some Parting Thoughts
THIS ISSUE
Most people associate the word nitrogen with the air we breathe, the fertilizers we use for growing our flowers and vegetables, and perhaps algal blooms in our lakes and rivers. There would certainly have been more than enough thematic material for an issue on the nitrogen cycle at the Earth’s surface. However, Guest Editors Gray Bebout, Marilyn Fogel, and Pierre Cartigny chose to focus on the large-scale cycle of nitrogen, ranging from the cosmos to the deep Earth and its surface. How did our atmosphere come to be made up of 78% nitrogen? Even though nitrogen is present only in trace amounts in minerals, this is where most nitrogen is stored. An interesting perspective, indeed!

ELEMENTS AT GOLDSCHMIDT
We thank Russell Rajendra and Kevin Murphy of the Mineralogical Society for staffing the Elements booth during the Goldschmidt Conference in Florence. The original plan was that the Mineralogical Society would help to man the Elements booth along with staffing their own booth. Early on during the conference, Russell decided to merge the booths together in the Elements location. The booth was well located near the front door and the registration desk, so traffic was good. Thanks also to the principal editors and members of the Executive Committee who spent time at the booth and answered questions. And thanks to the many visitors who came over to say how much they liked the magazine and the articles in it.

BUSINESS AS USUAL
As you will read in the advertisement in the next column, I have decided to step down at the end of 2014. I still love doing this job, and for me it is business as usual until December 2014. I am convinced that there is someone out there perfectly suited to take over, who will think as I do that this is the best job in the world—and who will have the energy to take Elements to greater heights in its second decade.

Pierrette Tremblay, Executive Editor

FROM THE EXECUTIVE COMMITTEE
Surrounded by exquisite art, delectable cuisine, and fascinating science, members of the Executive Committee of Elements diligently met for their annual meeting on August 26, 2013. Representatives from fourteen of the seventeen participating societies spent the afternoon discussing our most pressing issue: the upcoming retirement of our one-and-only managing editor, Ms. Pierrette Tremblay. It was a bittersweet afternoon as we celebrated nearly ten years of publication and Elements’ success, but we now look to a new future without the guiding hand and dedication of Pierrette. With Elements from the first issue, she helped Elements grow, providing the care she would extend to a family member, and she has placed Elements as a must-read for mineralogists, petrologists, and geochemists. We begin the search for her replacement now; it will take time to identify the best possible choice and have this person overlap with Pierrette to learn at least a portion of her job. As the list of her duties grew, it became apparent that she was more than a managing editor—likely three people wrapped into one. Better late than never… she’s been promoted to executive editor!

Although the position is now advertised—see the ad below—she is not leaving for another year! This month, we will celebrate her achievement by bestowing on her the MSA Distinguished Service Award, in part for her key role in the development and success of Elements.

Barb Dutrow, Chair of the Executive Committee
Quantifying Metamorphic Fabrics

FEI’s Automated Mineralogy technology is helping petrologists unravel the many and varied geological events that metamorphic rocks have undergone.

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The image is of a garnet-mica schist from Brittnay, France. Microtextures suggest the rock has undergone high-grade, regional metamorphism with associated poly-deformation. Image courtesy of Michael Garrick.
IMA MEDAL AWARDED TO NICK SOBOLEV

The International Mineralogical Association has awarded its 2013 Medal of Excellence in Mineralogical Sciences to Academician Dr Nikolay Vladimirovich Sobolev, professor at the V. S. Sobolev Institute of Geology and Mineralogy of the Siberian Branch of the Russian Academy of Sciences in Novosibirsk, Russia. Nick Sobolev, as most colleagues know him, is a distinguished scientist known worldwide, whose work on the petrology, mineralogy, and geochemistry of high-pressure and ultrahigh-pressure crustal and mantle rocks, kimberlites, and their xenoliths and diamonds has had a profound effect on many disciplines in Earth science. Nick has written several hundred peer-reviewed scientific papers on mantle mineralogy and petrology as revealed by diamonds and their mineral inclusions. He is the world expert in this field, and his name is synonymous with diamond-inclusion research. His h-index (48) and more than 8000 total citations are the highest for a Russian Earth scientist.

With his interest in diamonds, Nick Sobolev has followed in the footsteps of his world-famous father, Academician Vladimir Stepanovich Sobolev, who first predicted the probability of diamonds in Yakutia (northern Siberia); his three brothers are also all geologists. Nick’s 1974 book, Deep-Seated Inclusions in Kimberlites and the Problem of the Composition of the Upper Mantle, rapidly became not only the worldwide “Bible of Yakutian Kimberlites” but the most thorough collection and scientific evaluation of mantle mineralogy for decades. His work on inclusions provided the foundation for the current use of mineral compositions in diamond exploration. Work with colleagues on carbon isotope analyses of diamonds in the 1970s led to the first proposal that eclogitic diamonds form from crustal carbon recycled into the mantle by subduction, and in 1990, together with V. Shatsky, Nick proved that the continental eclogites he was studying in Kazakhstan contained microdiamonds, leading to the entirely new field of research of ultrahigh-pressure metamorphism.

You can read more at www.ima-mineralogy.org. A plenary lecture and medal presentation ceremony will be held at IMA2014 in South Africa. Many congratulations to Nick!

COLLINS MEDAL TO MICHAEL BROWN

Michael Brown was nominated for the 2014 Collins Medal of the Mineralogical Society of Great Britain and Ireland on two grounds: his science, which is truly international in quality, scope and breadth, and his contributions to the development of metamorphic geology.

Brown has published over 120 peer-reviewed papers in the fields of high-T metamorphism, including HP and UHT granulate metamorphism; crustal anatexis and melt segregation, extraction, ascent and emplacement; the P–T–t–d evolution and tectonics of metamorphic belts; and secular change in styles of metamorphism and tectonics. This work has played a fundamental role in developing understanding in these fields.

Brown’s main legacy, however, may be in how he has facilitated research. Brown founded the Metamorphic Studies Group of the Mineralogical Society and the Geological Society of London. This specialist group has consolidated the position of metamorphic studies in the UK. Brown was the founder of the Journal of Metamorphic Geology (JMG) and is still the driving force on the editorial board as the journal, with an impact factor of 3.418, enters its 30th year. It is difficult to imagine how the study of metamorphism could have reached its current strength in the absence of this journal. JMG has published seminal papers by Bell and by Holland and Powell, among others. An enthusiastic conference organizer, Brown has convened over 25 major thematic meetings.

HAP MCSWEEN, PRESIDENT ELECT OF GSA

Harry Y. (Hap) McSween, Chancellor’s Professor at the University of Tennessee and a former principal editor of Elements, has been elected vice president/president elect of the Geological Society of America (GSA). The GSA is an umbrella organization with 25,000 members, and Hap is the first planetary geoscientist to lead the GSA. He is also a member of the Mineralogical Society of America, the Geochemical Society, and the Meteoritical Society, all organizations that sponsor Elements.

ORDER OF MERIT TO DON DINGWELL

Dr. Wolfgang Heubisch, Minister of Research of the Free State of Bavaria, presenting the Order of Merit to Don Dingwell (left)

The President of the Federal Republic of Germany has honored Don Dingwell with the Order of Merit of the Federal Republic of Germany (Bundesverdienstkreuz am Bande), given by the Minister of Research of the Free State of Bavaria. The citation praises “Professor Dingwell’s tireless efforts between science and the public during the Volcanic Ash Crisis for Civil Aviation of 2010, his central role in advancing geosciences within Bavaria, Germany and Europe and the global importance of his service as the 3rd Secretary-General of the European Research Council.”
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A NEW FACILITY FOR THE GEOFORSCHUNGSZENTRUM

Regular readers of the Toolkit will have noticed its absence over the past eight months, as I have not contributed to Elements since the February 2013 issue. The reason for this prolonged silence is simple: here in Potsdam we have been busy with the installation of our new secondary ion mass spectrometry (SIMS) user facility. This is the first time in my 27-year SIMS career that I’ve faced this task, and these months have provided me with many challenges—challenges that fall outside the spectrum of the day-to-day work in an “average” geochemical laboratory. Lab installation has been an interesting exercise, including excursions into such domains as seismology, metallurgy, and the art of air conditioning.

The GFZ-Potsdam has, in fact, operated a SIMS user facility for the past fifteen years. From 1998 until the facility’s decommissioning in March 2012, our work was based on the capabilities of a so-called “small geometry” Cameca ims 6f instrument. Having joined the GFZ in December 1998, I took responsibility for a brand-new laboratory without having to face the many months of planning required for optimizing the facility. The raison d’être of this earlier facility was to provide the global geochemical community with access to SIMS technology, a service that the ims 6f instrument fulfilled for 13 years.

In the spring of 2011, funding became available for upgrading Potsdam’s SIMS facility. The first task was to produce a call for tenders, and here I was most grateful for the expert help from my institute’s purchasing department. In the end, a three-page document specifying 38 requirements was published, these requirements being divided into five categories: (1) hardware specifications, (2) operational specifications, (3) maintenance specifications, (4) desired options, and (5) financial and legal matters. In the end, we selected an ims 1280-HR “large geometry” instrument, again manufactured by Cameca in Paris.

The original intention was that the new instrument be installed in the same location as its predecessor once it was removed. Due to the much larger size of the new machine, it would be necessary to expand the space by incorporating part of an adjacent sample-preparation room; access for machine delivery would be via the windows, located three meters above ground level. However, before serious planning for the new facility could begin, it was first necessary to have the consent of the manufacturer regarding the proposed location. My main concern was the presence of a 12 tesla superconducting magnet, which had recently been installed in a nearby laboratory. My concerns were allayed by the test results: though producing a significant magnetic field gradient, this external magnetic field was very stable and presented no risk for the coming SIMS facility. It was now that the fates of seismology struck. The GFZ-Potsdam has, in fact, operated a SIMS user facility for the past fifteen years. From 1998 until the facility’s decommissioning in March 2012, our work was based on the capabilities of a so-called “small geometry” Cameca ims 6f instrument. Having joined the GFZ in December 1998, I took responsibility for a brand-new laboratory without having to face the many months of planning required for optimizing the facility. The raison d’être of this earlier facility was to provide the global geochemical community with access to SIMS technology, a service that the ims 6f instrument fulfilled for 13 years.

My first planning action for the new SIMS facility was to contact colleagues who operate similar instruments. All four responses came back the same: special attention should be paid to air-temperature stability in the new laboratory. This information was passed on to the engineering company in charge of designing the new facility. They supported a design that might be used for a high-end computing facility, where the air supply comes from below floor level and the warm air is extracted from above the machine. Furthermore, as the thermal stability of the voltage supplies is of particular importance, it was decided that the two main electronics racks would have independent air cooling from directly below as well as a hood extracting the heat from directly above. Based on thermal modeling, the laboratory was to receive a complete exchange of air every 2 minutes, with a target total temperature range of only ±0.1°C.

Late on the gloomy afternoon of 7 March 2013, a large truck arrived from France. On it were 11 pallets, the largest of which carried a wooden crate with the 3-tonne magnet inside. The next day was overcast, but fortunately it remained dry. The moving company was expert at such work, managing to complete the unloading by noon. Even the access door, with a mere 5 cm of spare width, presented little challenge (Fig. 2).
busily installing various components. After one more careful cleaning of the room, the four main segments of the SIMS vacuum system were unwrapped and assembled during a single week in late June. Amazingly, only two weeks later, on 11 July, we witnessed the first ions reaching our detector. All components were functioning by mid-August (FIG. 4).

So what recommendations would I make for others who might face this adventure in the future? Both your stress level and your success level are dependent on the support of others, be they from your facility’s building department or from your lab’s workshop—it is important to communicate well with these people. Second, it is really valuable to ask for advice from other laboratories operating similar equipment—best to learn from the mistakes of others rather than to repeat them yourself. Third, it is important to work closely with the instrument manufacturer early in the planning process. Finally, as most humans work to deadlines, it is necessary to establish a realistic timetable while retaining some flexibility at the tail end.

For me, this past year has certainly been most interesting and also relatively stress free. That everything ran so smoothly is largely due to the help from my many colleagues in Potsdam who supported this effort and who promptly responded when minor adjustments became necessary. To my coworkers I say thanks, and to the future users of the facility I say welcome.

Best regards from Potsdam,

Michael Wiedenbeck
(Michael.Wiedenbeck@gfz-potsdam.de)
Meet the Authors

Gray E. Bebout is a professor in the Department of Earth and Environmental Sciences at Lehigh University, USA. He received his PhD in 1989 from the University of California, Los Angeles. His primary research involves the use of nitrogen isotopes as tracers of biogeochemical cycling, and the application of field techniques and geochemistry of high- and ultrahigh-pressure metamorphic rocks to understand subduction zone chemical cycling. His other recent stable isotope work has been aimed at tracing fluid flow in foreland fold-and-thrust belts and reconstructing the Holocene paleoclimate through analysis of tree rings and lake sediments.

Vincent Busigny is an associate professor of geochemistry at Université Paris Diderot and the Institut de Physique du Globe de Paris. His research emphasizes the use of stable isotopes (N, Fe, C, H, O, S) as tracers of mineral-fluid-life interactions. Applications range from the behavior of fluid-mobile elements during alteration and subduction of oceanic lithosphere to the reconstruction of Precambrian environments and ecosystems. After completing his PhD in 2004 in Paris under the supervision of Marc Javoy, Pascal Philippot, and Pierre Cartigny, he worked with Nicolas Dauphas at the University of Chicago before returning to France.

Pierre Cartigny joined the Institut de Physique du Globe de Paris in 2000 as a CNRS research scientist. He completed his PhD in geochemistry from Université Paris Diderot in 1997, after which he moved to the University of Göttingen (Germany) as a postdoctoral fellow. Using stable isotope geochemistry, he explores the internal cycle of volatile elements (nitrogen, carbon, sulfur, water) and aims at identifying processes leading to volatile-element heterogeneities in the mantle. His recent interests include the application of multiple isotope compositions of sulfur and oxygen to mantle and Earth-surface problems.

Karen L. Casciotti is an assistant professor in the Department of Environmental Earth System Science at Stanford University. She received a BS in environmental engineering science at Caltech, an MS in oceanography from the Scripps Institution of Oceanography, and a PhD in geosciences from Princeton University. Her current research focuses on marine nitrogen cycle biogeochemistry, with an emphasis on using nitrogen and oxygen stable isotopes to understand how nitrogen is cycled in the ocean. She has participated in 10 research cruises in the Pacific, Indian, and Southern oceans.

Emily M. Elliott is an assistant professor in the Department of Geology and Planetary Science at the University of Pittsburgh. Her research program examines the tight coupling between human activities and reactive nitrogen distributions in atmospheric, terrestrial, and aquatic systems using stable isotope geochemistry. She is the director of the Regional Stable Isotope Laboratory for Earth and Environmental Science Research. Prior to joining the Pitt faculty, she received her PhD at Johns Hopkins University (geography and environmental engineering) and was a postdoctoral research associate at the U.S. Geological Survey.

Marilyn L. Fogel is a biogeochemist who uses stable isotopes to trace geochemical processes. She obtained her PhD from the University of Texas Marine Science Institute. She worked at the Geophysical Laboratory until January 2013, when she became a professor at the University of California, Merced. Fogel has worked on ecosystems in modern and ancient environments using stable isotopes in organic and inorganic materials, including meteorites. She was a member of the Space Studies Board and participates in NASA’s Astrobiology Institute. She served as program director in geobiology at NSF, is the 2013 recipient of the Alfred Treibs Medal in Organic Geochemistry, and is a fellow of the Geochemical Society.

Meredith G. Hastings is an assistant professor at Brown University. Her research interests span biogeochemistry, atmospheric chemistry, and climate. Her recent studies have focused on the isotopic composition of nitrate to investigate variations in the sources, chemistry, and transport of nitrogen oxides, both in the modern environment and through time using ice cores. Prior to joining the faculty at Brown in 2008, Meredith was a postdoctoral fellow at the Joint Institute for Study of the Atmosphere and Ocean (JISAO) at the University of Washington. She completed her PhD at Princeton University, working with researchers in the Department of Geosciences and at the National Oceanic and Atmospheric Administration’s Geophysical Fluid Dynamics Laboratory.

Bernard Marty is professor of geochemistry at the École Nationale Supérieure de Géologie (Nancy, France) and at the Institut Universitaire de France, and is a staff scientist at the Centre de Recherches Pétrographiques et Geochimiques (CRPG-CNRS), where he had previously been the director (2002–2008). Marty holds a PhD in physics (Toulouse, 1979), and a Doctorat d’Etat in geochemistry (Université Pierre et Marie Curie, Paris, 1987). His research interests encompass the isotopic geochemistry of volatile elements, including stable isotopes and noble gases, with application to the origin of isotopic anomalies in the Solar System, early-Earth dynamics and environments, mantle geochemistries, and the geological carbon cycle.

Dominic Papineau obtained his BSc in physics and biochemistry from McGill University in his home town of Montréal, Québec, Canada. He received his PhD in geological sciences and astrobiology from the University of Colorado at Boulder. As a postdoc, he was trained in and helped develop a correlated microanalytical approach at the Carnegie Institution of Washington. His interests include Precambrian biogeochemical evolution, biosignatures and microanalyses to search for life on other planets, world politics and social justice; he enjoys sailing and exploring geobiology in far away places. He is currently a lecturer in the London Centre for Nanotechnology and the Department of Earth Sciences at the University College London.

Andrew Steele, an astrobiologist who combines his expertise in microbiology with nanoscale chemical imaging, obtained his PhD from the University of Portsmouth. He is a senior scientist at the Geophysical Laboratory and is actively engaged in NASA’s Mars Science Laboratory mission as a co-investigator on the Sample Analysis at Mars (SAM) instrument. He is an active member of the Mars Exploration Program Analysis Group and a member of the NASA Advisory Committee on Planetary Protection. He has published on the characterization and chemistry of organic carbon and nitrogen compounds in Martian meteorites.

Christophe Thomazo is an associate professor of geochemistry in the Department of Biogeoosciences of the Université de Bourgogne, Dijon, France. He received a PhD from the Institut de Physique du Globe de Paris, France, and carried out postdoctoral research at the Westfälische Wilhelms-Universität, Münster, Germany. His research focuses on using the stable isotope geochemistry of elements related to metabolic processes (C, N, S, and Fe) and the mass-independent fractionation of sulfur isotopes to explore the evolution of biogeochemical cycles during ocean oxygenation changes, including the Precambrian Great Oxidation Event and the Cretaceous oceanic anoxic events.
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**a & b:** Chondrite-normalized REE profiles as determined by EPMA. Monazite cores contrast with monazite rims and associated xenotime.

**c & d:** WDS maps of Nd and Y distributions. Points marked on the Nd map show EPMA age determinations in Ma, 2σ.

Data acquired on the SX Ultrachron model, courtesy of Dr. Julien Allaz, Univ. of Colorado and Dr. Michael Jercinovic, Univ. of Massachusetts.

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2D projection of 70 million atom 3D dataset from a metamorphic zircon. Y atoms (red) are concentrated along microfractures.
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Nitrogen exhibits an intriguing combination of highly volatile behavior (particularly as N₂), 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 (1792) 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, ¹⁴N and ¹⁵N, with abundances of 99.636% and 0.364%, respectively. Stable isotope compositions of nitrogen are expressed as ratios of ¹⁵N/¹⁴N relative to a standard, the latter generally denoted as N₂ in Earth's atmosphere. The conventional notation for expressing nitrogen isotope compositions, in ‰ (delta notation), is:

\[
\delta^{15}N (\text{‰ versus atmospheric } N_2) = \left( \frac{^{15}N/^{14}N_{\text{sample}}}{^{15}N/^{14}N_{\text{AIR-N}_2}} - 1 \right) \times 1000.
\]

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Despite its relatively inert and volatile behavior (particularly as N₂), 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 N₂, 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 N₂, including NH₄⁺ (ammonium), NH₃ (ammonia), and NO₃⁻ (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 N₂ 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.
in N₂ (Boyd 2001; Goldblatt et al. 2009; see the potentially conflicting evidence presented by Marty et al. 2013). According to Goldblatt et al. (2009), N₂ 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]
- 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]

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 N₂ to NH₄, other microorganisms convert NH₄ to NO₃, and yet a third class of microorganisms convert NO₃ back to N₂, thus completing the cycle.”


Although high-temperature fractionations can produce significant shifts in nitrogen isotope composition in melt-fluid–rock settings (Busigny and Rebout 2013), it is the low-temperature nitrification/denitrification reactions that produce the largest stable isotope fractionations. With more than 30‰ normal 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; Vogel 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 ∆¹⁵N originated with studies by Hoering (1955), who also presented the earliest analyses of biological (e.g., rats and pigs) 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 $\text{NH}_4^+$, 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 $\text{NH}_4^+$) 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 $\text{NH}_4^+$ to substitute for $\text{K}^+$ 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 $\text{N}_2$ 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 nitrogen 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 loses. 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 $\delta^{15}\text{N}$ values near ~5‰ could reflect a relatively small input to the mantle of nitrogen with elevated $\delta^{15}\text{N}$ inherited from shallow processes. Another possibility is that sedimentary/organic nitrogen with positive $\delta^{15}\text{N}$ is preferentially delivered into volcanic arcs (Elkins et al. 2006), leaving the low-$\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ 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 $\delta^{15}\text{N}$ records through diagenesis and low-grade metamorphism and will have to evaluate issues of contamination and syngenericity (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
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 (Osisinki 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

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**Table 1**

<table>
<thead>
<tr>
<th>Reservoir size $(10^{21}$ g)</th>
<th>% in reservoir</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Goldblatt et al. (2009)</strong></td>
<td></td>
</tr>
<tr>
<td>Atmosphere</td>
<td>4</td>
</tr>
<tr>
<td>Continental crust</td>
<td>2.1</td>
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<tr>
<td>Oceanic crust</td>
<td>0.32</td>
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<tr>
<td>Mantle</td>
<td>8.4</td>
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<tr>
<td><strong>TOTALS</strong></td>
<td>14.82</td>
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</table>

<table>
<thead>
<tr>
<th>Reservoir size $(10^{21}$ g)</th>
<th>% in reservoir</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>Palya et al. (2011)</strong></td>
<td></td>
</tr>
<tr>
<td>Atmosphere</td>
<td>3.9</td>
</tr>
<tr>
<td>Continental crust</td>
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</tr>
<tr>
<td>Oceanic crust</td>
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</tr>
<tr>
<td>Mantle</td>
<td>0.17</td>
</tr>
<tr>
<td><strong>TOTALS</strong></td>
<td>7.8</td>
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</table>

**Galloway (2003) – surface/near surface only**

<table>
<thead>
<tr>
<th>Reservoir size $(10^{21}$ g)</th>
<th>% in reservoir</th>
</tr>
</thead>
<tbody>
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<td>Atmosphere</td>
<td>3.95</td>
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<tr>
<td>Sedimentary rocks</td>
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<tr>
<td>Ocean N$_2$</td>
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</tr>
<tr>
<td>Ocean NO$_3^-$</td>
<td>0.00057</td>
</tr>
<tr>
<td>Soil organics</td>
<td>0.00019</td>
</tr>
<tr>
<td>Land biota</td>
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</tr>
<tr>
<td>Marine biota</td>
<td>0.0000005</td>
</tr>
<tr>
<td><strong>TOTALS</strong></td>
<td>4.97</td>
</tr>
</tbody>
</table>

**Galloway (2003) – surface/near surface only**

<table>
<thead>
<tr>
<th>Reservoir size $(10^{21}$ g)</th>
<th>% in reservoir</th>
</tr>
</thead>
<tbody>
<tr>
<td>Deep ocean</td>
<td>0.00006</td>
</tr>
<tr>
<td>Surface ocean</td>
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<tr>
<td>Soils</td>
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</tr>
<tr>
<td>Biomass</td>
<td>0.0000043</td>
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<tr>
<td>Marine biota</td>
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</tr>
<tr>
<td>Terrestrial vegetation</td>
<td>0.000004</td>
</tr>
<tr>
<td><strong>TOTALS</strong></td>
<td>12.97</td>
</tr>
</tbody>
</table>

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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).

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 Lazzéri 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**
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 contemporary 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 Lehig 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.

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**Planetary Contributions to the Inner Solar System**

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Stable Isotopes as Tracers of Anthropogenic Nitrogen Sources, Deposition, and Impacts

Meredith G. Hastings1, Karen L. Casciotti2, and Emily M. Elliott3

T he global nitrogen cycle has been perturbed by human activities, including agriculture, land-use change, and fossil fuel burning. This perturbation ranges from the local to global scale, as anthropogenic reactive nitrogen can be transported over long distances in the atmosphere, in groundwater, and in stream networks and can even impact the open ocean.

Stable isotope signatures characteristic of reactive nitrogen can be used to trace its deposition in the present day, as well as in the past. Here we focus on the use of stable isotopes to trace the sources, transport, and impacts of anthropogenic nitrogen in the modern nitrogen cycle.

INTRODUCTION

The 20th century saw the emergence of humans as the major catalyst for environmental change, and by many measures we have entered an era aptly termed the “Anthropocene.” The modern, postindustrial nitrogen (N) cycle is fundamentally different from the N cycle that evolved between the geophysical environment and the natural biosphere. The ability of humans to create reactive nitrogen (i.e. by fixing nitrogen gas, \( N_2 \), to create ammonium and nitrate) has at least doubled the rate of input of reactive nitrogen (Nrr; here defined as ammonium [\( NH_4^+ \)], ammonia [\( NH_3 \)], nitrite [\( NO_2^- \)], nitrate [\( NO_3^- \)], nitrogen oxides [\( NO_x \)], and water soluble organic nitrogen [WSON]) to the Earth system (see FIG. 1 for NOx as an example).

Historically, nitrogen is considered a limiting nutrient, such that biospheric productivity would increase with the addition of more Nrr. However, the anthropogenic increases in Nrr and the biological, geological, and chemical links of the N cycle lead to a wide range of impacts characterized as a “nitrogen cascade” (FIG. 2). The “N cascade” framework (Galloway et al. 2003) describes how a single N atom moves along its biogeochemical pathway, linking one environmental system to another. For example, the combustion of fossil fuel releases nitrogen oxides (\( NO_x \)) into the atmosphere, where it contributes to poor air quality and affects climate (e.g. via ozone and particulate matter). In addition, that same N atom can be delivered to the terrestrial ecosystem as nitrate or ammonium, where it can contribute to forest degradation, soil acidification, and changes in biodiversity. If leached from the soil zone, this N atom can contribute to groundwater nitrate contamination, surface water acidification, and ultimately, to harmful algal blooms, hypoxia (low oxygen content), and ocean acidification. Understanding the origins and fluxes of Nrr throughout this complex cascade is critical to mitigating the impacts of excess N in these environmental systems.

Traditional tools, such as measuring the concentrations and fluxes of Nrr, have elucidated certain aspects of the N cycle, but their scope in space and time is limited. Models are often employed to build a broader understanding of the N cycle, but their comparison with concentration measurements alone cannot validate the assumptions needed to simulate the creation, transport, fate, and impacts of Nrr. Today, stable isotopes contained in Nrr compounds are providing new insights into the cascade of N through the environment. Given the extensive changes that have occurred in the N cycle in the recent past, of particular interest is the ability of stable isotope studies to discern and trace anthropogenic versus natural sources of Nrr. Isotopes are particularly powerful in this regard; Nrr sources that carry different stable isotope signatures can be used to assess how the flux of Nrr from different sources varies while the total loading of Nrr compounds in the environment may not appear to change.

Nitrogen has two stable isotopes (\(^{14}N, {^{15}}N\)) and oxygen has three (\(^{16}O, {^{17}}O, {^{18}}O\)), with \(^{14}N\) and \(^{16}O\) making up over 99% of the nitrogen and oxygen present on Earth, respectively. The mass differences between isotopes result in the discrimination of different elements and compounds based on their isotopic composition, in both biological and chemical processes. These relatively small differences in isotopic composition are typically quantified in delta notation, where \(\delta^{15}N\) (%o versus atmospheric \(N_2\)) = \((^{15}N/^{14}N_{sample} + ^{15}N/^{14}N_{ATM,N2} - 1) \times 1000\) and \(\delta^{18}O\) (%o versus Standard Mean Ocean Water) = \((^{18}O/^{16}O_{sample} + ^{18}O/^{16}O_{SMOW} - 1) \times 1000\). New methodologies involving the conversion of nitrate to nitrous oxide (\(N_2O\)) for isotopic analysis (e.g. Sigman et al. 2001) have allowed for order of magnitude improvements in sample-throughput and sample-size requirements. These improvements are particularly useful in environmental applications where sample concentrations, compositions, and availability vary over a large range.

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TRACING THE PRODUCTION AND FATE OF REACTIVE NITROGEN

The formation of Nr in the environment includes natural and anthropogenic sources, as well as natural sources that have been modified by human activity. An example of this latter category is an increase in biological nitrogen fixation caused by the intensification of nitrogen-fixing crops. The primary natural sources of Nr today include biological nitrogen fixation (i.e. the splitting of N\textsubscript{2} leading to Nr in terrestrial and oceanic ecosystems) and lightning. Anthropogenic sources include fossil fuel and biofuel combustion, biomass burning (i.e. deforestation), and fertilizer creation and application. While it is clear that anthropogenic sources of Nr have risen dramatically (e.g. NO\textsubscript{x} in Fig. 1), the uncertainty associated with estimating emissions is large and our understanding of the variability of natural sources, particularly with changes in climate, is limited (Galloway et al. 2004).

Delivery of Nr into terrestrial and oceanic ecosystems is a result of deposition from the atmosphere, surface water and groundwater transport on land, and runoff from land to the ocean (Fig. 3). Deposition from the atmosphere results from: (1) emissions of precursor gases such as nitrogen oxides, ammonia, and organic compounds; (2) chemical transformation of these precursors into soluble forms such as nitrate, ammonium, and water-soluble organic N; and (3) precipitation or reaction on the surface of particles. While the lifetimes of atmospheric nitrate, ammonium, and WSON are relatively short (i.e. days to weeks), the transport of Nr through the atmosphere and surface waters increases the scale of impact via the N cascade (Fig. 2).

Atmospheric Nitrate

Evidence of the reach of anthropogenic Nr has recently been underscored by isotopic studies of Nr. For example, Hastings et al. (2009) found a significant decrease (~12‰, from pre-industrial values of +11‰ to ~1‰ in the past decade) in the \( \delta^{15}N \) of nitrate in a Greenland ice core. This decrease is coherent with the increases in emissions of precursor NO\textsubscript{x} from fossil fuel combustion (Fig. 1), though it has also been hypothesized that NO\textsubscript{x} emissions from soils perturbed by the addition of industrial-scale fertilizer applications also contribute to the significant decrease in \( \delta^{15}N \) values (Felix and Elliott 2013). While previous ice-core studies had detected a change in nitrate concentration connected to the rise in anthropogenic NO\textsubscript{x} emissions, the isotopic record shows more distinct changes that occur earlier than those found when considering concentration alone. Furthermore, the isotopic record shows interannual to multiyear variability not captured by previous work. Holtgrieve et al. (2011) found similar decreases in the \( \delta^{15}N \) values of sedimentary N across 25 remote lakes in the Northern Hemisphere, starting early in the 20\textsuperscript{th} century. Despite a seemingly low amount of Nr input to these remote lakes today, the footprint of anthropogenic Nr and its incorporation into the biological system is clear based upon the isotope results.

Variability in the sources of atmospheric Nr and their impact via deposition are also much more apparent with the addition of isotopic measurements. For instance, multiyear studies of precipitation chemistry on the island of Bermuda found a surprising lack of change in seasonally averaged nitrate concentrations, despite a significant seasonal change in the amount of anthropogenically influenced air masses arriving at the island. The isotopes of nitrate and total N (i.e. nitrate, ammonium, and WSON), however, uncovered significant seasonal changes in \( \delta^{15}N \); these changes suggest a shift in the sources of Nr to the region (Hastings et al. 2003; Knapp et al. 2010).

In another study of nitrate deposition across the northeastern United States, the use of isotopes revealed correlations between \( \delta^{15}N \) of nitrate and precursor NO\textsubscript{x} emissions from power plants (Elliott et al. 2007). This correlation, combined with recent characterization of \( \delta^{15}N \) of NO\textsubscript{x} from U.S. power plants (~+9–26‰; Felix et al. 2012), indicates that power plants are an important source of NO\textsubscript{x} leading to nitrate deposition at rural monitoring sites in the eastern U.S. (Fig. 4). This contrasts with emissions inventories that suggest vehicular NO\textsubscript{x} is the largest source to the U.S. NO\textsubscript{x} budget. It also raises an important challenge: either the influence of vehicular NO\textsubscript{x} on landscape N deposition is underestimated based upon sampling at rural monitoring sites remote from NO\textsubscript{x} sources, or emission inventories, which are critical for models of air quality in the U.S., are not accurately addressing the contributions of NO\textsubscript{x} sources to atmospheric chemistry and/or nitrate deposition. At the continental scale, spatial patterns in \( \delta^{15}N \) are highly variable and often distinct from nitrate concentration patterns (Fig. 4). The difference in \( \delta^{15}N \) compared to concentration may be indicative of the contributions of natural and anthropogenic-source emissions having a sensitive impact on \( \delta^{15}N \) and/or that fractionating processes also contribute to the \( \delta^{15}N \) of nitrate captured in precipitation.

Another exciting advance in tracing the fate of Nr was the realization that the oxygen isotope composition of atmospheric nitrate is unique. In addition to elevated \( \delta^{16}O \) values (Fig. 5), atmospheric nitrate contains anomalously elevated \( \delta^{17}O \) values. The \( \delta^{16}O \) and \( \delta^{17}O \) of ozone are considerably elevated compared to other oxygenated compounds in the Earth system, and a 1:1 relationship between the ratios of \( ^{16}O/^{18}O \) and \( ^{17}O/^{18}O \) is found in ozone rather than the expected 2:1 relationship based upon mass differences alone. The discovery of this mass-independent\(^\text{1} \) signature (quantified as \( \Delta^{17}O = \delta^{17}O - 0.52 \times \delta^{16}O \)) of ozone has generated new understanding of gas-phase chemistry and dynamics in the atmosphere (Thiemens 1999). The result in terms of Nr is that nitrate generated in the

\(^{1} \) See Elements volume 5, number 6 for more on mass-independent fractionation.
The cascading impacts of nitrogen atmosphere by chemical reaction between NO\textsubscript{x} and ozone has elevated δ\textsuperscript{18}O, δ\textsuperscript{17}O, and δ\textsuperscript{15}N values (Michalski et al. 2003; Hastings et al. 2003). Global-scale modeling of the Δ\textsuperscript{17}O of atmospheric nitrate predicts significant variations in Δ\textsuperscript{17}O with season and latitude, dependent upon the amount of interaction between NO\textsubscript{x} and ozone (Alexander et al. 2009).

The isotopic composition of atmospheric nitrate provides a means to test our understanding of the sources and chemistry of NO\textsubscript{x} in the atmosphere. This has implications for diagnosing the influence of NO\textsubscript{x} loading on air quality, oxidation processes in the atmosphere, and climate. Moreover, the quantification of isotopic signatures in atmospheric nitrate provides a fundamentally new means by which to track atmospheric nitrate that is deposited on land and in the ocean.

**Nitrate in Streams and Rivers**

Sources of nitrate to streams and other surface waters can be difficult to quantify using concentrations or nutrient budgets alone, whereas the isotopes of nitrate have the advantage of relatively distinct ranges in δ\textsuperscript{15}N and δ\textsuperscript{18}O values for individual nitrate sources (Fig. 5). In particular, the use of paired isotopes (i.e. those of N and O) can distinguish atmospheric nitrate contributions from fertilizer-derived or microbially produced soil- and waste-derived nitrate contributions. In catchments impacted by land-use change and human activities, paired isotope studies of nitrate have successfully been applied to distinguish sources and processes contributing to nitrate present in streams, rivers, and groundwater (e.g. Kendall et al. 2007 and references therein). In these studies, δ\textsuperscript{15}N values generally increase with population density, reduced forest cover, and proportional contributions of nitrate derived from septic, sewer, or other waste streams. The additional application of nitrate Δ\textsuperscript{17}O measurements allows for robust quantification of atmospheric nitrate contributions to surface waters and groundwaters (e.g. Tsunogai et al. 2010), although relatively few studies have taken advantage of this new approach in a watershed context.

An important advance in our understanding of the movement of Nr in the terrestrial system comes from the ability to detail snowmelt dynamics in forested watersheds. In catchments subject to seasonal snowpack cover, episodic acidification of stream water occurs during early snowmelt in many small upland catchments. Advances in methods for the determination of isotopes of nitrate in natural waters (e.g. Sigman et al. 2001) have enabled the analysis of snowmelt samples collected at high frequency, revealing new insights into the dynamic nature of atmospheric and microbial nitrate contributions to stream water. Based on daily and subdaily sampling, Ohle et al. (2004) used paired isotopes of nitrate and solute chemistry to establish three distinct snowmelt phases. They determined that atmospheric nitrate is a large contributor to the early snowmelt nitrate pulse and that, with progressive snowmelt, the nitrate source switches from meltwater to soil water.

Sebestyen et al. (2008), using even higher-frequency sampling than the previous study, elucidated surface and subsurface flowpaths based on isotopes of nitrate coupled with dissolved organic carbon and nitrogen concentrations. Despite the fact that atmospheric nitrate contributed only 7% of watershed nitrate during the meltwater months (January–April), atmospheric nitrate dominated stream water nitrate export during early snowmelt, displacing nitrified nitrate from surface soils and shallow groundwater. Based on these findings, it was concluded that weekly or monthly sampling is not of sufficient resolution to properly assess nitrate sources to stream water.

**Nitrification Dynamics and δ\textsuperscript{18}O-NO\textsubscript{3}–**

Studies of nitrate isotopes, including those described above, have generally assumed that nitrate (NO\textsubscript{3}–) produced from nitrification reactions contains 2 atoms of oxygen from water (H\textsubscript{2}O) and 1 atom from molecular oxygen (O\textsubscript{2}) in a stoichiometric 2:1 ratio. This assumption, in turn, is used to assign δ\textsuperscript{18}O-NO\textsubscript{3}– values to nitrate derived from nitrification in end-member mixing models and apportion nitrate sources to groundwaters and surface waters. This biochemical ratio, in combination with typical δ\textsuperscript{18}O-H\textsubscript{2}O values (Michalski et al. 2003; Hastings et al. 2003), provides a new approach in a watershed context.
and δ²⁰O-O₂ values, generally predicts δ¹⁸O-NO₃⁻ values ranging between −10 and +10‰ for groundwater and between +7 and +12‰ for seawater. However, δ¹⁸O-NO₃⁻ values have recently been measured outside these ranges, calling into question the validity of the 2:1 assumption, our understanding of nitrification dynamics, and the associated implications for source apportionment.

Snider et al. (2010) conducted laboratory incubations of forest and agricultural soils using ¹⁸O-enriched H₂O with the aim of clarifying sources of O contributing to nitrification. The results indicated that under some conditions δ¹⁸O-H₂O is a stronger determinant of δ¹⁸O-NO₃⁻ than previously thought; the experiments showed that 79–96% of O atoms were derived from water, relative to the 67% predicted using stoichiometry alone. Further, the exchange of oxygen atoms between nitrate (an intermediate in both nitrification and denitrification reactions) and water in incubated soils resulted in the increased dependence of δ¹⁸O-NO₃⁻ on δ¹⁸O-H₂O. However, despite the obvious exchange of O between nitrate and water in these laboratory incubations, it is unclear how nitrate accumulation in soils and exchange with water contributes quantitatively to observed δ¹⁸O-NO₃⁻ values on a broader scale.

Parallel advances have been made in examining biotic and abiotic factors in oxygen-atom exchange and fractionation during nitrification. In pure cultures of ammonia-oxidizing bacteria, Casciotti et al. (2010) observed relatively low proportions of biologically catalyzed oxygen isotope exchange (1–25%) affecting the O atoms in nitrite. However, when nitrite was allowed to accumulate in solution, further abiotic exchange occurred. Similar studies conducted with ammonia-oxidizing archaea indicated that they, too, catalyze a modest amount of oxygen-atom exchange (Buchwald et al. 2012). More importantly, a high degree of isotopic fractionation occurred during incorporation of O from dissolved oxygen and water into nitrite during ammonia oxidation (Casciotti et al. 2010; Buchwald et al. 2012) and into nitrate during nitrite oxidation (Buchwald and Casciotti 2010). As a consequence, microbially produced nitrite and nitrate exhibited lower δ¹⁸O values than expected based on reaction stoichiometry alone, which has implications for interpreting nitrate sources in marine and terrestrial environments.

Vegetation
Given that nitrogen availability can limit plant growth, there has been a long history of studies dedicated to discerning N sources to plants and the controls on plant isotopic composition, both at the individual level and across larger spatial scales. While there are several controls on plant δ¹⁵N values, plant tissue can be effective "biomonitors" of Nr isotopic composition (Redling et al. 2013 and references therein). This is particularly true in landscapes where strong spatial gradients in Nr concentrations exist, such as transects perpendicular to highways. For example, Redling et al. (2013), using nitrogen isotopes in gaseous nitrogen dioxide (NO₂) and nitric acid (HNO₃) coupled with plant tissue δ¹⁵N and C:N ratios, documented the foliar uptake and fertilization effect of automobile NOₓ on nearby vegetation. They determined that the near-road N flux is four times higher than the background N flux, which has important implications for our understanding of Nr deposition fluxes to major metropolitan regions and near-road ecosystems. Despite such observed similarities in spatial patterns between δ¹⁵N in plant tissue and atmospheric Nr, the relative importance of foliar uptake of nitrate and ammonia has been difficult to quantify.

A new approach for examining the role of foliar uptake includes the examination of paired isotopes of nitrate extracted from plant tissue (Liu et al. 2012). In the Liu et al. study, nitrate extracted from epilithic moss reflected uptake of atmospheric nitrate, whereas nitrate from terricolous moss (i.e. those that live on the ground surface) reflected the δ¹⁵N of soil N. At urban sites, nitrate in epilithic moss was characterized by low δ¹⁸O values (+15 to +20‰) and high concentrations. In contrast, mosses from a remote mountainous region had nitrate δ¹⁸O values (+40 to +50‰) more similar to wet-deposition values (+77‰) and lower foliar N concentrations. Of particular interest in these results is that δ¹⁸O, not δ¹⁵N, is strongly correlated with moss nitrate concentrations and thus records the relative contributions of atmospheric nitrate. While further examination of fractionations resulting from nitrate reduction in plant tissue is needed, these studies illustrate how highly sensitive analytical methods for nitrate analyses can yield new insight into nitrogen dynamics between vegetation, the atmosphere, and hydrologic systems.
**Delivery and Impacts of Anthropogenic Nr in the Ocean**

Models suggest that much of the N delivered to the coastal ocean by rivers is converted to N$_2$ or buried in estuarine and coastal sediments, with relatively little conveyed into the open ocean (e.g., Seitzinger 2008). Atmospheric transport, on the other hand, can readily deliver Nr to both the coastal and the open ocean. Atmospheric inputs to the ocean are estimated to have increased by a factor of three in the last 150 years (Duce et al. 2008). This flux ($67$ Tg N y$^{-1}$) is now estimated to be about 50% of the input of new N from biological nitrogen fixation in the ocean. This additional input has a number of potential negative consequences (Fig. 2), including potential enhancement of greenhouse gas (N$_2$O) production. On the other hand, deposition of N could enhance carbon dioxide uptake by the oceans in remote regions that are currently N limited (Duce et al. 2008). Therefore, the impact of increased Nr delivery to the ocean depends strongly on the background conditions in the locations where it is deposited. Measuring atmospheric N fluxes to the ocean directly is difficult, due to the sporadic nature of precipitation events and the relatively low spatial coverage of sampling in remote regions. The combination of stable isotope measurements with other geochemical tracers can provide additional insight into the amounts and importance of Nr deposited to the open ocean.

While the oxygen isotope composition of atmospheric nitrate is significantly different from that of other sources (Fig. 5), in many areas the nitrate deposited in the surface ocean is likely to be consumed rapidly and lose its oxygen isotope signature. The N will be retained by phytoplankton, however, and ultimately will contribute to the $\delta^{15}$N of the sinking particulate flux and the $\delta^{15}$N of nitrate regenerated in the thermocline, the zone of strong thermal stratification below the sunlit surface ocean. Accumulation of low-$\delta^{15}$N nitrate in the thermocline has been observed in low-nutrient regions near Hawai‘i and Bermuda and has generally been attributed to N$_2$ fixation because of its low $\delta^{15}$N signature ($-1.5$ to $0\%$o). However, there is a need to account for atmospheric deposition when using $\delta^{15}$N-N$_2$O$_5$ to quantify the input of reactive N through N$_2$ fixation, and additional tracers of atmospheric deposition, such as trace element distributions, may be needed to do so (see below). Mara et al. (2009) used $\delta^{15}$N-N$_2$O$_5$ to successfully track local atmospheric input to the Mediterranean Sea. $\delta^{15}$N-N$_2$O$_5$ in samples of dry and wet deposition on Crete ranged from $-1.5$ to $-5\%$o, with an annual weighted estimate of $-3.1\%$o. Taking this as the input term required no additional N$_2$ fixation to explain the deep-Mediterranean $\delta^{15}$N-N$_2$O$_5$ values or the $\delta^{15}$N of algal biomass.

Other geochemical approaches have also been used to determine the accumulation of atmospheric N in the thermocline of the North Atlantic Ocean (Hansell et al. 2007). Of a total excess N accumulation rate of $7.8 \times 10^{11}$ mol y$^{-1}$, it was estimated that atmospheric deposition accounts for 38%, or $3.0 \pm 0.9 \times 10^{11}$ mol excess N y$^{-1}$. This surpassed dissolved organic matter remineralization ($2.2 \times 10^{11}$ mol excess N y$^{-1}$) and N$_2$ fixation ($2.6 \times 10^{11}$ mol excess N y$^{-1}$) as a source of excess N to the thermocline. Key uncertainties in this approach were the N:P ratios of sinking organic matter and the gradients in dissolved organic phosphorus. However, it illustrates the potential importance of atmospheric N as a source of new N to the oligotrophic North Atlantic, which is likely to grow in the future and contribute to carbon export as long as other potentially limiting nutrients (P, Fe) are available.

**Anthropogenic Nr**

Anthropogenic N will cascade through the ocean N cycle until it is ultimately consumed by anammox (anaerobic ammonia oxidation, which generates N$_2$ from NH$_4^+$ and NO$_2^-$) or denitrification (reduction of nitrate to form gaseous products, including N$_2$) in sediments and oxygen-deficient water columns. Pared nitrate isotopes have been used to track the cycling and loss of nitrite and nitrate in oceanic oxygen-deficient zones (Sigman et al. 2005). Unusual isotope effects associated with nitrite oxidation make $\delta^{15}$N-N$_2$O$_5$ a sensitive tracer of nitrite reoxidation compared to nitrite reduction, and incorporating $\delta^{15}$N measurements of nitrate along with paired nitrate isotopes has led to new insights into the mechanisms of N cycling in oxygen-minimum zones (Casciotti 2009 and references therein). Current estimates suggest that as much as 50% of nitrite removal occurs through reoxidation, which retains N in a reactive form rather than converting it back to N$_2$ gas.

**PROSPECTUS**

There is a rewarding road ahead for deepening our understanding of the global N cycle through the use of stable isotopes. The ability to measure the isotopic composition of Nr compounds in small sample volumes and with relative ease facilitates the production of data sets with significant spatial and temporal coverage. These data sets will, in turn, provide for a better grasp of the processes and mechanisms that define the modern N cycle, particularly through connections with models that include the biogeochemical cycling of N in the atmosphere, on land, and/or in the ocean.

Of particular significance will be the ability to use the $\delta^{15}$N of nitrate, nitrite, ammonium, and WSON as quantitative tracers of Nr sources. While there is evidence that emission sources must influence the $\delta^{15}$N found in Nr deposits, both the isotopic signatures of sources and potential fractionations associated with chemical transformations in the atmosphere need more constraint. For example, while new studies report large, distinct differences between $\delta^{15}$N associated with NO$_x$ emissions from soils and NO$_x$ emitted from industrial power plants, isotopic constraints are needed for vehicular NO$_x$ and biomass burning. Recent
advances in the detection of δ15N of ammonium and WSON at low concentrations will also allow for further constraints on the isotopic signatures associated with emission sources.

Combining isotopic techniques with other tracers will also be useful for detailing the sources and processes that result in Nr deposition. For example, trace elements such as aluminum (Al) have been found to be excellent tracers for atmospheric deposition in the ocean. The contribution of atmospheric N could potentially be quantified by the combination of measurements of the input of Al, the Al:N ratio of the aerosol, and the δ15N-NO3– value of the aerosol. To our knowledge, no one has taken this approach to quantify the N input to the surface ocean, although relevant data have been collected (e.g. Wankel et al. 2010). Despite recent advances, the ocean is still vastly undersampled for nitrate isotope measurements, although programs such as GEOTrACES will provide additional insight into the isotopic composition of atmospheric and oceanic nitrate in remote locations.

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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 (N₂) and is by far the most abundant gas in the atmosphere. Nitrite (NO₂⁻), nitrate (NO₃⁻), ammonium (NH₄⁺), 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 NH₄⁺ 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 ¹⁵N/¹⁴N 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 δ¹⁵N value of +5 to +7‰ of modern sedimentary organic matter in oceanic sediments reflects the ¹⁵N 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 δ¹⁵N (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 NO₂⁻ to NO₃⁻. Consequently, the growth of denitrifying bacteria and archaea, which breathe NO₃⁻ (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 N₂ fixation, glutamate synthetase for NH₄⁺ assimilation, and nitrite reductase for NO₂⁻ reduction into NH₄⁺ (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 Quebec), 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 δ¹⁵N 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 NH₄⁺ 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 δ¹⁵N

We present an extensive δ¹⁵N 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 δ¹⁵N values...
measured on various Precambrian sedimentary lithologies and materials, including kerogen, phyllosilicates, shales, carbonates, cherts, banded iron formations (BIFs), and N2-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 δ15N 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 δ15N preservation regarding secondary processes). The “SiZer” statistical approach referred to in FIGURE 2B is used to detect significant trends in δ15N 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. 2A) with different colors; these maps are a graphical representation of increasing (positive slope) and decreasing (negative slope) δ15N 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 δ15N values centered around +3‰ and ranging between –6.2‰ and +27.5‰. Considering that Eo- and Paleoarchean environments were anoxic and that NH4+ 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, N2-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 δ15N values between –0.7‰ and –2‰ (Nishizawa et al. 2007). These N2-bearing fluid inclusions data suggest that the δ15N value of the Paleoarchean

**Box 1** Interpreting δ15N in Sedimentary Rocks

Sedimentary nitrogen is mostly present as organic N and fixed ammonium substituting for potassium in phyllosilicates (Boyd and Philippot 1998). Sedimentary organic nitrogen reflects the residual nitrogen from particulate organic matter after (1) microbial respiration and fermentation through heterotrophic metabolisms during early diagenesis and (2) nitrogen loss concurrent with the thermal maturation of organic matter during burial diagenesis and metamorphism. The heterotrophic degradation of organic matter leads to only small nitrogen isotope fractionation effects on total nitrogen (less than 1‰), while other early diagenetic reactions in oxic or anoxic settings lead to larger, though still small, nitrogen isotope variations (on the order of 2–3‰; see Robinson et al. 2012 for a review). Later diagenetic processes appear to have a negligible effect on 15N/14N fractionations.

Although high-pressure metamorphism does not appear to impart significant nitrogen isotope fractionation (Busigny et al. 2003), high-temperature metamorphism has been shown to increase the 15N/14N ratio of ammoniated phyllosilicates (Bebout and Fogel 1992) because of Rayleigh distillation during nitrogen devolatilization. Residual nitrogen isotopes in phyllosilicates then have δ15N values increased by about 1–2‰ for greenschist facies, 3–4‰ for amphibolite facies, and up to 6–12‰ for upper amphibolite facies temperatures (Bebout and Fogel 1992; Boyd and Philippot 1998). This might be different for organic matter, which has been shown to retain its initial δ15N values (Ader et al. 2006). Such thermal effects must therefore be taken into consideration when interpreting data derived from rocks metamorphosed at temperatures higher than about 300°C (greenschist facies). Therefore, with these considerations, Precambrian paleoenvironmental nitrogen signatures are not completely obscured, and δ15N values from metamorphosed sedimentary rocks can sometimes be considered as upper limits of their premetamorphic values, especially if they can be reproduced for different types of rocks and locations.
TABLE 1 COMPARISON OF δ¹⁵N VALUES IN ARCHEAN METASEDIMENTARY ROCKS AND PROPOSED INTERPRETATIONS

<table>
<thead>
<tr>
<th>Geological terrain</th>
<th>Sample age (Ga)</th>
<th>Metamorphic grade</th>
<th>δ¹⁵N (source)</th>
<th>Interpretations</th>
<th>References</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isua Supracrustal Belt (Nain)</td>
<td>ca. 3.77</td>
<td>Amphibolite facies</td>
<td>+5.4 to +20.0‰ (WR BIF, magnetite in BIF, and WR metapelite)</td>
<td>Metamorphically altered pristine nitrogen possibly from chemosynthetic microorganisms</td>
<td>Pinti et al. (2001)</td>
</tr>
<tr>
<td>Isua Supracrustal Belt (Nain)</td>
<td>ca. 3.77</td>
<td>Amphibolite facies</td>
<td>−1.85 to +27.47‰ (biotite from metapelites)</td>
<td>Metamorphic nitrogen for highest values and BNF for lowest values</td>
<td>Papineau et al. (2005)</td>
</tr>
<tr>
<td>Isua Supracrustal Belt (Nain)</td>
<td>ca. 3.77</td>
<td>Amphibolite facies</td>
<td>−3.66 to +7.29‰ (graphite)</td>
<td>Modern atmospheric nitrogen or BNF for lowest values and D or metamorphism for highest values</td>
<td>Van Zuilen et al. (2005)</td>
</tr>
<tr>
<td>Isua Supracrustal Belt (Nain)</td>
<td>ca. 3.77</td>
<td>Amphibolite facies</td>
<td>−3.1 to +11.4‰ (WR BIF)</td>
<td>Derived from kerogenous material</td>
<td>Nishizawa et al. (2005)</td>
</tr>
<tr>
<td>Warrawoona Group (Pilbara)</td>
<td>3.4–3.5</td>
<td>Prehnite–pumpellyte facies</td>
<td>−11.0 to +12.1‰ (WR chert, chert separate)</td>
<td>Ammonium assimilation for lowest values, paleoatmospheric nitrogen for near-zero values, and metamorphic nitrogen for highest values</td>
<td>Pinti et al. (2001)</td>
</tr>
<tr>
<td>Warrawoona and Gorge Greek groups (Pilbara), Onverwacht (Kaapvaal)</td>
<td>3.4–3.5</td>
<td>Prehnite–pumpellyte to amphibolite facies</td>
<td>−6.2 to +13.0‰ (organic matter in chert)</td>
<td>Biological consumption of N₂ and/or NH₄⁺ for lowest values</td>
<td>Beaumont and Robert (1999)</td>
</tr>
<tr>
<td>Barberton Greenstone Belt (Kaapvaal)</td>
<td>ca. 3.2</td>
<td>Greenschist facies</td>
<td>−3 to +12‰ (chert)</td>
<td>Atmospheric signature with some metamorphic overprint</td>
<td>Sano and Pillinger (1990)</td>
</tr>
<tr>
<td>Harare Greenstone Belt (Zimbabwe), Penhalonga Formation (Kaapvaal), Abitibi terrain (Superior)</td>
<td>ca. 2.7</td>
<td>Greenschist facies</td>
<td>+14.8 to +23.4‰ (mica and carbonaceous shale)</td>
<td>Change in atmospheric δ¹⁵N composition through delivery of CI chondrite meteorites and comets with isotopically heavy nitrogen</td>
<td>Jia and Kerrich (2004)</td>
</tr>
<tr>
<td>Michipicoten Formation, Steeprock Group (Superior), Fortescue Group (Pilbara)</td>
<td>ca. 2.7</td>
<td>Greenschist facies</td>
<td>−4.1 to +35.8‰ (organic matter in black chert)</td>
<td>Biological consumption of N₂ and/or NH₄⁺ for lowest values and D for highest; increased redox states</td>
<td>Beaumont and Robert (1999)</td>
</tr>
<tr>
<td>Tumbiana Formation (Pilbara)</td>
<td>2.727</td>
<td>Greenschist facies</td>
<td>+8.6 to +30.4‰ (stromatolitic dolomite, mudstone, siltstone)</td>
<td>BNF and ammonia oxidation for lowest values and D for highest; increased redox states</td>
<td>Thomazo et al. (2011)</td>
</tr>
<tr>
<td>Campelland and Malmani formations (Kaapvaal)</td>
<td>ca. 2.67–2.50</td>
<td>Greenschist facies</td>
<td>−1.5 to +7.5‰ (kerogen, WR chert, carbonate, BIF)</td>
<td>BNF for lowest values followed by D for highest; increased redox states</td>
<td>Godfrey and Falkowski (2009)</td>
</tr>
<tr>
<td>Mt. McRay Formation (Pilbara)</td>
<td>2.50</td>
<td>Greenschist facies</td>
<td>+1.0 to +7.5‰ (WR shale, BIF, and carbonate)</td>
<td>BNF for lowest followed by D for highest; increased redox states</td>
<td>Garvin et al. (2009)</td>
</tr>
</tbody>
</table>

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

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

During the Meso- and Neoarchean, the average δ¹⁵N value increases to +15‰ and the range of δ¹⁵N variations also increases drastically in some paleoenvironments, reaching values up to +50.4‰. However, the detailed structure of the δ¹⁵N secular variation around 3.1 Ga (average δ¹⁵N value of +2.3‰) and the positive excursion recorded at 2.7 Ga (average δ¹⁵N 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 δ¹⁵N values has thus been supplemented by observations of highly ¹⁵N-enriched samples in the Neoarchean around 2.7 Ga (Table 1; Fig. 2A) and a long-term increase in δ¹⁵N (Fig. 2B). ¹⁵N-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 δ¹⁵N values in the Neoarchean to reflect a significant increase in atmospheric δ¹⁵N 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 N₂-bearing fluid inclusions in Precambrian cherts indicates...
no significant variation of the atmospheric $^{15}\text{N}/^{14}\text{N}$ ratio since ~3.5 Ga (Nishizawa et al. 2007). Moreover, because $\text{N}_2$ 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 $^{15}\text{N}$ values reach +31.6‰ (Papineau et al. 2009). After 2.0 Ga, $^{15}\text{N}$ 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 ($\text{NH}_4^+$) would be present in the deep anoxic ocean, $\text{NO}_3^-$ would accumulate at the oxic–anoxic interface during nitrification and denitrification cycles, and $\text{NO}_2^-$ 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 $\text{NO}_3^-$ 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 $\text{NH}_4^+$ 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 komatitic volcanism could have provided additional fixed nitrogen to the early-Earth environment (Mather et al. 2004). Experiments with lightning have also shown that nitrogen compounds can be synthesized from precursor $\text{N}_2$ gas, and, depending on the partial pressure of $\text{H}_2$, 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 $\text{N}_2$ to $\text{NH}_4^+$ (Schoonen and Xu 2001). Various Fe and Ni-bearing minerals can also catalyze the reduction of $\text{N}_2$ or oxidized nitrogen species to $\text{NH}_3$ 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 $\text{NH}_3$ before $\text{N}_2$ 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...
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 δ¹⁵N 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 δ¹⁵N value evolve during the Archean, if at all? What is the nature of the Neoarchean and Paleoproterozoic global secular variations in sedimentary δ¹⁵N 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 δ¹⁵N 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 cycles to better decipher the evolutionary history of the ancient nitrogen cycle and the early evolution of life on our planet.

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Nitrogen is the main constituent of Earth’s atmosphere and a key component of the biosphere, but it is a trace element in the major silicate reservoirs. The relatively low concentrations (parts per million level) complicate efforts to constrain the nitrogen speciation and abundance in the mantle and crust. In most silicates, nitrogen occurs as NH$_4^+$ (substituting for K$^+$), whereas its speciation in hydrous fluids and silicate melts can vary widely depending in large part on redox conditions. Current knowledge of nitrogen isotope fractionation among relevant mineral and fluid/melt phases is limited by the lack of experimental data to confirm theoretical predictions of these fractionations. Modeling of modern and long-term nitrogen cycling on Earth will be advanced by better constraints on the sizes and isotopic compositions of the major crust and mantle nitrogen reservoirs.

INTRODUCTION

Nitrogen (N) is generally regarded as a volatile element with a behavior similar to that of the noble gases. However, nitrogen reactivity and its multiple stable redox states make it compatible in rocks and an important trace element in the silicate Earth. Estimates of the distribution of nitrogen on modern Earth place the majority of the nitrogen in the mantle, which has a very low nitrogen concentration but constitutes the largest fraction (~50%) of the Earth by volume (e.g. Kerrich et al. 2006; Palya et al. 2011; Bebout et al. 2013a this issue). Nitrogen’s large range in stable isotope compositions makes it a useful tracer of mass exchange between the surface and deep-Earth reservoirs and of fluid/melt–rock interactions in the crust and mantle. The majority of the work on nitrogen isotopes has focused on marine environments (Sigman et al. 2009) and involves anthropogenic and natural exchanges among the atmosphere, biosphere, soils, and oceans (see Bebout et al. 2013a). The behavior of nitrogen isotopes in high-temperature, crust–mantle systems has been investigated by a relatively small number of laboratories, in part because of the difficulty inherent in analyzing the very small amounts of nitrogen typically residing in silicate materials (see the Analytical Box in Cartigny and Marty 2013 this issue). In this paper, we provide a brief overview of the present knowledge of the nitrogen cycle in the silicate Earth, focusing on speciation in mineral–fluid–melt systems in the crust and mantle and on the utility of nitrogen as a tracer of sedimentary/organic components in the deep Earth.

NITROGEN IN CONTINENTAL CRUST: A LONG-TERM STORAGE SITE?

The nitrogen cycle within continental crust can be described in terms of the successive effects of sedimentation, diagenesis, metamorphism, and magmatism. Nitrogen is introduced into the crust mostly via organic matter deposited in sediments. This organic nitrogen typically has a range of $\delta^{15}$N$_{air}$ values between 0 and $+10\%$, with an average value of about $+5\%$ (Sigman et al. 2009; for the definition of $\delta^{15}$N notation, refer to Bebout et al. 2013a). Nitrogen concentrations in sediments are strongly dependent on lithological variations and organic matter input flux, and they show a wide range, from less than 100 to more than 10,000 ppm. During biological and thermal diagenetic degradation of organic matter, a large amount of nitrogen is released into pore fluids as NH$_3$ (ammonia), which is rapidly transformed to NH$_4^+$ (ammonium) by protonation; during these processes, nitrogen largely preserves its organic $\delta^{15}$N signature (Thomazo and Papineau 2013 this issue). Although $>90\%$ of the nitrogen initially present in organic matter is liberated during diagenesis, a small amount of nitrogen is preserved within its structure, seemingly with limited change in $\delta^{15}$N, up to greenschist facies metamorphic grade (Ader et al. 2006).

In rocks extremely rich in organic carbon, such as coals, this residual organic nitrogen constitutes the majority of the “rock” nitrogen. The nitrogen released into porewaters from organic matter in the form of NH$_4^+$ substitutes for K$^+$ in detrital phases such as K-feldspar and authigenic clays such as illite and is thus trapped in the sediment. With an increase in pressure ($P$) and temperature ($T$), both feldspar and clays participate in low-grade metamorphic reactions and illite progressively transforms into micas, with NH$_4^+$ substituting for K$^+$ in interlayer sites. For metasedimentary rocks, this affinity of NH$_4^+$ for clays and micas is illustrated by strong correlations between bulk nitrogen and large-ion lithophile elements (LIL.Es) such as K, Rb, and Cs (Fig. 1; see also Bebout et al. 2013a).

During metamorphism in the continental crust, particularly at greenschist and higher grades, NH$_4^+$ can be released by continuous metamorphic reactions, thermal decomposition (i.e. complete breakdown of mineral hosts such as mica), cation exchange, or redox reactions. Over wide ranges in pressure and temperature, continuous metamorphic devolatilization reactions can result in changes in mica chemistry in an evolving mineral assemblage, with or
without a decrease in mica modal abundance (Bebout and Fogel 1992; Bebout et al. 2013b). In a sufficiently oxidizing environment, NH$_4^+$ from micas can be stabilized as N$_2$ in fluids and lost from the rock (Duit et al. 1986; Bebout and Fogel 1992; Svensen et al. 2008). During progressive devolatilization, isotopically “light” nitrogen is preferentially fractionated into the metamorphic fluids, leading to an increase in the residual mica δ$^{15}$N value by up to a few per mil (Bebout et al. 1999; Jia 2006; Svensen et al. 2008). At higher grades of metamorphism, the breakdown of mica can result in partial melting (i.e. by dehydration melting). Melting can lead to appreciable loss of nitrogen from the rock, depending on whether or not there are suitable host mineral phases in the melting residue. Palya et al. (2011) demonstrated the retention of significant amounts of nitrogen in rock residues during melting, not only as NH$_4^+$ in residual K-feldspar, but also as N$_2$ in the channels of cordierite (FIG. 2A) produced by mica dehyydration-melting reactions. Nitrogen loss through these different pathways can potentially be traced by coupling variations in nitrogen concentrations and isotope compositions with Cs/K (FIG. 1) and Cs/Rb ratios. Cesium is highly mobile in fluids relative to K and Rb; this mobility is due to the large ionic radius of Cs, such that the size of the Cs ion is much greater than the size of the crystallographic sites in which K resides (Busigny et al. 2003; Palya et al. 2011; Bebout et al. 2013b; see FIG. 1). Theoretical calculations of fluid speciation and fluid inclusion studies indicate that, at continental crust metamorphic conditions (lower-greenschist to granulite facies), nitrogen in fluids in metasedimentary rocks is dominantly present as N$_2$ (Duit et al. 1986). N$_2$-bearing fluids liberated by metamorphic reactions can be (1) trapped as fluid inclusions or in microporous phases, (2) incorporated as NH$_4^+$ into newly formed silicate minerals, or (3) returned to the surface and recycled back to the atmosphere–hydrosphere system.

Melts derived from metasedimentary rocks at higher-P/T conditions in the amphibolite and granulite facies can contain a large amount of nitrogen that is incorporated as NH$_4^+$ into potassic minerals, such as micas and alkalifeldspars, during crystallization. NH$_4^+$ can be stabilized within melts under reducing conditions, particularly if the melted metasedimentary rocks contain graphite (Hall 1999). Ammonium has been shown to be present in all of the major mineral phases in granites except quartz (Honma and Ithihara 1981; Boyd et al. 1993) and to preferentially enter into biotite (Bi), followed (in order of decreasing concentration) by muscovite (Mu), K-feldspar (Kf), and plagioclase (Pl), with partition coefficients $D_{\text{Mu/Bi}}$, $D_{\text{Kf/Bi}}$, $D_{\text{Pl/Bi}}$ of 0.43, 0.38, and 0.11, respectively (Honma and Ithihara 1981). Total nitrogen concentrations in granites (average of 35 ppm; Hall 1999) are relatively low compared with those of sedimentary rocks, and peraluminous granites (S-type granites, resulting from melting of metasedimentary rocks) are significantly more enriched in nitrogen than peralcaline granites (crystallized from evolved mantle-derived melts). Nitrogen concentrations in granites can also be increased by hydrothermal alteration (Hall 1999), in some cases involving hydrothermal fluid produced by dehydration reactions in the wall rocks of contact aureoles (Bebout et al. 1999). The work to date on the nitrogen isotope compositions of granites indicates a relatively wide range of δ$^{15}$N values (+1 to +10‰), reflecting heterogeneity of the nitrogen sources and complex metamorphic–magmatic processes (Boyd et al. 1993; Bebout et al. 1999).

One of the strongest NH$_4$ enrichments in continental crustal rocks occurs in hydrothermal deposits in the vicinity of volcanic systems, where ammonium salts such as sal ammoniac (NH$_4$Cl) or ammoniojarosite ([NH$_4$HFe$_2^{3+}$(SO$_4$)$_2$(OH)$_6$]) can be identified. Significant NH$_4^+$ enrichment also occurs in buddingtonite (NH$_4^+$-feldspar, NH$_4$AlSi$_3$O$_8$), which is commonly associated with mercury- and gold-bearing hot spring deposits and occurs as an authigenic diagenetic phase (Svensen et al. 2008).
NITROGEN IN OCEANIC CRUST: MAGMATIC VERSUS HYROTHERMAL CONTRIBUTIONS

Oceanic crustal sections contain a variety of lithologies, including sediments, basalts, gabbros, and serpentinized peridotites. As in sediments and metasedimentary rocks of the continental crust, nitrogen in oceanic sediments is initially fixed by organic matter and then released as NH$_4^+$, which can substitute for K$^+$ in K-bearing minerals (Fig. 1). During subduction zone metamorphism of these sediments, the extent of change in the nitrogen concentrations and $\delta^{15}$N values resulting from devolatilization depends on the $P$–$T$ path they follow. Along warm $P$–$T$ paths (e.g. $>13^\circ$C/km), significant amounts of NH$_4^+$ are released from the rocks into fluids, as N$_2$ or NH$_3$, with nitrogen isotope fractionation enriching the residual rock in $^{15}$N (Haendel et al. 1986; Bebout and Fogel 1992). In contrast, cold $P$–$T$ paths ($<10^\circ$C/km) to depths of $\sim$100 km are not associated with significant loss of nitrogen into fluids, reflecting the high stability of NH$_4^+$ in phengite (high-pressure, low-temperature ferromagnesian white mica) and the lower degree of dehydration that occurs (Bebout and Fogel 1992; Busigny et al. 2003; Bebout et al. 2013b).

In oceanic mafic and ultramafic rocks formed at ridge axes, nitrogen concentrations are low relative to those in sediments. Nitrogen solubility in basaltic melts is low, similar to that of Ar; thus nitrogen is strongly partitioned into gas vesicles and escapes from the melt during degassing. Consequently, fresh basalts erupted onto the seafloor usually have total nitrogen concentrations lower than 1 ppm, including N in gas vesicles and nitrogen dissolved in glass. Nitrogen in vesicles of fresh MORB glass extracted by crushing techniques is in the form of N$_2$ and displays a large range of $\delta^{15}$N values, converging on the typical mantle value of about $-5 \pm 2\%$ (Cartigny and Marty 2013). However, the speciation of nitrogen dissolved in fresh basalt glasses is poorly constrained. Experimental studies suggest that nitrogen is mostly dissolved as N$_2$ in basaltic melt when the oxygen fugacity ranges between that of the iron-wüstite buffer and that of air; however, a fraction of the nitrogen may be present as the nitrosyl group (i.e. the monovalent radical -NO) in highly depolymerized melts (Roskosz et al. 2006). These experiments were performed under strictly anhydrous conditions, and nitrogen speciation in the melt could be different if water is added to the system, possibly producing H$_2$ under reduced conditions. At high $f$H$_2$, amine groups (e.g. NH$_3$, NH$_2$–) are formed and stabilized (Mysen and Fogel 2010).

Interaction of oceanic crust with seawater over a wide range of temperatures produces new mineral phases able to store nitrogen. Nitrogen concentrations in altered oceanic basalts from several DSDP/ODP sites range from $-1.3$ to 18.2 ppm, with $\delta^{15}$N values ranging from $-11.6$ to $+8.3\%$ (Li et al. 2007 and references therein). Relationships among nitrogen enrichments, mineralogy, and major and trace element concentrations suggest that nitrogen in these rocks resides dominantly as NH$_4^+$ in secondary minerals such as celadonite, feldspar, and smectite. Nitrogen concentrations and $\delta^{15}$N values of eclogitic metabasalts ($2-20$ ppm and $-1$ to $+8\%$, respectively) fall in the ranges for altered oceanic basalts; these data were interpreted as reflecting nitrogen enriched on the seafloor and preserved in subduction settings to depths approaching 100 km. Relationships between the concentrations of nitrogen and other trace elements suggest that nitrogen in these eclogitic metabasalts occurs mostly as NH$_4^+$ in phengites (Halama et al. 2010), again demonstrating the significance of micas in controlling deep-Earth nitrogen budgets and cycling. Although the nitrogen geochemistry of fresh gabbros from the oceanic crust has not yet been explored, a recent study of ophiolitic metagabbros from the Western Alps (Europe) demonstrated nitrogen concentrations and $\delta^{15}$N values of 2.6 to 55 ppm and $+0.8$ to $+8.1\%$, respectively (Busigny et al. 2011). The dominant nitrogen species in these rocks was proposed to be NH$_4^+$ substituting for Na–Ca in minerals such as feldspars, amphiboles, and clinoxyroxenes.

Peridotites serpentinized in oceanic and subduction settings contain 1.4 to 15 ppm nitrogen and have positive $\delta^{15}$N values of $+4$ to $+15\%$ (Philippot et al. 2007; Halama et al. 2012). Unaltered lithospheric peridotites have very low nitrogen concentrations ($<1$ ppm; Yokochi et al. 2009). Thus it appears that serpentinization is accompanied by nitrogen enrichment. This nitrogen could be present...
as NH$_4^+$ bound in tremolite (Halama et al. 2012) or as fluid inclusions in sealed voids or cracks produced during serpentinitization (Philippot et al. 2007).

**THE ENIGMATIC SPECIATION OF NITROGEN IN THE MANTLE**

The upper mantle is depleted in $^{15}$N relative to shallower reservoirs, including the oceans, the atmosphere, and continental and oceanic crust. Numerous studies of mid-ocean ridge basalts and diamonds point to a mean mantle $\delta^{15}$N value around $-5 \pm 2\%$o (Cartigny and Marty 2013). In contrast with this widely accepted $\delta^{15}$N value, the average nitrogen concentration in the mantle remains uncertain, with estimates spanning two orders of magnitude, from 0.27 to 36 ppm. This large uncertainty is due to the assumptions employed in various models, particularly as related to whether nitrogen behaves as a compatible or an incompatible element during partial melting of mantle peridotite (Cartigny and Marty 2013). Beyond this crucial question lies the problem of the speciation of nitrogen in the mantle. A detailed study of peridotite xenoliths from the lithospheric mantle showed bulk nitrogen concentrations between 0.1 and 0.8 ppm (Yokochi et al. 2009), near the lower estimates derived in the modeling studies. Comparison of crushing and step-heating extractions of these xenoliths indicated that only a small fraction of the total nitrogen (<10%) is carried in fluid inclusions. Analyses of mineral separates demonstrated that nitrogen is bound in crystal structures, with the highest affinity for phlogopite, followed by amphibole, clinoxyroxene, and olivine. Nitrogen and rubidium partition in a similar way among mantle peridotite minerals, suggesting that nitrogen occurs as NH$_4^+$ (Yokochi et al. 2009). However, the authors pointed out that their samples may not be representative of the average mantle because peridotite xenoliths can be modified by host-magma–mineral interactions (potentially inducing loss or addition of nitrogen) and/or metasomatic processes at crustal levels. Watenphul et al. (2010), in multianniv experiments at ultrahigh-pressure conditions (9.5–12.8 GPa), showed that a significant amount of nitrogen could be stored in the deep mantle as NH$_4^+$ in clinopyroxene. More-oxidized and lower-pressure conditions in the shallow mantle would lead to the oxidation of nitrogen into N$_2$ and the loss of nitrogen by magma degassing.

Diamond also carries important information regarding the global nitrogen concentration, the isotopic composition of nitrogen and, possibly, the generation of nitrogen-bearing fluid/melt in the mantle. In diamond, nitrogen substitutes for carbon and concentrations are as high as 3500 ppm, making nitrogen the main impurity. Nitrogen concentrations in diamond were initially thought to reflect the concentrations of the growth media (i.e. mantle fluid or melt enriched in carbon) and particularly their C/N ratios. However, further study showed that nitrogen concentrations in diamond depend primarily on growth rate. The speciation of nitrogen in mantle fluids and melts, from which diamonds precipitate, is poorly constrained. This is mostly due to the lack of nitrogen isotope fractionation factors (i.e. the distribution of nitrogen isotopes between two chemical species; see caption for Fig. 3) between diamond and any other molecular species. Such data would be useful particularly for cases where the nitrogen isotope compositions of a diamond population reflect progressive diamond growth and fluid/melt chemical evolution (see Thomassot et al. 2007).

Nitriles have also been proposed as possible host phases for nitrogen in the deep mantle. They form under highly reducing conditions, can be stable at very high pressures in the mantle, and could also be a significant nitrogen host in the Earth's core. In the deep mantle, nitrogen may be present in solid phases such as osbornite, a titanium nitride (TiN), and/or dissolved in melts, where it could occur in N$^3$- groups (Roskosz et al. 2006).

**TRACKING MINERAL–FLUID INTERACTION IN THE SILICATE EARTH**

In considering the distribution of nitrogen in the silicate Earth, one emerging theme is that the predominant nitrogen species in minerals (at least in the crust) is NH$_4^+$, which substitutes for K$^+$, Na$^+$, and/or Ca$^{2+}$ in phases such as illites, micas, feldspars, clinoxyroxenes, and amphiboles. A part of the nitrogen in sediments and metasedimentary rocks is likely preserved in organic matter affected to varying degrees by metamorphism (Ader et al. 2006). In the mantle, diamonds and nitriles are possible nitrogen hosts, but their abundance, and thus their importance for the mantle nitrogen inventory, remains uncertain. Metamorphic fluids under crustal conditions are likely dominated by N$_2$ and NH$_3$ (e.g. Duit et al. 1986). The stability of nitrogen oxides (NO, N$_2$O, NO$_3^-$) requires highly oxygenated conditions, and thus these species are mostly limited to surface/near-surface environments. The exchange of nitrogen among minerals and fluid species can be tracked by coupling nitrogen concentrations and isotope compositions with other geochemical tracers considered compatible with mobile fluid circulation (such as Al and Ti) or by normalizing to C for assessments of the chemical evolution of the organic components. Tracers tightly associated with NH$_4^+$ in minerals (e.g. the LILEs) can also be used (Fig. 1).

Nitrogen isotope compositions have been shown to be powerful tools for delineating mineral–fluid interaction in crust–mantle systems. However, experimentally determined nitrogen isotope fractionation factors are conspicuously lacking. The currently available fractionation factors for these systems have mostly been derived by theoretical calculations using spectroscopic data (Scalan 1958; Richet et al. 1977; Hanschmann 1981; see Fig. 3). Needed are (1) a critical evaluation of the quality of the spectroscopic data on which these calculations are based, and (2) experimental studies of nitrogen isotope fractionation in relevant mineral–fluid systems. **Figure 3A** reports the temperature dependence of available fractionation factors for pairs of molecular species relevant to study of the silicate Earth (NH$_4^+$–NH$_3$, NH$_4^+$–N$_2$, and NH$_3$–N$_2$). This figure clearly shows the discrepancies among the various calculations (for instance, for NH$_3$–N$_2$), with a range of uncertainty significantly higher than natural $\delta^{15}$N variation. The origin of these discrepancies is difficult to determine but may derive from error-inducing approximations made in the calculations and/or imprecise spectroscopic data. Nevertheless, a number of authors have suggested that the directions and magnitudes of isotopic evolution in natural crustal settings match the fractionation factors for NH$_4^+$–N$_2$ and NH$_3$–NH$_4^+$ calculated by Hanschmann (1981) (see Haendel et al. 1986; Behout and Fogel 1992; Jia 2006). As an example, **Figure 2B** shows that, in pegmatite samples containing both beryl and muscovite, the $\Delta^{15}$N$_{\text{beryl-muscovite}}$ (mean = +2.9‰; $\sigma$ = 1.1‰; where $\Delta^{15}$N$_{\text{beryl-muscovite}}$ = $\delta^{15}$N$_{\text{beryl}}$ – $\delta^{15}$N$_{\text{muscovite}}$) closely matches that predicted theoretically by Hanschmann (1981) for the fractionation between N$_2$ and NH$_3$ for geologically plausible crystallization temperatures of 550 ± 50°C (data from Lazzerei et al. 2011; see the plot of fractionation factors in Fig. 3A). In these nearly bimodal pegmatite samples, the beryl is assumed to contain nitrogen as N$_2$ and the coexisting muscovite is assumed to contain nitrogen as NH$_4^+$. Another possibility to consider, in interpreting nitrogen data for silicate systems, is that crustal minerals and fluids are not necessarily fully equilibrated with respect to nitrogen concentrations and isotope compositions, pointing to the need for experiments aimed at determining kinetic fractionation factors (Li et al. 2009).
Given the various magnitudes and directions of nitrogen isotope fractionations among the different fluid species of nitrogen, it is evident that changes in redox conditions can exert a strong influence on the nitrogen isotope signature in any given system (see Fig. 3). At high metamorphic grades and in magmatic systems, where mineralogy and melt/fluid chemistry evolve during changes in temperature and/or redox conditions, nitrogen isotope fractionation could occur among hydrous fluids, melts, and minerals (Roskosz et al. 2006; Mysen and Fogel 2010). Finally, it is not yet known whether nitrogen isotopes are fractionated during partial melting reactions or provide a true record of the $^{15}$N of their sources.

**OUTLOOK**

**Nitrogen as a Biogeochemical Tracer in the Deep Earth** For the most part, nitrogen in the deep Earth owes its existence to initial incorporation by biological processes at the Earth’s surface, followed by mobilization at depth via sediment burial, devolatilization, and melting. Nitrogen should see expanded use, in tandem with C and the LILEs, via sediment burial, devolatilization, and melting. Nitrogen as a biogeochemical tracer in any given system (see Fig. 3). At high metamorphic grades and in magmatic systems, where mineralogy and melt/fluid chemistry evolve during changes in temperature and/or redox conditions, nitrogen isotope fractionation could occur among hydrous fluids, melts, and minerals (Roskosz et al. 2006; Mysen and Fogel 2010). Finally, it is not yet known whether nitrogen isotopes are fractionated during partial melting reactions or provide a true record of the $^{15}$N of their sources.

**Continental Crust** Continental crust is extremely heterogeneous. Current estimates of deep continental crust concentrations and $^{35}$N (see Bebout et al. 2013a) are based on a very small number of analyses of exhumed suites and xenoliths. Badly needed are additional studies of nitrogen in exposed continental crust sections to evaluate, among other issues, the possible role of continental crust formation in the uptake of nitrogen from the atmosphere during the early evolution of the biosphere (Goldblatt et al. 2009).

**Oceanic Crust Sections** The evaluation of the nitrogen reservoir in variably altered oceanic crust is hampered by low N concentrations. The analysis of nitrogen at these levels requires specialized extraction methods and high-sensitivity mass spectrometry (see the Analytical Box in Cartigny and Marty 2013).

Studies of nitrogen in modern and ancient oceanic crustal sections are crucial for determining the fluxes of nitrogen from external reservoirs (atmosphere, hydrosphere, biosphere) into the deep mantle through subduction zones.

**The Mantle** Our knowledge of the nitrogen concentration and isotopic composition of the mantle is based on the fragmentary record of exhumed rocks, xenoliths/xenocrysts, and mantle-derived igneous rocks. Future work on mantle nitrogen (and carbon) should seek to better constrain the magnitude of isotope fractionation among minerals and “fluids” within the mantle and to determine whether subduction inputs can locally result in deviations from more “normal” mantle isotopic compositions. Better knowledge of the nitrogen isotope composition of the mantle would elucidate (among other issues) processes of early-Earth formation, core–mantle segregation, atmospheric evolution, and the recycling of surface material to the mantle.

**Need for Fluid/Melt–Mineral Studies of Fractionation Factors** There is a critical need for experiments to determine nitrogen isotope fractionation associated with fluid–mineral or melt–mineral exchange. Particularly useful would be studies of fractionation between fluids of various types—and with varying nitrogen speciation (particularly as N$_2$ and NH$_3$)—and micas (muscovite and biotite), K-feldspars, cyclosilicates (beryl and cordierite), and diamonds. For example, knowledge of nitrogen speciation in diamond-forming fluids could place constraints on the oxygen fugacity of the mantle. The availability of experimentally confirmed nitrogen isotope fractionation factors for mica–fluid pairs would improve estimates of the proportions of initially subducted nitrogen either released into fluids during subduction of oceanic crustal sections or returned to the deep mantle.
Diffusion Rates for Nitrogen in Silicate Materials

Still unknown are the rates and mechanisms by which nitrogen diffuses in minerals such as the micas, alkali feldspars, clinopyroxenes, and cyclosilicates, potentially affecting closure temperatures. This information is important for evaluating the extent to which these minerals can preserve information regarding nitrogen behavior during high-temperature processes.

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Biogeochemical cycling of nitrogen on the early Earth. Elements 9: 345-352


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Nitrogen shows unique features among the volatile elements. To be cycled, atmospheric di-nitrogen (N\textsubscript{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 (\(15\text{N} \) depleted) and the Earth’s surface (\(15\text{N} \) 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\textsubscript{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\textsubscript{2} is massively cycled by biological activity (at a rate of \(\sim 2 \times 10^{21} \text{g N/y} \); 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 (\(4 \times 10^{21} \text{ g N} \)) 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\textsubscript{4}\textsuperscript{+}). Having similar charge and ionic radius as potassium, ammonium then substitutes for – and follows – 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 \(15\text{N} \)-depleted homogeneity of the mantle (\(\delta^{15}\text{N} = -5 \pm 2 \text{ per mil [‰]} \)) compared to the atmosphere (\(\delta^{15}\text{N} = 0 \text{‰} \) by definition) and crust/sediments (\(\delta^{15}\text{N} > 0 \text{‰} \)). 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 \(15\text{N} \) values that converge towards an endmember value of around ~9‰. 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. Ololdinyo Lengai volcano; Fischer et al. 2009). Another important result, inferred from the observation of near-constant N\textsubscript{2}/40Ar\textsuperscript{*} ratios in MORB (where 40Ar\textsuperscript{*} stands for 40Ar 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\textsubscript{2}/40Ar\textsuperscript{*} ratios should be representative of the mantle source value (Marty 1995). Coupled to He flux, N\textsubscript{2}/40Ar\textsuperscript{*} ratios constrain the outgassing mantle flux to about \(0.7 \times 10^{13} \text{g N/y} \) (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 40Ar results from the decay of 40K over time (40K half-life = 1.25 Gy), the calibration of N to 40Ar lets us link nitrogen to non-volatile, mantlerecyclable potassium and to time. Thus N\textsubscript{2}/40Ar\textsuperscript{*} 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 \(\delta^{15}\text{N} \) values measured in some MORB samples (Fig. 1), generally associated with low 40Ar/38Ar ratios, might reflect contamination by surface material, source heterogeneity (in particular,
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 N2 or ammonium (Watenehul et al. 2009), both likely behaving incompatibly during partial melting. In addition, the scale 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 δ15N 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 15N than present-day mantle nitrogen, possibly as low as δ15N = −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 \times 10^{21}g N) is the main reservoir of nitrogen at the Earth’s surface and, by convention, has a δ15N value of 0‰. Crustal nitrogen (in sedimentary and crystalline rocks) represents approximately one fifth of the surface inventory (−1.1 \times 10^{21}g N) and has a mean δ15N 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 \times 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](image-url) Comparative histograms of δ15N 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 $\delta^{15}$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/yr; 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 $\delta^{15}$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/yr; 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 specification 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 $\delta^{15}$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 (1.32 × 10$^{11}$ g N/yr), 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/yr (Hilton et al. 2002), the net recycling flux of nitrogen is 10.4 × 10$^{11}$ g N/yr. 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.

\[ \text{Primordial Nitrogen Isotope Composition} \]

**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 reflect 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.
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 ARCHAEOAN 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 $10.4 \times 10^{11}$ g N/y minus a degassing flux of $0.7 \times 10^{11}$ 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. 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 $\delta^{15}$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 \( \delta^{15}\text{N} \) values (Sano and Pilinger 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 \( \delta^{15}\text{N} \) 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 \( \delta^{15}\text{N} \) values, from –40 to +18‰. This range is commonly interpreted to reflect the interplay between source heterogeneity (for the most \( ^{15}\text{N} \)-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 +9‰. This view is how ever difficult to recon-cile with positive \( \delta^{15}\text{N} \) 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 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 \( \delta^{15}\text{N} \) 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^{27}g N) by the N flux from the mantle approximated by its mid-ocean ridge flux, is \( \sim 7 \times 10^{10} \) 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. \( 5 \times 10^{13} \) y for \(^{36}\text{Ar} \), 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 \( ^{15}\text{N} \)- 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 (\( ^{15}\text{N} \)- 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 \( ^{15}\text{N} \)-O groups), ammonium and \( ^{15}\text{N} \) 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 unsuit- able owing to late-stage recycling. The absence of a direct and undisputable secular record for mantle \( ^{15}\text{N} \) could reflect limited N recycling as a consequence of high N scavenging by other experiments and no direct quantitative observation. Thus, the evidence is not yet in for satisfactorily interpreting ancient secular variations.

**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 isotopic fractionation of atmospheric N during hydrodynamic escape, N isotope fractionation during mantle–core segregation, the late accretion of \(^{15}\text{N} \)-rich volatiles to form the atmosphere and oceans of the Earth, the recycling of light \(^{15}\text{N} \)-depleted nitrogen metabolized during ancient times (but see}
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 $\delta^{15}$N value, contrasting with the negative $\delta^{15}$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 $\delta^{15}$N values as low as $-40‰$ (i.e. the lowest value for $\delta^{15}$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 $\delta^{15}$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 $\delta^{15}$N would have progressively decreased the $\delta^{15}$N values of surface reservoirs, while the recycling of surface N via subduction zones would have increased the upper mantle $\delta^{15}$N value. All these possibilities remain to be confirmed and quantified.

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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 $^{15}N_2 – H^+$, $^{13}C – ^{16}O^+$ or $C_2H_2^+$) not separable by most low-resolution ion-ratio mass spectrometers (IRMS). For example, Beaumont et al. (1994) reported an increase in $\delta^{15}N$ for many samples 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). $N$ being a reactive element, additional difficulties have recently been recognized, 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 sub-mole-size procedural blanks can now be achieved (e.g., Kendall and Grim 1990; Boyd et al. 1993).

$N$ 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 instruments. 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).

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.

$N$ 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 $\sim$5 orders of magnitude. Samples as small as $10^{-11}$ mol N (0.1 ng N) can now be routinely analyzed with sub-permille 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.
REFERENCES


15N value. Geochimica
Nitrogen is a critical element for living organisms on Earth. While atmospheric N₂ is plentiful, organisms find it difficult to metabolize, requiring chemical modifications that are rare or absent in abiotic chemistry. Living organisms reduce N₂ to NH₃ with elaborate, energy-intensive, biochemical processing to create nitrogen-bearing carbon compounds essential for life. Astrobiologists have long discussed what role nitrogen could play in shaping life on other planets. Work on Martian meteorites has provided new insights into nitrogen cycling on Mars. Research on meteorites ties into investigations by NASA’s Mars Science Laboratory that are providing on-the-ground information to piece together a more cohesive picture of the importance of nitrogen for establishing a habitable environment.

**INTRODUCTION**

In aquatic, oceanic, and terrestrial environments on Earth, nitrogen (N) is a limiting nutrient and, as such, controls both the amount of biomass and the diversity of organisms that can exist in a given environment. Nitrogen is critical in biological processes because carbon’s interactions with N, O, and other heteroatoms (atoms that are not carbon or hydrogen) are critical for the synthesis and metabolism of compounds such as purines, pyrimidines, amino acids, and porphyrins. These molecules provide the basis for information storage, enzymatic activity, and metabolism in all living organisms. Indeed the majority of metabolism involves interactions between functional groups containing C–N, C–O, and other heteroatomic bonds. Active cycling of N between various oxidation states is the purview of living organisms on Earth. Therefore, active N cycling beyond that attributable to abiological processes on another solar system body may be a sign of extraterrestrial life, even if all the enzymatic reactions and processes found there are completely different.

As is typical for any chemical system, nitrogen cycling exists in the absence of biology, for example, in the deep Earth (Cartigny and Marty 2013 this issue). Beyond Earth, N is found in dense interstellar clouds, where it has many forms, including CN, HCN, C₂N₂, CNO, N₃H, NH₃, and NO (Charnley and Rodgers 2002; Àleon and Robert 2004). We also expect that, given the abundance of N in the Solar System (Halliday 2013), as a gas it will interact with higher-temperature silicate phases much like it does on Earth. The Earth, however, is an exception, because it is the only planet currently known to have the vigorous tectonic cycle needed for sustaining N cycling. Titan, Triton, and Kuiper Belt objects are intriguing reservoirs of N chemistry in the Solar System. Abundant N₂ and CH₄ (Imanaka et al. 2004) in the atmospheres of these bodies have contributed to the formation of cyanide, cyanogens, and, in some cases, tholins; the latter are complex molecules formed on icy bodies by the reaction of ultraviolet (UV) light with simple organic molecules like CH₄ (Niemann et al. 2005; Atreya et al. 2008). Remarkably, tholins are among other complex organic molecules that have also been detected in the circumstellar disk of star HR4796A (Debes et al. 2007), a hint that building blocks to support life might be common in other planetary systems. We also know from studies of meteorites that N can be a prominent element in organic matter from carbonaceous chondrites, where it occurs as soluble amino acids, HCN, NH₃, benzonitrile, and a range of heterocyclic nitrogen compounds, such as pyrimidine.

After outlining new technologies for finding nitrogen, this paper will highlight three areas of active research into nitrogen’s biosignature, detection, and characterization in extraterrestrial environments: N cycling in terrestrial analogue study sites; N on Mars and some of the Solar System’s moons; and N in carbonaceous chondrites, asteroidal meteorites that contain abundant organic matter.

**NEW TECHNOLOGIES FOR FINDING NITROGEN**

Laser-induced breakdown spectroscopy (LIBS) is a remote sensing technique designed to measure the elemental composition of rocks and minerals (Sinha et al. 2011). In this method, a laser is fired onto a sample surface and high-temperature plasma is generated. As the plasma cools, the elements present release light of characteristic wavelengths; these emissions are measured through a telescope and transmitted via an optical fiber to multiplexers, spectrometers, and data processing equipment. An instrument is currently housed on Mars Science Laboratory’s Curiosity rover to help mission scientists decide where the rover should go to make more detailed measurements with other analytical instrumentation, i.e. CheMin and SAM (discussed below). Also, the instrument is designed to

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remove and analyze rock dust to understand weathering on Mars. For light elements, LIBS is most sensitive for the detection of H and C, but has the potential to measure N. Although LIBS may steer the rover to interesting sites, the instrument with the greatest potential for detecting N compounds is the Sample Analysis at Mars (SAM) instrument (Mahaffy et al. 2012), which has a gas chromatograph coupled to a mass spectrometer, in addition to a tunable laser spectrometer. SAM is measuring the molecular composition of the atmosphere and compounds in rocks and soils. At this time, no definitive measurements of oxidized or reduced N compounds have been recorded on Mars. NH₄, NO₃, and CN molecules may have been detected in the Rocknest suite of samples, but these observations need to be confirmed (Navarro-González et al. 2013; Stern et al. 2013; Wray et al. 2013).

Laser ablation–miniature mass spectrometer (LA–MMS) for elemental and isotopic analysis has yet to be deployed on a rover, but this technique has the potential for measuring astrobiologically relevant isotopic compositions. The technique starts with laser ablation; the ablated sample then enters an ion source where it undergoes secondary ionization, separation by a magnetic sector, then counting by a 2140-element charge-coupled device (CCD) detector array. The technique works well for the alkali metals and oxygen but has yet to be used for the detection of low abundances of N in rocks, although the potential is there (Sinha et al. 2011).

TERRESTRIAL ANALOGUE SITES

Microbes are the dominant biological agents in terrestrial N cycling, and it is reasonable to expect that this would be true on other planets as well. Nitrogen in all its oxidized and reduced forms is shuttled back and forth through oxidation states by various enzymes in microorganisms. Although higher organisms participate in these reactions, it is the microbial world that is most influential and varied in processing nitrogen. Recently, scientists have discovered and confirmed several new pathways for reduction of NO₃, particularly in anaerobic processes. The question of how and where these pathways take place on Earth is studied by molecular and isotopic methods (Hastings et al. 2013 this issue). In terrestrial analogue research, the goal is to observe an environment or ecosystem on Earth that has analogous relevance to the Solar System body of interest, usually Mars or Europa (FIG. 1). In astrobiology studies, these analogues usually are areas where microbial life dominates environments that are similar to those found on Mars; such areas include, but are not limited to, the Antarctic Dry Valleys, the Atacama Desert, the Rio Tinto mine, Axel Heiberg Island, Yellowstone National Park, White Sands National Monument, and Svalbard (Navarro-González 2003; Steele et al. 2010).

Ecologists engaging in analogue research take a broad and abstract approach in order to create the big picture. They examine aspects of N pools (e.g. NH₄, NO₃, and organic N) and their isotopic compositions, distributions of organisms, and environmental parameters, and they seek to create conceptual models of how energy and materials flow in a particular ecosystem. Analytical chemists who have the expertise to design instruments and understand the types of chemical and biochemical reactions that are important for analogue work are called upon to step out of their laboratories and into extreme environments, where they often encounter very practical problems. For example, these scientists have developed new methods for field-based genetic analysis and also handheld instruments for point-of-sampling analysis (e.g. Raman and laser-induced breakdown spectroscopy) for measuring biological and environmental parameters. Engineering advances are key to ensuring that the measurements made by robotically deployed instrumentation are correct, until astronauts are able to travel to Mars or other planetary bodies. Furthermore, engineers with the technical background to design, build, and implement the technology needed to carry out the necessary analyses are key participants. Last, but not least, planetary scientists interacting with these three groups provide the background for linking the terrestrial analogue environments used to test analytical methods and instruments with the extraterrestrial environments to be studied. Rarely do such diverse scientists work together; however, in the past 15 years or so, NASA’s Astrobiology Program has led the world in establishing this type of collaborative work.
One example of a terrestrial analogue site using nitrogen cycling as a biosignature is gypsum deposits, which have been detected on Mars (Glamoclija et al. 2012; López-Lozano et al. 2012). At White Sands National Monument in the United States (Glamoclija et al. 2012), scientists searched for key genes responsible for the oxidation and reduction of N using a functional gene analysis approach. They found novel N pathways associated with microbial communities within mat-like layers in dune and ephemeral-lake sediments and correlated the molecular genomic data to elemental N cycling of nitrate and ammonia. Together, elemental and molecular pathway assays revealed “signatures” of elemental cycles created by microbes rather than patterns seen in simple weathering patterns.

Unusual concentrations of N in the environment can also be thought of as biosignatures, because living organisms move and can therefore transfer elements from one place to another. For example, elemental and stable isotope signatures in soil and plant material have been used to trace the movement of nitrogen from the marine to the terrestrial environment by the Arctic fox (Fogel et al. 2007). This study showed a distinct signature of N isotopes and concentrations caused by the fox within an Arctic landscape containing very little N, an observation that clearly demonstrates the principle that living organisms, whether they are microbes or larger organisms, cause distinct and measurable changes in the distribution of nitrogen in the environment. Concentrations of N on Earth are called hot spots—patches in space and time that have disproportionately higher reaction rates of N cycling relative to surrounding areas (McClain et al. 2003); on the other hand, hot moments are short periods of time when disproportionately high reaction rates occur relative to longer time intervals. Hot spots occur particularly in areas where hydrous environments converge and meet substrates that are missing reactants. On Earth, this could be the confluence of two rivers with different chemistries, for example. In sediments, hot spots could occur at oxic–anoxic interfaces where organic matter from the oxic zone is transported into the anoxic zone. Essentially, hot spots can produce a highly heterogeneous biogeochemical landscape, particularly in terms of N concentrations and reactions (McClain et al. 2003). Variations in N elemental concentrations and isotope ratios in any kind of landscape or rock sample can be a potential biosignature, if other abiotic formation mechanisms can be excluded.

It is possible to distinguish abiotic formation and cycling of oxidized and reduced N forms from similar processes by biological processes using stable isotope tracers (for example, $\Delta^{15}O$ and $\delta^{15}N$; for definitions, see Bebout et al. 2013 this issue) and elemental distributions. The Atacama Desert has been another important analogue site for determining whether nitrogen distributions are biotically or abiotically controlled. Atacama soils contain high concentrations of nitrate and ammonia. They are thought to have originated via atmospheric deposition, but within the soil, microbial processes have modified their oxidation states. Michalski et al. (2004) found $\Delta^{17}O$ signatures in nitrites that suggested they were derived primarily from atmospheric sources via photochemical reactions in the troposphere and stratosphere. They also found isotopic signals pointing to a microbial source—these signals increased in prominence with higher moisture content and milder conditions. Sutter et al. (2007) developed infrared techniques for detecting nitrites in Atacama Desert soils. Although there were numerous interferences, NO$_3^-$ could be detected in these soils because they lacked primary silicates. Walvoord et al. (2003) found that deserts contain vast stores of nitrites in subsurface layers, accumulated by long-term leaching from moisture-poor soils. This finding may be significant to the search for concentrations of oxidized N on Mars.

**MARS AND MOONS OF ASTROBIOLOGICAL INTEREST**

Mars

Mars is not tectonically active; therefore, N trapped in deep reservoirs cannot be recycled to the atmosphere as it is on Earth. Nonetheless, both N$_2$ and NO produced via cosmic ray interactions with N$_2$ are present in the Martian atmosphere. There has also been debate about “missing” N compounds on Mars, which could have escaped to space or been buried in the regolith (Manning et al. 2008). Mancinelli and Banin (2003) hypothesized that typical Martian soils may resemble dry, desert soils on Earth and are likely to contain N as nitrate or as NH$_4$ bound to aluminosilicate minerals. Stepped combustion analysis of one of the SNC group (shergottites, naklites, and chassignites) of Martian meteorites released $^{15}$N-enriched N$_2$ at high temperature, as well as noble gases with isotopic ratios similar to those measured by the Viking mission to Mars. These findings helped tie SNC meteorites to Mars, but required the presence of an indigenous, “missing,” $^{15}$N-depleted phase to mix with the atmospheric component (e.g. Bogard and Johnson 1983). SNC meteorites, both archived and freshly collected, provide an opportunity to use state-of-the-art instrumentation (e.g. nano-SIMS, confocal Raman imaging spectroscopy) to actively search for N in organic compounds. In 13 of these meteorites, organic carbon phases that formed from both igneous and hydrothermal processes were identified (Steele et al. 2012, 2013).

Finding bound N in Martian meteorites raises questions as to how these phase(s) were formed and why they are present. Recently, Aoudjehane et al. (2012) measured N in different phases from the freshly collected Tissint meteorite (Fig. 2), using similar stepped temperature-release techniques as Becker and Pepin (1984). They found N$_2$ dissolved in basaltic glasses and measured Ar/N ratios with respect to $\delta^{15}$N values. Using this method, they calculated the $\delta^{15}$N of the Martian atmosphere to be +643‰, strikingly similar to the value of +740‰ for the Martian atmosphere measured by Viking (Nier et al. 1976). The Tissint sample was then combusted to find an organic matter pool with an isotopic composition of –26.6‰ for $\delta^{13}$C and –4.5‰ for $\delta^{15}$N, with a C/N ratio of 13.6. Above 600°C, the gas released gave values of +16‰ for $\delta^{13}$C and +300‰ for $\delta^{15}$N, isotopic compositions that are far outside those of any possible terrestrial sources. Following heating at high temperature, a fraction of the C ($\delta^{13}$C of –26.3‰) and N ($\delta^{15}$N of less than +10‰) that was released was deduced to be of magmatic origin. Steele et al. (2013) reported similar values to those of Aoudjehane et al. (2012), with some noticeable differences in the isotopic compositions of the high-temperature phase. They detected fragments of organic nitrogen compounds (e.g. CN, CNO) within inclusions completely enclosed by volcanic glasses (Steele et al. 2013). These N molecules are housed in organic phases formed at high temperature and are not the remains of biological material. On Earth, the C and N relationships of compounds from organisms survive relatively high-temperature metamorphism in sediments and rocks (Busigny and Bebout 2013 this issue); further work is needed on Martian samples to begin to make similar comparisons. These recent findings indicate that multiple pools of Martian N are not only contained in these meteorites but are also widespread in many Martian soils and rocks, thus accounting for the “missing” nitrogen phase.
The atmosphere on early Mars probably contained 0.5 mbar of $N_2$, which may have resulted in slight greenhouse gas warming of the planet (Paris et al. 2013). The presence of liquid water is essential for abiotic fixation of $N_2$ by several mechanisms, including the formation of HNO by dissolution of $N_2$ (Boxe et al. 2012). In addition, NO could be produced by photodissociation of $N_2$ in the atmosphere and ammonia could be produced by reduction of $N_2$ by ferrous iron. Recently Steele et al. (2013) postulated the presence of CN species from the reduction of $N_2$ by pyrrhotite in hydrothermal systems during either volcanism or meteorite impact (Manning et al. 2008). Other impact-generated processes include deposition of meteoritic nitrogen and formation of short-lived hydrothermal systems that allow $N_2$ fixation through abiotic reactions (Manning et al. 2008).

The current Martian atmosphere contains only 0.2 mbar $N_2$. Even with this lowered atmospheric concentration, it has been postulated that there is enough biologically available N in the form of HNO$_3$ in the subsurface to support a limited microbial population (Boxe et al. 2012). Steele et al. (2000) observed that terrestrial microbes on carbonate globules in the Martian meteorite ALH 84001 show morphological signs of growing under conditions of limited nitrogen, indicating that Martian igneous rocks are habitable to terrestrial-type organisms.

The planets of the inner Solar System show signs of evolution from a primordial, presumably impactor-delivered, nitrogen budget. Earth's $N_2$ is similar in abundance and isotopic composition to nitrogen in CI chondrites—presumably material that originally formed the Earth. Both are depleted relative to the solar composition. On Venus, the concentration of nitrogen in the atmosphere is about the same as on Earth, whereas the concentration on Mars is significantly less (by 4 orders of magnitude). The solar bulk composition is much higher (by a factor of $10^6$), as are the bulk compositions of comets and CI chondrites. Venus, Earth, and Mars probably all had the same original composition, but Mars is now depleted in key volatiles with respect to Earth and Venus. Although little is known about N in deeper environments on Mars and Venus, the dominant atmospheric process on Mars is degassing from multiple impacts (Halliday 2013). In particular, we do not know whether there is a sink for N in the metallic cores of the terrestrial planets.

A final possibility for N storage on Mars is in clathrates (molecule-trapping atomic structures). Mousis et al. (2012) calculated the stability of clathrate hydrates at low temperature and low pressure in the conditions prevailing in the atmosphere and at the surface of Mars. If clathrates were present on Mars, they would easily be able to incorporate $N_2$ in their caged structures. Martian clathrates would probably take the form of a CO$_2$-based clathrate, unstable in the close subsurface during the Martian summer and stable during the winter. The stability of presumed clathrates on Mars may control an aspect of the Martian N cycle by releasing and trapping gases at different times of the year and in different locations in the subsurface. Atmospheric methane, a powerful greenhouse gas, may control the Martian climate and may vary in abundance in response to the formation of CO$_2$/N$_2$/Ar/CH$_4$ hydrates in the seasonal polar caps.

**Moons of Astrobiological Interest**

Although Mars is currently the main target for investigating the potential for extraterrestrial life, several of the moons surrounding Jupiter and Saturn are thought to be excellent candidates, in particular because they contain active hydrothermal systems. Enceladus, one of Saturn’s smaller moons, contains significant amounts of liquid water, then thermal decomposition might form molecular N$_2$ as well. Alternatively, N$_2$ may have been the original carrier of N to Enceladus via clathrates. Tectonic activity, geysers, and volcanoes may be producing the constant source of N-containing compounds necessary for life.

Compared to the atmosphere on Mars, Titan, the largest of Saturn’s moons, has a dense atmosphere, dominated by N$_2$ and CH$_4$. Titan’s atmosphere extends to at least 130 km above the surface (Niemann et al. 2005). Methane...
Nitrogen is present in significant abundance in the organic matter isolated from meteoritic materials. The insoluble organic matter (IOM) isolated from the matrix of carbonaceous chondrites has a C/N ratio of 24, indicating a substantial amount of N relative to organic carbon. In the Tagish Lake meteorite, up to 0.2% of the total rock is N, with nearly 50% of the N in the form of IOM (Alexander et al. 2013). The N in the bulk rock not included in the IOM could be in the form of soluble organic N, such as amino acids, amino sugars, and other small N-containing compounds (Alexander et al. 2013). Additionally, the $^{15}$N of the amino acids from the Murchison meteorite indicates that most of these acids are extraterrestrial (Engel and Macko 1997). Ammonia has been found associated with IOM from carbonaceous chondrites, in addition to significant quantities of amino acids and other amines (Pizzarello et al. 2011). Therefore, meteoritic NH$_3$ may have been a ready source of NH$_3$ for early prebiotic chemistry and, indeed, possibly the first living organisms. Callahan et al. (2013) confirmed earlier work by Martins et al. (2007) by finding widespread occurrences of nucleobases in 11 out of 12 carbonaceous chondrites they tested. Clearly N can be found not only as inorganic molecules but also in combined organic forms that, on Earth, have originated principally through biological reactions.

Meteorites also contain “nanoglobules” embedded in insoluble organic matter. Nanoglobules are nanometer-sized, round objects that can be hollow or filled and are composed primarily of aromatic carbon. Busemann et al. (2006) found what they called “hot spots” of $^{15}$N in IOM, which could explain the enrichment of $^{15}$N in bulk IOM and could potentially originate from processes in molecular clouds. De Gregorio et al. (2011) examined the $^{15}$N of nanoglobules and compared them to bulk IOM and nonglobular regions having enriched $^{15}$N values. They determined that the primary source of the hot spots was within the IOM rather than the nanoglobules. They found that the chemistry of nanoglobular nitrogen for the most part was determined by the type of meteorite and reactions with the parent body. Those globules with highly enriched $^{15}$N, like the hot spots in IOM, were most likely formed outside the solar nebula where $^{15}$N-enriched ammonia condensed on ice grains at extremely low temperatures (e.g. 10 K) (Charnley and Rodgers 2002).

**PROJECTIONS**

Nitrogenous compounds on Earth are highly reactive and largely processed by microorganisms. Diagenesis and degradation change the molecular form of living biomass drastically, but the isotopic and elemental concentrations are preserved when nitrogen is subducted into the deep Earth. N$_2$ gas is then expelled during volcanic eruptions, and the cycle is completed when N$_2$ is fixed by microbes. What would we expect on a planet showing no sign now of active plate tectonics? We would expect a depletion of N$_2$ in the atmosphere and an accumulation in oxidized and reduced forms in the near surface. A soil devoid of life would interact with ultraviolet light to produce N$_2$ gas, which would eventually be lost to space. For Mars, this picture would change if the surface were wet because nitrate and ammonium could then leach into deeper strata and sediments and avoid destruction by UV processes. In this case, we would expect that N concentrations and isotopic compositions be related to rock type (e.g. gypsum or phyllosilicate-bearing rock) and remain in surface layers on the mostly dry Martian surface. Some buried nitrogen would be continuously lost through impact “gardening,” in the absence of subsurface sequestration of water. If we were to discover “hot spots” in Mars’s geological record, that might be an important clue to finding life on another planet.

**ACKNOWLEDGMENTS**

The authors thank Marc Fries (Johnson Space Flight Center) and Mihaela Glamoclija (Carnegie Institution and Rutgers University) for their reviews. We thank the AMASE team and acknowledge support from NASA ASTEP NNX09AB74G and the CIW-NASA Astrobiology Institute (NNA09DA81A).
Nitrogen forms a variety of compounds that are significant in the interstellar medium, star formation, planetary formation and the evolution of life. Through the study of planetary materials, we recognize three generations of nitrogen and nitrogen-bearing compounds: primary, secondary and tertiary. Species from different sources are recognized by characteristic isotopic compositions or specific modes of occurrence (e.g. Grady and Wright 2003).

**PRIMARY NITROGEN**

Primary nitrogen is nitrogen that has been inherited directly from the molecular cloud from which the Solar System evolved. The isotopic composition of primary nitrogen reflects the original source reservoirs and is preserved in presolar grains, organic molecules and high-temperature condensates.

Presolar grains are found in primitive meteorites. These grains originated from other regions of the molecular cloud, beyond the protoplanetary disk from which our Solar System formed ~4.567 billion years ago. Presolar grains were first recognized because they host isotopically unusual noble gases (Zinner 2007). Subsequent characterization has shown them mainly to be grains of silicon carbide (SiC) and graphite, plus oxides and, possibly, nanometre-sized diamonds. The isotopic composition of the grains themselves is often, but not always, unusual, because the grains come from stars which experienced different nuclear processes from our Sun (e.g. carbon-burning stars, supernovae). Their isotopic composition is related to the production of individual species from our Sun (e.g. carbon-burning stars, supernovae). Their isotopic composition reflects the original source reservoirs and is preserved in presolar grains, organic molecules and high-temperature condensates.

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**SECONDARY NITROGEN**

Second-generation nitrogen-bearing species are those produced on parent bodies by alteration (aqueous or thermal) of primary nitrogen-bearing species. Such processes may lead to modification of the primary species, for example, the graphitization of amorphous carbon during metamorphism, and may or may not alter the original isotopic compositions. The most primitive types of meteorites, the CI, CM and CR chondrites (Fig. 2), contain ~500–5000 ppm nitrogen, with overall δ15N ranging from +15‰ to +150‰ (see Fogel and Steele 2013 this issue).

**HIGH-TEMPERATURE CONDENSATES**

High-temperature condensates: Primary nitrogen is also present within highly reduced minerals thought to be grains that condensed at high temperatures as the presolar nebula cooled (Meibom et al. 2007; Feng et al. 2012). These minerals include osbornite (TiN), sinoite (Si2N2O) and nierite (Si3N4), and they occur in varying abundances in interstellar space, transport and processing in the protoplanetary disk and their distribution through asteroidal parent bodies make it likely that presolar grains also survive alteration on the parent bodies of primitive meteorites.

**ORGANIC MATERIAL**

The interstellar medium is rich in organic molecules formed by several different processes, such as ion–molecule reactions on the surface of icy grains. The effect of such reactions is to increase the heavier isotope over the lighter one, producing material with characteristic isotopic signatures (e.g. Herbst 2003). Inventories of interstellar molecules (e.g. www.astro.uni-koeln.de/cdms/molecules) indicate that there are ~60 N-bearing species, most of which are organic in nature. As a result, a variety of N-bearing organic species are available for incorporation into meteorite parent bodies, and these species may be subsequently altered during parent-body evolution. These interstellar species include molecules (e.g. ammonia, amines, carboxylic acids) that are important both as building blocks and as intermediates in the chain of evolution from simple to complex molecules, which ultimately led to the formation of DNA. Although precursor molecules have been identified, there have been no confirmed observations of amino acids in the interstellar medium. Glycine was thought to have been discovered in the interstellar medium (Kuan et al. 2003), but the conclusion was later overturned (Jones et al. 2007).

**NITROGEN IN PLANETARY MATERIALS**

Nitrogen forms a variety of compounds that are significant in the interstellar medium, star formation, planetary formation and the evolution of life. Through the study of planetary materials, we recognize three generations of nitrogen and nitrogen-bearing compounds: primary, secondary and tertiary. Species from different sources are recognized by characteristic isotopic compositions or specific modes of occurrence (e.g. Grady and Wright 2003).

**THE CNO CYCLES**

The CNO cycles (Fig. 1A), as a result of which the abundance of 14N is gradually increased over that of 15N. If a star reaches the end of the CNO cycles, it will attain a 14N/15N ratio of 5000, which corresponds to a δ15N value of –945‰. In contrast, grains produced during nova outbursts are more enriched in 15N, and reach a 14N/15N ratio ~ 5, which means a δ15N value of +54,000‰.

**FIGURE 1**

FIGURE 1B is a summary of nitrogen (and carbon) isotope compositions of presolar grains; where fields overlap in C versus N space, the grains can be separated by silicon isotope composition (Nittler 2003). It is clear that the isotopic extremes generated by nucleosynthetic reactions in different types of stars are inherited by the materials produced within the stars, and these materials can be identified as discrete grains within meteorites. FIGURE 1A shows that we can identify the astrophysical location in which a particular group of presolar grains was produced. The presolar grains that have been extracted from meteorites are refractory materials, resistant to dissolution in acids and solvents. Their survival in interstellar space, transport and processing in the protoplanetary disk and their distribution through asteroidal parent bodies make it likely that presolar grains also survive alteration on the parent bodies of primitive meteorites.

**FIGURE ADAPTED FROM ZINNER (2007) AND SOURCES THEREIN**

**SECONDARY NITROGEN**

Second-generation nitrogen-bearing species are those produced on parent bodies by alteration (aqueous or thermal) of primary nitrogen-bearing species. Such processes may lead to modification of the primary species, for example, the graphitization of amorphous carbon during metamorphism, and may or may not alter the original isotopic compositions. The most primitive types of meteorites, the CI, CM and CR chondrites (Fig. 2), contain ~500–5000 ppm nitrogen, with overall δ15N ranging from +15‰ to +150‰ (see Fogel and Steele 2013 this issue).
TERTIARY NITROGEN

Tertiary nitrogen species are introduced into meteorites by implantation, mainly during exposure to cosmic and solar radiation, during both residence at the parent-body surface and transit in interplanetary space.

Cosmogenic (or spallation) nitrogen is produced by the interaction of cosmic rays with silicate minerals, where the main target elements are $^{16}$O and $^{24}$Mg. Both $^{14}$N and $^{15}$N are produced, with a $^{14}$N/$^{15}$N ratio of approximately 1 (Reedy 1981; Silberberg et al. 1998), which translates to a $\delta^{15}$N value of $+270,000$‰. The abundance of cosmogenic nitrogen is related to the length of time that material is exposed to radiation – the cosmic ray exposure age of a sample – and is generally very low, at the parts per billion level.

Solar nitrogen: The solar wind is a stream of highly energetic particles that “blows” from the surface of the Sun. The energetic nature of the particles causes them to become implanted within grains when they impact a planetary surface. Two types of material have acted as collection surfaces for the solar wind from which measurements have been made: lunar soils and collectors from NASA’s Genesis mission. Examination of mineral grains from Apollo soil samples revealed that they had glassy rims (Fig. 3) produced by a combination of cosmic and solar radiation. Nitrogen from these grains had $\delta^{15}$N values as low as about $-240$‰ (Frick et al. 1988; Hashizume et al. 2000), which was inferred to have been implanted by radiation.

The Genesis mission exposed an array of collector plates (Fig. 4) to the solar wind for a period of just over 2 years. Analysis of nitrogen in the plates found that the solar wind was depleted in $^{15}$N, with $\delta^{15}$N about $-400$‰ (Marty et al. 2011). This finding fits well with the nitrogen isotope composition of the second-largest nitrogen reservoir in the Solar System: the atmosphere of Jupiter, which has $\delta^{15}$N values of about $-375 \pm 100$‰ (Owen et al. 2001). It also confirmed that the nitrogen implanted into the outer layers of grains from the lunar regolith was almost certainly from the solar wind.

An additional, and so far unique, example of tertiary nitrogen is that which occurs in many Martian meteorites, where clasts of glass act as hosts of gases trapped from the Martian atmosphere (see Fogel and Steele 2013).

SUMMARY

Through the study of nitrogen in meteorites, we can identify and track several generations of nitrogen-bearing species. Primary material formed in stars and molecular clouds and became incorporated into the protoplanetary nebula from which the Sun and Solar System formed. Secondary nitrogen resulted from the alteration of primary species on parent bodies. Some meteorites also contain tertiary nitrogen implanted by solar or cosmic radiation. Lunar and asteroidal surfaces also record tertiary nitrogen, and Martian meteorites carry samples of the planet’s atmosphere, trapped inside grains/melt pockets at the time the meteorite was ejected from the surface of Mars by impact. On Earth, the structural and isotopic signatures of original parental materials have been modified by tectonic cycling and biological processing. Only in meteorites can we look back through the different generations of nitrogen to understand the reservoirs from which planetary nitrogen was originally sourced.

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REFERENCES

SEM 2013: 33rd MEETING OF THE SPANISH MINERALOGICAL SOCIETY

The 33rd Meeting of the Spanish Mineralogical Society (SEM 2013) was held in Caravaca de la Cruz (Murcia, Spain) between 24 and 28 June 2013. The meeting was coordinated by Francisco Guillén Mondejar (University of Murcia). The organizing committee included members of nine other institutions.

The meeting achieved two main objectives: (1) To give a well-deserved posthumous tribute to Rafael Arana Castillo, professor of crystallography and mineralogy (University of Murcia), who died in 2011, and (2) To promote the conservation and cultural and touristic use of our mineralogical heritage by holding the 10th International Seminar of the Spanish Mineralogical Society and several scientific field trips.

Scientific Communications and Lectures

Fifty communications were presented, 24 oral and 26 posters, involving nearly 200 scientists. Contributions covered topics on mineralogy, petrology, geochemistry, mineral resources, environmental sciences, archaeometry, the conservation of historical, geological and mining heritage, among others. The SEM 2013 program featured four plenary lectures: “Current status of the teaching of geology” (Amelia Calonge), “Origin of the southeastern Spanish volcanoes” (José Lopez Ruíz), “The strength of phyllosilicate-rich fault zones” (Daniel R. Faulkner) and “Remediation of marine mining waste in Chile and Peru” (Bernard Dold). All scientific contributions were published in volume 17 of Macla, the journal of the SEM.

Awards for Young Researchers

Awards for the best communications were given to: Cristina Fernández-Barranco, for “Thermal ageing of sepiolite / polyamide 6,6 nanocomposites,” and Catalina Sánchez-Roa, for “Injected clastic dykes in the Galera fault zone.”

Field Trips

Three field trips were held to highlight the rich mineralogical and petrological diversity of the region of Murcia:

- Geosites (IUGS, UNESCO) in Murcia: Neogene volcanoes of ultrapotassic rocks (Calasparra Moratalla, Cancarix and Jumilla) and the apatite deposit of Mina La Celia
- Ornamental rocks from Cehegín: Visit to the Marble Technology Center and the “Ivory Cream” ornamental-rock quarry of the Sierra de la Puerta
- Mineralogical and mining heritage of La Union mining area: La Union Mining Museum (Mina Groups-Vicenta), Mina-Cueva Victoria and Cabeza Rajo. Regeneration of Portman Bay

Other Scientific Activities

Exposition “Original or Replica” of the Instituto Geológico y Minero of Spain, which includes a replica of Spain’s largest meteorite, the Molina de Segura meteorite. House of Culture of Caravaca de la Cruz, 17–28 June.

Documentary “The mystery of the giant crystals.” House of Culture of Caravaca de la Cruz, 27 June.
Most important countries in the world for meteorite finds. (NWA) meteorites, including some rare specimens, is indeed one of the treasures of such extraterrestrial research in countries adjacent to the Sahara and Arabia, in which meteorites abound and impact craters exist. With the help of several colleagues, John carried out extensive studies of the isotopic abundances of gases in the lunar regolith, and in particular for his attempts to understand the striking variability of implanted nitrogen. In retirement, John kept abreast of developments in work on the solar compositions and on the currently unknown origin of the abundant nonsolar nitrogen component. He also enjoyed competing in vintage car races with his lovingly rebuilt 1926 Frazer-Nash.

IN MEMORIAM

JOHN KERRIDGE (1937–2013)

John Kerridge passed away on March 25, a few weeks after his 76th birthday, losing his battle with mesothelioma. John was a fellow of the Meteoritical Society, and members remember him well for his service to the Society in initiating and then editing the first volume of Meteorites and the Early Solar System (1988). In this impressive volume, John assembled the collective visions of 69 coauthors to assess the progress and discuss options regarding the use of meteorite data in studying the environment and processes in the early solar nebula. He put emphasis on a requirement that solar nebular properties must be placed in the appropriate astrophysical context, an issue that is still central in our research approaches a quarter of a century later.

Peter Eberhardt received his PhD in 1956 from the University of Bern. As part of his thesis work on the decay products of natural technetium in molybdenite, Peter designed and built the first mass spectrometer at the Physics Institute. Peter became interested in meteorites, and after finishing his PhD, he did postdoctoral research in Chicago and La Jolla with Harold Urey. There he met his future wife, Anita. Back in Bern, he led, together with Johannes Geiss, the meteorite and lunar-sample research program and the work on the aluminum foils deployed on the lunar surface by the astronauts of Apollo 11 to 16. A more complete outline of Peter’s scientific achievements can be found in the Leonard Medal citation by Edward Anders in Meteoritics 26, page 70 (1991).

Peter Eberhardt was an exceptionally good experimental physicist. Under his guidance, six more mass spectrometers for noble gas research were built. He was very systematic and careful, and he never published results that were not absolutely correct. He had a sixth sense for things that could go wrong in the laboratory. For example, he would rush into the lab, and his first words might be: “Why is the emission not on 200 mA?” And the student might say: “Oh, yes, I did not see!” Or a power failure could occur in the building, and within seconds he would be in the lab, ordering what to do to avoid damage to the mass spectrometers.

Later in his career, space research became important at the Physics Institute. Under Peter’s guidance, mass spectrometers for high-altitude rockets, satellites, and space probes were designed, such as for the mission to the comet Giotto and the ongoing mission to the comet Churyumov-Gerasimenko. Unfortunately he will not experience the encounter, in 2014, of the Bernese ROSINA instrument with this comet. The research community thanks Peter Eberhardt for his commitment and devotion to our scientific goals.

Otto Eugster

Kurt Marti and Kevin McKeegan

2014 ANNUAL MEETING INVITATION

You are cordially invited to attend the 77th Annual Meeting of the Meteoritical Society, to be held on 7-13 September 2014, in Casablanca, Morocco. Casablanca is Morocco’s largest city. Located in the northwest of Morocco on the Atlantic Ocean, Casablanca is known all over the world. Besides being the economic capital of a fast-developing country, “Casa” is a prestigious center of art and architecture, showing a unique blend of traditional Moorish architecture and Art Deco. To be immersed in this atmosphere, the meeting will be held in the Hyatt Regency Casablanca in the city center, within walking distance of hotels and the railway station. For tourist information, visit the website www.tourisme.gov.ma/.

Plenary, oral, and poster sessions will be held in the conference center at the Hyatt Regency Casablanca, which will also provide accommodation for meeting attendees. Scheduled events include an icebreaker during registration, a banquet, an award ceremony, and several excursions. Two preconference workshops will be held the weekend before the meeting, and a 5–6 day postconference field trip will be held in the south of Morocco. The 3rd Arab Impact Cratering and Astrogeology Conference (AICAC III) will take the form of a special impact symposium during the Meteoritical Society conference.

This meeting will be a unique opportunity for researchers from Africa and the Middle East to meet planetary science experts for discussions on the most advanced techniques for studying meteorites, cosmic dust, asteroids, and comets, and their implications for the origin and evolution of the Solar System. The conference will also outline the importance of such extraterrestrial research in countries adjacent to the Sahara and Arabia, in which meteorites abound and impact craters exist or are yet to be discovered. Morocco, the site of most Northwest Africa (NWA) meteorites, including some rare specimens, is indeed one of the most important countries in the world for meteorite finds.

Conference information and announcements, as well as details about Morocco, are posted on the conference website: www.metsoc2014casablanca.org.

Hasnaa Chennaoui Aoudjehane (h.chennaoui@fsac.ac.ma)
Conference Chair

ANNUAL MEETING SCHEDULE

- 2014 Casablanca, Morocco, September 7-14
- 2015 Berkeley, California, USA, July 27-31
- 2016 Berlin, Germany, August 7-12
- 2017 New Mexico, USA, dates and exact location TBD

http://meteoriticalsociety.org
This year, 40 students attending the annual meeting of the Society in Edmonton, Alberta, Canada, received travel grants. Student travel grants and travel grants for scientists from countries with limited financial resources are generously sponsored by the Barringer Crater Company, the Planetary Studies Foundation, NASA (Cosmochemistry Program), The Meteoritical Society Endowment Fund, the International Mineral Collectors Association (Brian Mason Award), and the Royal Astronomical Society of Canada, Edmonton Centre.

**Barringer Crater Company Awardees**

Moritz Barth, Universität Münster
Jean-David Bodéan, The Open University
Edivaldo dos Santos Filho, Centro Brasileiro de Pesquisas Físicas
Lauren Flor Tores, Universidad del Valle
Christopher Fry, Carleton University
Alexandre Garenne, Université Joseph Fourier
Marian Horstmann, Universität Münster
Melinda Krebsz, Hungarian Academy of Science
Agata Krzesińska, Polish Academy of Sciences
Haruka Kusuno, Risshu University
Kuljeet Kaur Marhas, Physical Research Laboratory
Annemarie Pickersgill, Western University
My Riebe, ETH Zürich
Jared Shivak, University of Western Ontario
Katrina van Drongelen, University of Toronto
Niel Williams, The University of Manchester
Yakovlev Grigoriy Alekseevica, Ural Federal University

**Planetary Studies Foundation Awardees**

Katherine Armstrong, Portland State University
Nicole Lunning, University of Tennessee

**NASA Cosmochemistry Program Awardees**

Evan Groopman, Washington University
Pierre Haenecour, Washington University in St. Louis
Jangmi Han, University of New Mexico
Romy Hanna, University of Texas in Austin
Ellen Harju, University of California, Los Angeles
Niel Williams, The University of Manchester
My Riebe, ETH Zürich
Jared Shivak, University of Western Ontario
Katrina van Drongelen, University of Toronto

**Royal Astronomical Society of Canada, Edmonton Centre Awardees**

Daniel Applin, University of Winnipeg
Michael Bramble, Western University
Maxim Ralchenko, Carleton University
Diego Uribe, Western University

**International Collectors Association – Brian Mason Award**

In 1997, Joel Schiff, the first editor of the popular *Meteorite* magazine, created a travel award in honor of Brian Mason, who was born in New Zealand. The award is given to a student attending the annual meeting of the Society who submits an abstract that presents clearly explained, exciting results of particular interest to readers of *Meteorite* magazine. The recipient is required to write a popular account of his or her work for the magazine. Since 2008, the award has been generously funded by the International Meteorite Collectors Association.

**Meteoritical Society Endowment Fund Awardees**

Mahaveer Sisodia, J. N. Vyas University, India
Hasnna Chennaoui Aoudjehane, Hassan II University, Morocco

**HANDBOOK OF IRON METEORITES NOW ONLINE**

Electronic versions of volumes 1 and 2 of the *Handbook of Iron Meteorites*, by Vagn F. Buchwald, are now available at the University of Hawai‘i website (http://evols.library.manoa.hawaii.edu/handle/10524/33750), or you can Google *Handbook of Iron Meteorites*. Volume 3 is still being scanned and will be up soon. Permission for scanning was granted by the copyright holder, Mini Wadhwa (Arizona State University Center for Meteorite Studies), and the NASA Cosmochemistry Program funded the project. Jeff Grossman and Ed Scott (University of Hawai‘i) and John Wasson (UCLA) launched the website, which will be hosted by the University of Hawai‘i.

The *Handbook of Iron Meteorites* was published in 1975 and, although no longer in print, is still an extraordinarily valuable resource. This monumental book contains 1426 pages, 2124 figures, eight appendices, and a supplement. Volume 1 provides a general introduction to meteorites, fireballs, and impact craters and to the mineralogy, composition, and properties of iron meteorites. It also contains appendices of information about iron meteorites. Volumes 2 and 3 contain descriptions of about 600 iron meteorites—nearly all those that were known and accessible in 1975. These descriptions include information about the structure, mineralogy, and composition of each iron meteorite, its discovery and subsequent history, and a list of museum holdings. A guide for users can be found on page 245 at the beginning of volume 2. At the end of volume 3, on pages 1376–1418, a supplement contains information about eleven meteorites studied by Vagn Buchwald after 1973, plus additional notes and photographs for a few other iron meteorites.

**CALL FOR AWARD NOMINATIONS**

Please consider nominating a colleague for one of the Society’s awards. Nominations should be sent to Secretary Greg Herzog (metsocse@gmail.com) by January 15 (January 31 for the Service Award and the Pellac-Ryder Award). For more information and details on how to submit a nomination for any of these awards, please see the latest Newsletter at the Society website or e-mail the secretary.

The Society gives a number of awards each year. The **Leonard Medal** honors outstanding contributions to the science of meteoritics and closely allied fields. The **Barringer Medal and Award** recognize outstanding work in the field of impact cratering and/or work that has led to a better understanding of impact phenomena. The **Nier Prize** recognizes outstanding research in meteorites and closely allied fields by scientists who are under 35 or within 7 years of the PhD. The **Service Award** honors members who have advanced the goals of the Meteoritical Society to promote research and education in meteoritics and planetary science in ways other than by conducting scientific research. The **Paul Pellac–Graham Ryder Award** is given for the best student paper in planetary science and is awarded jointly by the Meteoritical Society and the Planetary Geology Division of the Geological Society of America.
FROM THE PRESIDENT

**IAGS 2013**

The 26th International Applied Geochemistry Symposium (IAGS) in Rotorua, New Zealand, is fast approaching. The 18–21 November program is full of varied and interesting presentations, as well as pre-meeting workshops and pre- and post-meeting field trips. Concurrent sessions during the meeting will whet any applied geochemist’s appetite. The 35th New Zealand Geothermal Workshop, incorporated in the IAGS, will hold geothermal-related sessions. The Society of Economic Geologists is cosponsoring sessions on ore deposits. All of the above plus nearly 60 posters and numerous keynote talks over four days will ensure intellectual stimulation and animated discussions.

Workshop topics include exploration for orogenic gold deposits, molar element ratio analysis, the environmental geochemistry of mine drainage, quality assurance in geochemical analyses, the use of portable XRF in mineral exploration, and the basics of geothermal science and practical geothermal geochemistry. An informal student-publishing workshop will also be held. Pre- and post-meeting field trips will focus on active and fossil geothermal and epithermal systems, active volcanoes, orogenic gold mines, environmental geochemistry, wine terroirs, geothermal resources, and the Rocklabs factory.

In the tradition of previous IAGSs, there will be an extensive social program. The partners program includes numerous sightseeing tours and visits. The official symposium dinner will include presentation of the best student paper award and the AAG’s Gold and Silver Medals. This is certain to be a memorable IAGS, thanks to Tony Christie and his dedicated local organizing committee. Numerous corporate, university, and society sponsors and a promising trade exhibition are helping to ensure the meeting’s success. Support for students includes very low registration and conference dinner fees, prizes for best student oral and poster presentations, and limited student travel grants. Further information is available at [www.gns.cri.nz/iags/](http://www.gns.cri.nz/iags/).

Bob Eppinger (eppinger@usgs.gov)
U.S. Geological Survey, AAG President

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**Chile**

Applied geochemistry in Chile has slowly been growing, as geochemistry is being used in ever broader applications, such as geothermal energy exploration and evaluation, environmental baseline and impact studies, mining, geo-mineral metallurgical characterization, and exploration. Workers trained in geochemistry are still few, but young Chilean geologists returning from overseas graduate programs and a growing number of our own graduates are showing increasingly more interest in applied geochemistry. The number of students engaged in applied geochemistry field courses and graduate and undergraduate studies has increased.

Recent ongoing applied research projects include rutile and tourmaline chemistry in porphyry copper environments (AMIRA project, Universidad de Concepcion); geochemistry in geothermal environments (Andean Geothermal Centre of Excellence–CEGA, Universidad de Chile); geochemistry applied to geo-mineral metallurgical characterization (Department of Geology, Universidad de Chile–DGUCH); and, recently the Advanced Mining Technology Center–AMTC at the Universidad de Chile; exploration geochemistry (DGUCH), including geochemistry applied to exploration in areas of transported overburden, and caliche geochemistry, including isotopic geochemistry; various projects in environmental geochemistry (Universidad de Concepcion, Universidad de Chile, and Universidad Catolica del Norte); and, soon to begin, geochemistry, mineralogy, and geology applied to the characterization of terroir in the wine industry (DGUCH together with the Chilean Wine Consortium).

On an interesting note, upcoming environmental legislation will include baseline geochemical regulations and the evaluation of geochemical environmental impacts, likely to become mandatory as of 2013–2014. The definition of environmental baseline studies was developed by a multidisciplinary group from the departments of geology, geophysics, and civil engineering of the Universidad de Chile.

Ravi Anand, AAG’s 2013–2014 Distinguished Lecturer, visited Chile during the first week of March and gave two talks at the Central Codelco Auditorium in Santiago, Huerfanos.

**NEWS FROM AAG REGIONAL COUNCILLORS**

**Chile**

Brian Townley (btownley@ing.uchile.cl)
Universidad de Chile
THE PRESIDENT’S CORNER

This month, the CMS is celebrating its 50th anniversary at its annual meeting, held this year at the University of Illinois in Urbana-Champaign, Illinois, USA. The number of participants will likely be larger than the combined attendance of the last two annual meetings. This is an encouraging basis for an excellent anniversary annual meeting. In this issue we conclude a series of short contributions on the history of the Society prepared by Dr. Duane (Dewey) Moore, previously at the Illinois State Geological Survey in Urbana and currently at the University of New Mexico. We are grateful to Dewey for his efforts in preparing this article. The complete article and additional information are available on the CMS website, www.clays.org/CMS%20ORGANIZATION/CMShistory.html.

Best wishes,

Peter Komadel (peter.komadel@savba.sk)
President, The Clay Minerals Society

HOW THE CLAY MINERALS SOCIETY GOT STARTED, PART III

Before World War II, there were stirrings of interest in clay science in all parts of the world. After WW II, interest blossomed across the globe. The group that had been sponsored by the U.S. National Research Council, which had originally met in St. Louis in 1951, applied for incorporation as a nonprofit organization on July 18, 1962, in Washington, D.C. This led to The Clay Minerals Society’s first meeting as an incorporated entity, the Twelfth Clay Minerals Conference (counting those before incorporation), which was held in Atlanta on September 30–October 4, 1963—this was the birth of The Clay Minerals Society. Attendees came from many diverse scientific disciplines with a common interest in clays and clay minerals.

In that first year of incorporation, The Clay Minerals Society had 33 charter sustaining members. The disciplines of the officers and the associate editors emphasized the broad and balanced interests of the Society—three geologists, three chemists, two soil scientists, one civil engineer, one oil company employee, and two persons from government agencies. As of 2011, CMS included seven corporations and 21 individuals as sustaining members. The notably successful twelve years of operation as a committee under the aegis of the National Research Council served as a model for conducting the business of this new organization. Several available histories related to The Clay Minerals Society thoroughly cover the subject up to 30 years ago; two are by Ralph E. Grim (1961, 1988) and one is by Richards A. Rowland (1968).

Beginning in about 1985, interest in clays and clay-sized minerals and compounds, and in mineralogy and geochemistry in general, grew rapidly. At about the same time, the term nano came suddenly into widespread use in a variety of contexts. One consequence of this spreading interest in clays was that The Clay Minerals Society combined its meetings with those of other societies: the Soil Science Society of America; the American Chemical Society; the Mineralogical Society of America; the clay societies of France, Japan, and Spain; and the Association Internationale pour l’Étude des Argiles (AIPEA). This latter organization, coincidentally, is celebrating its 50th anniversary in 2013, as is The Clay Minerals Society.

The following awards were presented at the CMS annual meeting at the University of Illinois at Urbana-Champaign. More awards news will appear in the December 2013 issue of Elements.

The G. W. BRINDLEY LECTURE AWARD went to Dr. Andrey Kalinichev, Research Director, Radiochemistry Group, École des Mines de Nantes, France. Andrey has been a pioneer in the use of molecular dynamics modeling and other computational techniques to study clays and related materials, with a focus on understanding the structure, dynamics, energetics, and reactivity of clay-fluid interfaces. He also puts special effort into integrating spectroscopic and computational studies, working with NMR spectroscopists and more recently with high-energy neutron techniques, to deepen our understanding of clay and surface science. Among his many published papers, he is a key author on one of the most influential papers in molecular modeling of phyllosilicates and other oxide minerals: the CLAYFF molecular dynamics forcefield. Andrey’s current research involves modeling organo-mineral interactions and the development of larger, more structurally diverse models of clay minerals.

The PIONEER IN CLAY SCIENCE LECTURE AWARD went to Dr. Thomas J. Pinnavaia, Emeritus Distinguished University Professor, Michigan State University. Professor Pinnavaia has had an illustrious career spanning the fields of dynamic stereochemistry of higher coordination number metal complexes, the intercalation chemistry of smectitic clay minerals and related lamellar solids, the role of metal ions in the self-assembly of nucleotides, and the supramolecular assembly of inorganic mesophases. He has advised over 80 PhD students and an equal number of postdoctoral and visiting scientists. He has authored more than 400 technical publications and holds 80 patents. He is a Distinguished Member of CMS and served as president in 1990–1991.

2013 CMS Awardees

The University of Illinois at Urbana-Champaign, More awards news will appear in the December 2013 issue of Elements.


Duane Moore
University of New Mexico

2014 CMS ANNUAL MEETING

May 17–21, 2014, at Texas A&M University, College Station, Texas, USA

“Everything is Big: From Nanoparticles to Planets”

Events: Workshop on surface modification of clays and nanocomposites, field trips, 18 technical sessions

Information: http://cms2014.tamu.edu
It seems that it was just a short time ago that I wrote my first President’s Letter for the society pages in Elements. A lot has happened in the past year, and the pace will only pick up for the Mineralogical Society of America in the next few years. As I turn over the reins to incoming President David J. Vaughan, I am pleased with the state of the Society and look forward to contributing to it however I can in the future. The MSA is coming upon a signal event in its history as we reach our centennial during the period of 2016–2019, and I hope that all members will take part in the celebrations.

That we will celebrate our centennial over four years comes from the historical vagaries of the Society. In July 1916, a new publication appeared, The American Mineralogist, and the first paper in volume 1, number 1, traces the lineage of the new journal in an article entitled “Arthur Chamberlain and His Magazines” (a copy of the original publication can be viewed at www.minsocam.org/msa/collectors_corner/amtoc/toc1916.htm). The journal has been published continually since that time (note that the last volume with “The” in the title was volume 57, 1972), and since then it has become the leading journal in mineralogy/crystallography/petrology in the world. The editors of the journal are already planning for marking the centennial in 2016, and I would urge authors to consider putting their landmark papers in that centennial volume.

The journal continued to be published without the support of a formal society until 1919. In the February 1919 issue of the journal, it was noted: “At the meeting of the Geological Society of America in Baltimore, December 27–28, 1918, the question of the formation of a Mineralogical Society of America was informally discussed by mineralogists present.” Discussions apparently continued, and in the January 1920 issue of The American Mineralogist an article entitled “Organization Meeting of the Mineralogical Society of America” described the formation of the Society on December 30, 1919, at a meeting held at the Geological Museum of Harvard University.

Thus the centennial of the Mineralogical Society of America and the journal that is its signature publication spans the period of 1916–2019. The Society will recognize that milestone in many ways, and I urge all members to recognize it as well. We are fortunate and privileged to belong to a robust society that continues to thrive nearly a century after its founding. It has been the members of the MSA and the authors who contribute to American Mineralogist who have brought about that success. I look forward to the celebration of the first century and the inauguration of the second century in the coming years.

It has been a privilege to serve the Mineralogical Society of America as its president, and I thank all of you for your support over the past year.

With my sincere thanks to all members of the Society,

John M. Hughes (jm Hughes@uvm.edu)
2013 MSA President
Frank Hawthorne will receive the 2013 Roebling Medal, given for a lifetime of outstanding original research in mineralogy. He is Distinguished Professor and Canada Research Chair in Crystallography and Mineralogy at the Department of Geological Sciences, University of Manitoba. He is a theorist by inclination and an experimentalist by necessity.

Dr. Hawthorne has addressed the most fundamental problems in mineralogy in his theoretical work: (1) the factors controlling the bond topology of oxide and oxy salt minerals, (2) the factors affecting the chemical formulae of complex minerals, (3) how pH controls the complexation of cations and anions in aqueous solution, and (4) the relation between crystal structure and stability of low-temperature minerals. In his experimental work, Dr. Hawthorne has addressed major issues in the crystal chemistry of rock-forming minerals, allowing accurate activity models to be derived for thermodynamic modeling of geological processes.

The Mineralogical Society of America Award is given for outstanding contributions by a scientist beginning his or her career. Dr. Wendy Li-Wen Mao, assistant professor of geological and environmental sciences, Stanford University, Stanford, California, USA, is the 2013 MSA Award recipient.

A common theme of Dr. Mao’s research is the understanding of the nature of minerals and other materials in extreme environments, including direct observations of chemical bonding changes, phase transitions, and the elasticity of Earth and planetary materials under extreme pressure–temperature conditions. Her principal accomplishments are detailing the nature of materials of the core–mantle boundary region (oxides, silicate perovskite, and post-perovskite) and the Earth’s core (iron and iron alloys). She has used and helped develop synchrotron radiation techniques, and she has combined them with high-pressure methods to reveal altogether new materials phenomena. She has also helped to develop the new field of radiation-induced chemistry and physics at high pressure, which builds on her studies of the water–hydrogen system.

The Mineralogical Society of America’s Distinguished Public Service Medal is awarded for distinguished contributions to public policy, to furthering the vitality of the geological sciences, especially the fields of mineralogy, petrology, and crystallography, or for service to, or on behalf of, the mineralogical community.

Pierrette Tremblay, managing editor of Elements magazine, Québec City, Québec, Canada, is the 2013 medalist.

Ms. Tremblay’s contributions embody the ideal of the award through her unrelenting energy and passion for promoting mineralogy, petrology, and geochemistry in many ways, but especially by her work with Elements magazine. From the inception of Elements, through the next nine years of sustained growth and activity, she has been the driving force behind the vision and continued success of Elements. She has forged ahead on nearly every front (managing editor, financial officer, marketing director, advertising agent, etc.) to make Elements the widely read, international magazine that it is today, with 17 international professional societies as members of the Elements family. Because all members of these societies and their institutional subscribers receive Elements, each issue of Elements is in the hands of over 14,000 scientists and 1000 libraries.

Mineralogy and Optical Mineralogy
M. Darby Dyar and Mickey E. Gunter

Now available in an electronic version, under “textbooks”


And all the rest. You can also purchase single chapters from these and all Reviews volumes (v1 [1974]–present), and you can use chapters from any and all Reviews volumes for course packs and add to them articles from the American Mineralogist (v85 [2000]–present) and Elements (v1 [2005]–present).

For more description and ordering instructions, visit www.minpubs.org or contact the Mineralogical Society of America, 3635 Concorde Pkwy Ste 500, Chantilly, VA 20151-1110, USA; phone: +1 (703) 652-9950; fax: +1 (703) 652-9951; e-mail: business@minsocam.org. Cost is $45 ($33.75 for members of MSA, GS, CMS).


Geothermal fluids span large variations in composition and cover wide ranges of temperature and pressure. Their composition may also be dynamic and change in space and time on both short and long timescales. In addition, the physicochemical properties of fluids, such as density, viscosity, compressibility, and heat capacity, determine the transfer of heat and mass by geothermal systems, whereas, in turn, the physical properties of the fluids are affected by their chemical properties. Quantitative models of the transient spatial and temporal evolution of geochemical fluid processes are, therefore, very demanding with respect to the accuracy and broad range of applicability of thermodynamic databases and thermodynamic models (or equations of state) that describe the various data sets as a function of temperature, pressure, and composition. The application of thermodynamic calculations is, therefore, a central part of geochemical studies of very diverse processes, ranging from the aqueous geochemistry of near-surface geothermal features including chemosynthetic and thermal biological activity, through the utilization of crustal reservoirs for CO2 sequestration and engineered geothermal systems, to the formation of magmatic–hydrothermal ore deposits, the devolatilization of subducted oceanic crust, and the transfer of subduction fluids and trace elements into the mantle wedge.

For a description and ordering online, go to www.minsocam.org or contact the Mineralogical Society of America, 3635 Concorde Pkwy Ste 500, Chantilly, VA 20151-1110, USA; phone: +1 (703) 652-9950; fax: +1 (703) 652-9951; e-mail: business@minsocam.org. Cost is $45 ($33.75 for members of MSA, GS, CMS).
**Japan Association of Mineralogical Sciences**

**JAPAN ASSOCIATION OF MINERALOGICAL SCIENCES Awardees**

The Japan Association of Mineralogical Sciences (JAMS) is proud to announce the recipients of its 2013 society awards. The Japan Association of Mineralogical Sciences Award is given to two scientists (maximum) per year for exceptional contributions to the mineralogical and related sciences. The Manjiro Watanabe Award—named in honor of Professor Manjiro Watanabe, a famous Japanese mineralogist, and funded by his contribution—is awarded every year to one scientist who has contributed significantly to the mineralogical and related sciences over his/her long career.

**Japan Association of Mineralogical Sciences Award to Hiroko Nagahara**

**Ritsuro Miyawaki,** of the National Museum of Nature and Science, Japan, is a chemist and crystallographer who has studied the crystal chemistry of rare earth (RE) minerals. He has been involved in the description of more than thirty new mineral species, of which one-third are RE minerals: kimuraite-(Y), kozoite-(Nd), bastnäsite-(Nd), hingganite-(Ce), uedaite-(Ce), iwashiroite-(Ce), magnesiorowlandite-(Y), and others. He has determined crystal structures to clarify the nomenclature of inadequately described RE minerals, such as tengerite-(Y) and rowlandite-(Y). He began his research on RE minerals with an undetermined herderite-like mineral found in a granitic pegmatite in Gifu Prefecture. Later on, the mineral was described as hingganite-(Ce), a new member of the gadolinite–datolite group. He carried out a structural refinement of gadolinite-(Y) and compared the structure with the structures of other members of the gadolinite–datolite group; the result was published in 1984 as his first contribution to mineralogy. He reviewed a total of more than 100 crystal structures of RE minerals. He demonstrated differences in structural features, such as coordination numbers and coordination polyhedra, in the crystal structures of RE minerals containing the smaller Y or the larger Ce ion. He pointed out that the slight difference in ion size, which is related to the lanthanoid contraction, apparently affects the crystal structure of RE minerals without infinite 3- or 2-dimensional frameworks, i.e., carbonates and phosphates; on the other hand, RE minerals with tight frameworks, such as silicates and niobates, usually form the same crystal structure even with varied RE ionic sizes.

**Japan Association of Mineralogical Sciences Award to Takeo Matsumoto**

**Takeo Matsumoto** received a doctor of science degree in 1962 from the University of Tokyo on the subject “The study on the application of Ito’s method to analyze powder X-ray diffraction data,” under the supervision of Profs. T. Ito and R. Sadanaga. He then accepted an academic position in the Faculty of Science at the University of Tokyo. He worked at Bern University in Switzerland as a visiting researcher from 1964 to 1968; during this time, he studied the densest packing of the three-dimensional ellipsoid and published a paper entitled “On densest packing of ellipsoids.” This paper made a large contribution to the field of mathematical and theoretical crystallography. He moved to Kanazawa University in 1968 and began the structural analysis of various crystals, providing important crystallographic data. At the same time, he continued to study mathematical and theoretical crystallography, in areas such as the statistical distribution of symmetrical groups, the higher-dimensional space group, the packing of ellipsoids, and crystallographic orbits. In particular, he published “Non-characteristic orbits for all space groups” in 1984 with his colleagues (Engel, Steinmann, and Wondratschek). In 1992–1993, he superintended the project “General research on experimental and theoretical studies for macro and micro structure and physical properties of minerals.” He successfully analyzed the crystal structure of micron-scale crystals and found a new technique for the determination of the Laue group. He continues to carry out research, with his coworkers, on the deformation of sphere-packing structures and on heterogeneous cylinder packing.
The general assembly of the SFMC was held at the Université Pierre et Marie Curie, Paris, on 2 July 2013. Marc Blanchard, secretary, welcomed the members in the name of Bruno Goffé, president of the Society. The 2012 budget was presented by Stéphanie Rossano, treasurer. Then, Marc Blanchard reported on the main actions in 2012. The most remarkable event organized by the Society was the third edition of Serpentine Days, held on Porquerolles Island, France, on 2–6 September 2012 (see *Elements* v8n6). The implication of the Society in conferences and schools was also detailed at the meeting. After these formal reports, the Haüy-Lacroix Prize for the year’s best PhD theses in mineralogy was awarded by Etienne Balan, jury chairman, to Julien Feneyrol and Pierre Lanari (photo). The two laureates gave short overviews of their work, followed by general presentations on the topics by their supervisors, Gaston Giuliani and Olivier Vidal.

### Julien Feneyrol

*(Université de Lorraine)* – “Pétrologie, géochimie et génèse des gisements de tsavorite associés aux gneiss et roches calco-silicatées graphiteux de Lemshuku et Namalulu (Tanzanie)"

Tsavorite is a (V, Cr, Mn)-bearing green grossular and a gemstone mined within the Neoproterozoic Mozambique belt. A complete study of the Lemshuku and Namalulu deposits in northeastern Tanzania shows that tsavorite deposits formed during metamorphism and metasomatism of silico-calcareous sedimentary sequences, enriched in organic matter and containing evaporite intercalations, which are interpreted as coastal-marine sabkha formations on the eastern margin of Congo and Kalahari cratons during Neoproterozoic time (http://neon.crpg.cnrs-nancy.fr/MEMOIRES).

### Pierre Lanari


The topic of this thesis is the construction of detailed *P-T* paths in metamorphic rocks by combining forward and inverse modelling techniques using micro-structural characterization of successive local equilibria and a micro-mapping approach. New solid solution models were derived and a set of programs was developed, such as XMapTools for the microprobe X-ray image processing, which were successfully used to decipher the metamorphic history of metamorphic rocks from the Alps and the Himalaya (http://tel.archives-ouvertes.fr).
WRI-14 – AVIGNON, FRANCE

The 14th Water–Rock Interaction Working Group conference was held in Avignon, France, on 9–14 June 2013 and was attended by 280 scientists from 32 countries. WRI-14 Secretary General Pierpaolo Zuddas organized an unforgettable experience for delegates in the famous medieval Palais des Papes in Avignon. The primary goals of the conference were to increase the fundamental and applied understanding of water–rock interactions at varying scales and to identify new WRI environmental issues. A wide range of topics was covered during WRI-14, and all the speakers did an outstanding job of presenting and sharing their expertise. The planning committee is pleased to announce that WRI-15 is scheduled to be held in Portugal in 2016. A full report on the Avignon meeting will be included in a future issue of *Elements* and in the IAGC fall Newsletter.

URBAN GEOCHEMISTRY WORKING GROUP MEETING

The newest IAGC working group, Urban Geochemistry, will hold its first meeting on 5–7 August 2014 on the campus of Ohio State University in Columbus, Ohio, USA. We anticipate a small number of plenary talks, a series of poster sessions, and a discussion on the future of this new group. Keep a look out on the IAGC website, in *Elements*, and in other venues for more details. If you have already signed up to receive news of the Urban Geochemistry Working Group, you will receive these details via e-mail; if you would like to sign up, please e-mail Chris Gardner at IAGeoChemistry@gmail.com.

**Berry Lyons** (Ohio State University) and **Dave Long** (Michigan State University)

CALL FOR 2014 AWARD NOMINATIONS

Now is the time for 2014 IAGC award nominations! The window of opportunity for nomination submission will extend through 1 December. Nominations may be made for the following 2014 awards: the Vernadsky Medal, the Ebelman Award, the Distinguished Service Award, the IAGC Fellow award, and the IAGC Certificate of Recognition. For a summary of the awards and instructions on how to submit your nomination, visit www.iagc-society.org/awards.html.

MEMBERSHIP RENEWAL FOR 2014

New for 2014 memberships: In an effort to keep our operating costs low and provide convenient payment options to our members, we now accept credit card payments through Square Market (http://squareup.com/market/iagc) in addition to PayPal. Don’t miss any issues of *Elements* – renew your IAGC membership for 2014 today! Visit www.iagc-society.org and click on “Society, Membership” to select your payment option.

**Donation Request – Ignacio Torres**

Our friend and colleague Ignacio Torres passed away unexpectedly on January 15, 2012. Ignacio S. Torres Alvarado, known as “Nacho” to his friends, leaves behind his wife, Gaby, and two children. The IAGC is happy to collect donations on behalf of his family. Please visit our website to make a donation. All major credit cards are accepted: www.iagc-society.org/Ignacio_Torres_Donation.html.
One hundred and twenty people attended the ‘Minerals for Life’ conference held in Edinburgh in June 2013. The prime objective was to bring together academics and people from regulatory agencies and industry to talk about matters of mutual interest.

The mineral sciences span an increasingly broad range of subjects. The traditional core disciplines of characterization and classification have burgeoned in recent decades, as the range of analytical tools available has grown rapidly, along with our systematic understanding of mineral chemistry. Similar advances in exploration, mining and process engineering bring these fields to a state of advancement such that they would be unrecognizable to a practitioner of fifty years ago. Over the same timescale, our environmental awareness has developed greatly, and our subject remains at the core of many methods of environmental remediation. Moreover, it has helped foster environmental responsibility in operational practice. The science underlying minerals as functional materials covers many new fields, with wide applications spanning medicine, electronics, construction and many others, as we develop new applications for minerals and their products. The contribution of minerals to human well-being has never been more prominent than it is today. After all, if we don’t grow it or catch it, we must dig it from the ground!

Copies of many of the presentations are available from the conference website at www.minersoc.org/minerals-for-life.html.

One very significant take-away from the meeting was the realization amongst some that the work done on characterization of materials (natural and otherwise) by mineralogists is invaluable and should be promoted more to industry.

SOCIETY AWARDS FOR 2013

Society Awards for 2013 were presented during the conference banquet in Edinburgh, a very pleasant evening indeed.

MINERALS FOR LIFE:
OVERCOMING RESOURCE CONSTRAINTS

(F. Brenker and G. Jordan, editors)

Vol. 9 (2010): Advances in the Characterisation of Industrial Minerals (G. Christidis, editor)


(M. F. Brigatti and A. Mottana, editors)

(D. Dubessy, M. C. Caumon and F. Rull, editors)

Vol. 13 (2013): Environmental Mineralogy II
(D. J. Vaughan and R. A. Wogelius, editors)

(F. Nieto and K. J. T. Livi, editors)

These, and the previous seven books in the series, are all available from the Mineralogical Society’s online bookshop (www.minersoc.org).
FROM THE PRESIDENT

Report on Council Meeting

The MAC annual Council meeting was held May 20–21 at the Marlborough Hotel in Winnipeg. Outgoing councilors Andrew Conly and Chris Weisener were thanked for their service, and incoming councilors Roberta Flemming, Heather Jamieson, and Steve Piercey were welcomed. Michelle DeWolfe, who has been interim secretary since June 2010, is now officially secretary, and Neil Banerjee became the new finance chair as of July 1. Marc Constantin, treasurer, reported that the Association’s finances are good, with a treasury reserve sufficient to operate for at least two years.

Council reviewed the awards and scholarships given during the past year. The Peacock Medal was awarded to David Patterson at the University of Calgary. The Hawley Medal, given annually for the best paper in The Canadian Mineralogist, was awarded to B. Lalinská-Voleková, J. Majzlan, T. Klimko, M. Chovan, G. Kučerová, J. Michňová, R. Hovoric, J. Göttlicher, and R. Steininger for their paper titled “Mineralogy of weathering products of Fe-As-Sb mine wastes and soils at several Sb deposits in Slovakia.” The Young Scientist Award was given to Kim Tait, and the Pinch Medal was won by Renato and Adriana Pagano. MAC Foundation Scholarships were awarded to Olivier Gagne (PhD) and Mitchell Kerr (MSc). A total of $10,777 in Travel and Research Grants was distributed to 3 BSc, 3 MSc, and 6 PhD applicants.

Ron Peterson reported on the 2012 St. John’s GAC-MAC meeting. Thanks to the efforts of the Local Organizing Committee (LOC) to raise sponsorship, there was a $178,000 profit, the largest ever for a GAC-MAC meeting. The LOC’s share of the profit will go towards funding geoscience in Newfoundland. Nancy Chow from the Winnipeg 2013 LOC summarized key features of the meeting, including field trips and outreach programs. With 721 registrants and $58,000 in sponsorship, the Winnipeg LOC expects a modest profit of $24,000. In addition, short course 43, Uranium: Cradle to Grave, had excellent attendance, with a strong student representation.

Short course 44 will be an updated version of the Geology of Gem Deposits short course (SC39), held in Yellowknife in 2007. It will take place in February 2014 just prior to the Tucson Gem & Mineral Show. The University of Arizona is helping with the organization of the short course.

The next GAC-MAC meeting will be held in Fredericton in 2014 at the University of New Brunswick. Chris McFarlane from the LOC summarized the plans for the meeting, including short course 45, titled Cathodoluminescence and Its Application to Geoscience. The meeting will feature tributes to John Jambor and André Lalonde, and the 2014 Peacock medalist will give a keynote address at the MAC luncheon.

The Montreal 2015 GAC-MAC meeting will be held in conjunction with the AGU conference. Lee Pigage from the Whitehorse LOC presented preliminary plans for the 2016 meeting at Yukon College, to be held probably in the first week of June.

Lee Groat recommended a MAC presence at the 2013 GSA meeting in Denver, as Frank Hawthorne is being honored. The 2013 Québec Mines conference will be attended by Joanne Caron, MAC business manager. In 2014, MAC will have a presence at the Mineral Exploration Roundup (Vancouver), the Tuscon Gem and Mineral Show, and the PDAC meeting (Toronto).

Mackenzie Parker, managing editor of The Canadian Mineralogist, reported on events at the journal: three special issues and three regular issues were published in 2012. The June 2013 issue has gone to press. Online journal management will help to correct current delays; there is evidence that online submissions are resulting in faster submission-to-acceptance times. The John Jambor thematic issue is being aimed for January 2015, and a thematic issue for André Lalonde is planned. MAC will start the process of gathering manuscripts for these issues now, perhaps looking to conferences and symposiums for potential authors. Council decided to increase page charges for The Canadian Mineralogist to $50/page, starting with the June issue, but with a 20% discount for current members of the MAC and no additional charges for color.

In order to support MAC publications and their sales, Joanne Caron has been pursuing contractors for the website and online database. We are studying the possibility of adapting the MSA system to the MAC’s needs and how such a system would be maintained.

It was generally agreed that a more active approach to increasing MAC membership is needed, and Neil Banerjee volunteered to take a lead role in this initiative. He advised that the Association needs to do more targeted activities, such as sending e-mails, posters, etc., and he suggested that we set a goal of increasing membership from 700 to 1000 in the next year.

The Council meeting closed with a decision to present an honorary life membership in the MAC to Robert Martin in recognition of his many years of service.

Lee Groat, MAC President
2014 MAC AWARDS
CALL FOR NOMINATIONS

PEACOCK MEDAL
The Peacock Medal is awarded to a scientist who has made outstanding contributions to the mineralogical sciences in Canada. There is no restriction regarding nationality or residency. The medal recognizes the breadth and universality of these contributions in mineralogy, applied mineralogy, petrology, crystallography, geochemistry, or the study of mineral deposits.

YOUNG SCIENTIST AWARD
This award is given to a young scientist who has made a significant international research contribution in a promising start to a scientific career. The scientist must be 40 or younger at the time of the award. He or she must be a Canadian working anywhere in the world or a scientist of any nationality working in Canada. The research areas include mineralogy, crystallography, petrology, geochemistry, mineral deposits, and related fields of study.

BERRY MEDAL
The Leonard G. Berry Medal is awarded annually for distinguished service to the Association. The award recognizes significant service in one or more areas, including leadership and long-term service in an elected or appointed office. The medal is named after Leonard G. Berry (1914–1982), a founding member of MAC, editor for 25 years of The Canadian Mineralogist and its predecessor, and first winner of MAC’s Past-Presidents’ (now Peacock) Medal.

Please submit your nominations by December 31, 2013. Check our website, www.mineralogicalassociation.ca, for additional details.

STUDENT TRAVEL/RESEARCH GRANTS
The Mineralogical Association of Canada awards travel and research grants to assist honors undergraduate and graduate students in the mineral sciences to:

- Present their research at a conference
- Visit a facility, laboratory, or field area to gather data for their research
- Pay for analyses that cannot be acquired at their university or equipment for an independent research project

The maximum grant value is CDN$1200 per student. Grants will fund up to 50% of costs incurred for registration, travel, and subsistence, and up to 100% of other research costs (e.g. equipment, analyses).

Quotations and receipts may be requested for any equipment purchased.

Eligibility
- Graduate students and honors students at the undergraduate level in one of the fields covered in The Canadian Mineralogist (mineralogy, crystallography, petrology, economic geology, geochemistry)
- Grant recipients must submit a report on their travel or research for possible publication by MAC.

For more information, see www.mineralogicalassociation.ca.

Deadline to apply: January 15, 2014

MINERALOGICAL ASSOCIATION OF CANADA
SHORT COURSE
GEOLOGY OF GEM DEPOSITS

DATES: Monday and Tuesday, February 10–11, 2014, prior to the Tucson Gem and Mineral Show
VENUE: University of Arizona, Tucson, AZ, USA
ORGANIZER: Lee A. Groat, University of British Columbia, BC, Canada
E-mail: groat@mail.ubc.ca
PRICE: Professional $450, students $250 (taxes included)
REGISTRATION: www.mineralogicalassociation.ca

Topics and Speakers
- Diamond: Jeff Harris, University of Alberta, Edmonton
- Corundum, ruby, sapphire: Gaston Giuliani, Nancy, France
- Geology of gems and their geographic origin: Gaston Giuliani, Nancy, France
- Emerald: Lee Groat, University of British Columbia
- Non-emerald beryl: David Turner, University of British Columbia
- Chrysobery: Dan Marshall, Simon Fraser University
- Tanzanite and tsarovite: Dan Marshall, Simon Fraser University
- Topaz: Dan Marshall, Simon Fraser University
- Pegmatite gem deposits: William "Skip" Simmons, University of New Orleans
- Jade: George Harlow, American Museum of Natural History, New York
- Colored gem stones from Canada: Bradley Wilson, Alpine Gems Ltd., Kingston, Ontario

BERRY SUMMER SCHOOL
OPTICAL MINERALOGY, 2014

VENUE: University of Ottawa, Ontario, Canada
QUESTIONS AND INQUIRIES: Jim Nicholls
(jim.nicholls@shaw.ca)
REGISTRATION: www.mineralogicalassociation.ca

VINTAGE TECHNOLOGY, NOVEL APPLICATIONS
The polarized light microscope has been an important investigative instrument in the mineralogical sciences for nearly two centuries. In spite of its vintage, all its capabilities have not yet been realized. This Berry School will provide a time and place for graduate students, upper-level undergraduate students, and professional geoscientists to learn how to use the instrument in traditional and novel applications. The school will cover the theory, practice, and application of the polarized light microscope in the interpretation of the origin and development of minerals as revealed in thin sections, polished sections, aggregates, and single crystals.

BACKGROUND REQUIREMENTS
An undergraduate knowledge of crystallography and mineralogy is necessary. Priority will be given to graduate and upper-level undergraduate students. Enrollment is limited to 20 by the number of Olympus BX41 polarized light microscopes available.

SPONSORS
- Mineralogical Association of Canada
- Mineralogical Society of America
- University of Ottawa (lab and microscopes)
Diversity

One of the goals of my predecessor, Sam Mukasa, was to increase the diversity of the Geochemical Society (GS), in topical coverage, in gender, and in regional distribution of the membership. As I support this goal 100%, I have tried in my nearly two years as president to make some changes to address this issue. I can report some notable successes, but also some glaring failures in my attempts to increase the diversity of the GS. Of the 59 members of the 10 volunteer committees serving various society tasks, 32 are male, 27 female, 30 from North America, 17 from Europe, and 12 from countries outside North America and Europe. The regional distribution of committee membership thus reasonably well matches the regional distribution of the GS membership. Of the 91 members of the rebuilt Board of Associate Editors for the GS’s journal, Geochemica et Cosmochimica Acta, 77 are male, 14 are female, 46 are employed in North America, 30 in Europe, and 15 are from outside North America and Europe. In this case, the regional distribution is appropriate for the GS, but there is a gender imbalance that Executive Editor Marc Norman and the Joint Publication Committee are aware of and are actively trying to correct. In both GCA and GS committees, the range of topical coverage is broad and covers a reasonable fraction of the many subjects that can be addressed by geochemical approaches. The leadership of the GS shows poor gender diversity (12 male, 4 female) and particularly poor regional diversity (11 from North America, 4 from Europe, and one from Australia). However, there is some good news to report on this front. First, the next president of the GS will be Barbara Sherwood Lollar, only the third woman in GS history to serve in this role. Bylaw changes have ensured that the upcoming election will elect a regionally diverse group of directors, including the requirement that the next vice president will not be from the same region as the current vice president. This will result in a non–North American GS president for only the second time in the history of the Society.

While more can and will be done to diversify the GS leadership, the area where our record is poorest is in Society awards. The Patterson Award has been won only by men from Europe or North America. The Treibs Award has been presented to only one woman, with the remainder of the awards given to males from Europe or North America. With only a marginally better record, the Goldschmidt Award has been won by only one woman and only 4 men from outside North America or Europe. The Clarke Award has a slightly better record, but still nothing to brag about: 35 males, 6 females, 33 North Americans, 6 Europeans, and 2 from outside North America and Europe. As bad as this record of diversity in GS awards is, comparison with other geoscience societies shows clearly that the GS is not the only one with this problem. See, for example, the data reported by Sam Mukasa in his Triple Point column in the April 2009 issue of Elements.

My attempt to correct the lack of diversity in awards includes formation of the Awards Nomination Committee, whose sole task is to reach out to the community to identify and solicit nominations for worthy award candidates. Increasing diversity in the awards is one of the committee’s explicit charges, and through a lot of hard work, they are beginning to make a difference by increasing the diversity of the nominations considered by the various award committees. Ultimately, however, the task of correcting the lack of diversity in GS awards lies with the membership. The award committees cannot select award winners who are not nominated. Nominations are the responsibility, duty, and privilege of the GS membership. If you consider diversity an important issue and you know of someone who you believe has been passed over for an award they deserve, make a difference: submit a nomination for that person. With your assistance, we hopefully will be able to reach a state where all aspects of the Geochemical Society well match the diversity of its membership.

Richard Carlson, GS President

GS AT GSA-DENVER

Dr. Rebecca Lange (University of Michigan) will deliver the 2013 F. Earl Ingerson Lecture. Her talk, “The origin of highly evolved, voluminous rhyolites by progressive, multiple episodes of partial melting: The resolution of some paradoxes,” will be presented on Sunday, 27 October 2013 at 9:20 am in CCC Room 205. The Geochemical Society will again be sponsoring a ticketed reception with MSA and the GSA-MGPV Division, as well as welcoming attendees to our exhibit booth (Booth 1107).
Many members contribute to the Geochemical Society each year, often by including a donation with their dues. Thank you for your contributions! Everything we do at the Geochemical Society is made possible through the generosity of our members, volunteers, and contributors.

If you would like to contribute to the Geochemical Society, please log in to your account on our website and select “donate,” or contact the business office at gsooffice@geochemsoc.org.

**GEOCHEMICAL SOCIETY CONTRIBUTIONS**

Through the generosity of our members, volunteers, and contributors.

By including a donation with their dues. Thank you for your contribution!

**International Participation Program**

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**Organic Geochemistry Division**

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**Student Travel Grant Program**

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**General Support Fund**

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**ANNUAL MEMBERSHIP DRIVE**

If you have not done so already, please take a moment to renew your membership in the Geochemical Society. Members joining by 31 January 2014 will benefit from a US$5 discount (member rates with the discount are $30 professional, $10 student, and $15 senior). You may renew online or download a membership form from our website: www.geochemsoc.org/join.

Please consider making a donation with your membership. Donations are tax deductible where applicable. Remember to indicate how you would like your donation to be used. And finally, word of mouth is a valuable part of our membership growth. If you know of a peer or student who isn’t a member, please encourage them to join.
GOLDSCHMIDT2013: A MEDIA HIT

The Florence 2013 Goldschmidt Conference was marked by a major effort to reach out to the world’s media to promote our research. It was a big success, but like many conference-related matters, this result required careful planning over the preceding months.

The media primarily want to know what new work is being presented at a conference. The different session chairs and subject experts first identified, from over 4300 abstracts, those that might have some press potential. The Goldschmidt media committee, chaired by EAG Vice President Liane Benning, selected 20 of these abstracts. After consultation with CampusPR, a UK-based science media company, the selection was reduced to 10 abstracts that both represented top-quality science and were attractive to the media. To achieve as wide a media reach as possible, CampusPR interviewed the lead authors of these abstracts and wrote draft press releases for each. I came on board, as Goldschmidt press officer, to work with Abigail Chard at CampusPR and distribute the press releases internationally.

Abigail’s job was difficult. She had to turn the research into understandable science without over-simplification or over-dramatisation. As the work went on, it became obvious that some of the science being presented would not make it to the final press release stage. There can be many reasons for this. Some authors might be concerned that the media will take things out of context or take them out of their area of expertise. More than one author was worried about whether advance publicity might put a subsequent publication at risk. Or it may simply be that as the work is explained it becomes less newsworthy than was originally thought. These are all valid reasons not to proceed, and we set it as a rule that no press release would be issued unless all parties were happy with the final version. Eventually we arrived at a final five:

- Bacteria supplemented their diet to clean up after the Deepwater Horizon oil spill
- We may all be Martians – new research supports the theory that life started on Mars
- Research suggests terror bird’s beak was worse than its bite
- Harmful particles in Icelandic volcanic ash fell first, says new research
- Chelyabinsk meteorite had a previous collision or near miss

Goldschmidt is an international conference, so our audience is international. This means that we need to reach the science journalists at their desks in London, Rome or San Francisco, as well as the journalist who comes to the congress. In fact, we considered staging an advance press conference in London, where there is a whole raft of specialist journalists, but logistics and time eventually worked against us. We did hold a small press conference in Florence for attending journalists, but most of our press releases were distributed via agencies and e-mail. Simon Redfern from Cambridge had just finished a media scholarship at the BBC, and his contacts and insight were also invaluable.

It’s fair to say we had great success, much more that I had anticipated. Steven Benner’s work on the evolution of early life on Mars went global, with reports in many languages and in many top-rank media outlets, such as the Los Angeles Times, Reuters, New Scientist, all the main UK papers, French and Italian news agencies, and so on. Perhaps the highlight was Steve’s live appearance on BBC Radio’s Today show, which is the top news outlet in the entire BBC. Some of the other stories also achieved great international coverage, but the good thing is that they were all firmly grounded in geochemistry.

In summary, I’d say that we had some good stories, well-written press releases, and authors who were happy to work with us (we can’t thank them enough for that). You also have to be lucky: a big story elsewhere can relegate your work to a footnote. But in the end we can be very pleased with the way it went: we learned a lot from Florence, and we have set ourselves a high standard for future Goldschmidt conferences.

Tom Parkhill, Goldschmidt Press Office

If you want to talk to Tom Parkhill about any aspect of dealing with the media at Goldschmidt, e-mail him at tom@parkhill.it. A full report on Goldschmidt2013 will be available in the next issue of Elements.

WHY NOT JOIN EAG OR RENEW YOUR MEMBERSHIP, AND FORGET ABOUT IT FOR A FEW YEARS?

As the end of the year is approaching, you are probably starting to receive reminders about renewing your membership. We would like to summarize why it is in your interest to renew your membership or to join the EAG:

For 25 euros or, if you’re a student, 15 euros:
- you benefit from reduced registration fees at Goldschmidt2014
- you receive 6 printed issues of Elements plus online access to all back issues
- you receive 4 printed issues of Geochemical Perspectives plus online access to all back issues
- you benefit from reduced subscription rates for Chemical Geology and Geofluids
- you can request sponsorship for short courses your institution may organize

And to save you from having to renew your membership every year, we propose multi-year memberships with a discount: professionals can take a 5-year membership for 100 euros, and students can take a 3-year membership for 35 euros.

Think about it, just once: a professional taking a 5-year membership now receives reduced registration fees for all Goldschmidt conferences until 2018, 30 issues of Elements, and 20 issues of Geochemical Perspectives (plus online access to all back issues of those publications), and that person will not receive a reminder from the EAG for another five years.

So if you think this offer is worth it, please go to www.eag.eu.com/membership.
WORKSHOP REPORTS

This past August, the International Association of Geoanalysts co-sponsored two workshops. Here we report on these activities.

Biennial Secondary Ion Mass Spectrometry Workshop

The 7th Biennial Geochemical SIMS Workshop (BGSW7) was held on 20–22 August 2013 at the Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences. This two-and-a-half-day event attracted 50 delegates from 14 countries on 5 continents. The first afternoon of the workshop featured six invited keynote talks from leading experts in the field of secondary ion mass spectrometry (SIMS). The talks covered diverse applications as nuclear forensics, accelerator-based Super SIMS, and the operational design of the emerging Helmholtz SIMS network. The remaining two days were devoted to poster and oral technical presentations from world-leading SIMS facilities; these reports described current activities, recent analytical breakthroughs, and newly refined data-collecting strategies. Altogether, 33 abstracts were submitted for presentation at the workshop.

Both the IAG and Wiley Publishing, publishers of the IAG’s official journal, Geostandards and Geoanalytical Research, generously supported the evening cultural program, and they deserve particular recognition for having made possible a visit to the site of the 1945 Potsdam Conference and the historic Cecilienhof Palace. Generous corporate donations from Cameca and Australia Scientific Instruments also contributed to the relaxed and collegial setting, including a dinner cruise to Berlin on the Havel River and an evening barbeque on the laboratory terrace. Delegates also had the opportunity to visit Potsdam’s newly installed SIMS facility as well as historical places on the GFZ campus, including the site of the world’s first teleseismic observation, made in April 1889.

Thanks to the scientific contributions of the many delegates and the financial support provided by the sponsors, BGSW7 provided a near-perfect setting for the exchange of ideas among many of the most active geo-SIMS laboratories. The interactive nature of the workshop combined with the presence of leading members of this highly specialized community contributed to the advancement of this top-end analytical technology.

Michael Wiedenbeck (michael.wiedenbeck@gfz-potsdam.de)

BORON ISOTOPE WORKSHOP

Just prior to the Goldschmidt 2013 conference, the Pisa Boron Working Group and the IAG organized a workshop to bring together the geochemical boron (B) isotope community. Hosted by the Istituto di Geoscienze e Georisorse (CNR Pisa), this workshop provided a forum for discussing the various methodologies and mass spectrometric techniques available for boron isotope analysis.

Attracting 35 scientists from around the globe, including delegates from Asia, North America, Europe, and Australia, the workshop began on Saturday, August 24. The morning session started with a presentation about measurement uncertainties in B isotope data, which was followed by a block of talks presenting the different mass spectrometric techniques and chemical methodologies currently in use for determining B isotope ratios. The afternoon session began with the results from the Boron Isotope Intercomparison Project on carbonates. This was followed by a talk presenting the state of the art in B isotope matrix-matched reference materials characterization, assessing which materials are most urgently needed. After a coffee break, the afternoon session focused on new applications and methodologies, with presentations on B isotope ratios in bioapatite, plants, and silicates, as well as on a newly devised method for online B-matrix separation. The social part of the workshop featured an exquisite dinner in the old town of Pisa and concluded at 2:30 Sunday morning in front of a student pub.

Most discussions touched on issues such as quality control in B isotope analysis, data comparability, and realistic measurement uncertainties in B isotope data. A major issue that repeatedly arose during the workshop was the shortage of well-characterized reference materials for carbonate work, and in particular the challenges faced by in situ analyses using SIMS and LA–MC–ICP–MS. The presentations at the workshop, as well as recent papers, highlighted MC–ICP–MS as a powerful mass spectrometric technique for determining precise, reproducible, and accurate B isotope ratios on a broad spectrum of matrices.

The B workshop in Pisa was the most recent in a series of meetings involving the geochemical B isotope community at which new analytical developments and applications have been discussed. The primary intent of this ongoing effort is to solve analytical problems through joint, community-wide approaches. The organizers would like to highlight the International Association of Geoanalysts and its journal, Geostandards and Geoanalytical Research, as suitable platforms for geo-analytical projects, and they hope that the B isotope workshop in Pisa will stimulate new cooperations within the B isotope community.

Samuel Agostini (s.agostini@igg.cnr.it) and Martin Rosner (martin.rosner@isoanalysis.de)
South Africa is currently home to 75 type species of minerals. Daltry (1997) published an exhaustive work on the region’s type mineralogy, and this was subsequently updated by Gait (2002). This short article serves to bring the listing up to date as of 2012. Of the 75 South African type species approved by the IMA, 42 are named after people and 15 derive from names, most based on chemical composition.

**TYPE MINERALS FROM SOUTH AFRICA**

South Africa is world renowned for its rich economic mineral deposits, so it is no coincidence that many of the type species were discovered during the exploration of the country’s commodities, such as platinum, chrome, and manganese. To date, the Kalahari manganese field (KMF), located north of Kuruman in the Northern Cape Province, is the most productive type field for manganese, surpassing the Bushveld Complex, which long held the number one spot. There are 13 valid type species known from the Bushveld Complex (and these are mostly platinum-group minerals; Table 1), while the Kalahari manganese field has produced 20, with two new species awaiting validation by the IMA. Furthermore, the most prolific single producer in South Africa is the Wessels mine located in the KMF. It is interesting to note that seven of the type species from the KMF contain copper. This metal is extremely rare in these manganese deposits and appears to be partitioned into rare and esoteric species.

| 1980 | Braunite II | Ca(Mn³⁺,Fe³⁺)₃SiO₄ |
| 1983 | Sturmanite | Ca₂(Fe⁴⁺,Al,Mn⁴⁺)₂(SO₄)₂[B(OH)₄] (OH)₄·2SH₂O |
| 1990 | Orlymanite | Ca₂Mn³⁺₂Si₆O₁₈(OH)₄·2SH₂O |
| 1992 | Vonbezingite | Ca₄Cu₂(SO₄)₂(OH)₂·2H₂O |

**REFERENCES**


**Dr Sabine Verryn**, IMA2014 Conference Chair, and **Dr Desh Chetty**, IMA2014 Scientific Committee Chair

**IMA2014: THE 21ST MEETING OF IMA – CALL FOR ABSTRACTS AND REGISTRATION**

For the first time in its history, the International Mineralogical Association (IMA) will hold its General Meeting on the African continent, and it has selected South Africa as the host nation. Taking place at the Sandton Convention Centre in Johannesburg on 1–5 September 2014, the prestigious forum will showcase research excellence in the field of mineralogy. Preparations are coming along well, with close to 70 session proposals received. A wide variety of topics and themes has been put forward, making for a comprehensive and stimulating scientific programme of oral and poster sessions, workshops and short courses. The call for abstracts opened on 1 August 2013, and those interested in submitting abstracts are encouraged to respond to the call. A number of exciting field trips have also been proposed, and these alone promise to attract many people. Please visit our website, www.ima2014.co.za, to submit an abstract and for updates on the conference, or e-mail us at info@ima2014.co.za with any queries.

Registration also opened on 1 August, and early-bird registration will close on 15 January 2014. We look forward to welcoming you to South Africa in 2014.

**Prof. Bruce Cairncross**
University of Johannesburg, South Africa

**TABLE 1**

| 1992 | Poldervaartite | Ca₅(Cu₄⁺,Mn²⁺)₅(SO₄)_(2+3)(OH) |
| 1993 | Hennomartinitie | SrMn³⁺₁₂Si₄O₁₂(OH)₂·H₂O |
| 1994 | Effenbergerite | (K,Na)⁶(Na,Li)₂(Mg,Mn³⁺,Li,Fe³⁺)₂Si₆O₂₂ (OH)₂ |
| 1995 | Nchwaningite | Mn₂⁺₂Si₃O₆(OH)₂·H₂O |
| 1996 | Wesselsite | SrCu₃Si₆O₁₈ |
| 2002 | Manganvesuvianite | Ca₁₀Mn³⁺₄(Mg,Mn²⁺,Fe³⁺)₁₀(Mg,Mn²⁺,Fe³⁺)₂Si₁₄ O₉(H₂O) |
| 2005 | Holststamite | Ca₄Al₂(SiO₄)₂(OH)₄ |
| 2006 | Manganipiromontelite-(Sr) | CaSr(Mn³⁺,Fe³⁺)₂Al[SiO₄]₂(OH) |
| 2007 | Olmiite | CaMn₃(SiO₃)₉(OH) |
| 2010 | Guidottite | (Mn₂⁺Fe³⁺)₅(SiO₃)₂O₃(OH)₄ |
| 2012 | Lavinskyite | K₂LiCu₃(SiO₄)₂(OH)₄ |
| 2013 | Cairncrossite | Sr₂Ca₄Cu₉(Si₄O₁₁)₂(OH)₂·15H₂O |
| 2012 | Diegogattaite | Na₂Ca₄Cu₉(Si₄O₁₁)₂·H₂O |

Two new type species are pending, one from Wessels mine and one from N’Chwaning II mine.

- Black Rock mine;
- Wessels mine;
- N’Chwaning II mine

* Incorrectly attributed to Black Rock mine; most likely from N’Chwaning II mine
* Not approved by the IMA

**TABLE 2**

| 1997 | Atokite | Pd₁Sn |
| 1997 | Braggite | PtS |
| 1997 | Cooperite | PtS |
| 1997 | Genkinite | Pt₂Sb |
| 1997 | Geversite | Pt₂Sb |
| 1997 | Hollingworthite | RhAsS |
| 1997 | Irarsite | IrAsS |
| 1997 | Merenksyite | PdT |
| 1997 | Platarsite | PtAs |
| 1997 | Rustenburgite | Pt₁Sn |
| 1997 | Stibiopalladinite | Pd₂Sb |
| 1997 | Stumpfite | PtSb |
| 1997 | Tetraferroplatinum | PtFe |

* Atook mine; * Rustenburg mine; * Rustenburg Layered Suite; * Onverwacht dunite pipe; * Dreekop dunite pipe; * Tweefontein; * Mooihoek dunite pipe
This year marks the 50th anniversary of the International Clay Conferences of AIP EA, the Association Internationale pour l’Étude des Argiles. AIP EA held its 15th International Clay Conference (ICC) in Rio de Janeiro, Brazil, from July 7 to 11, 2013, on the campus of the Federal University of Rio de Janeiro. The conference was organized by the Brazilian Clay Group of the Brazilian Geochemical Society (SBGq), in cooperation with the Brazilian Association of Petroleum Geologists (ABGP), under the auspices of the AIP EA. A total of 205 participants from 30 countries attended the meeting, which was sponsored by Petrobras (Diamond Sponsor), Halliburton, Schlumberger, and GeoHub, with further support from Dairix, Bruker and Zeiss.

A significant pre-meeting activity was the second edition of the AIP EA School for Young Scientists (ASYS). The school, entitled Magnesian Clays: Characterization, Origin and Applications, was organized by Manuel Pozo of the Universidad Autonoma of Madrid, Spain. The ASYS was held at the Brazilian Center for Physics Research (CBPF) on July 6 and 7. Young (and not-so-young!) researchers had the opportunity to discuss the following topics with renowned scientists:

- **Introduction to Mg-rich clay minerals:** structure and composition (S. Guggenheim, USA)
- **Properties and applications of Mg-clays:** (J. Santaréns, Brazil)
- **Geology of Mg-clays in sedimentary and non-sedimentary environments:** (J. P. Calvo, Spain)
- **The origin of Mg-clay deposits:** mineralogical assemblages and textures (M. Pozo, Spain)
- **Geochemical pathways to Mg-clay formation:** (N. Tosca, Great Britain)
- **Methodology for the identification and characterization of Mg-clays:** (E. Galan, Spain)
- **Mg-clays in Brazilian basins:** (D. Barbosa Alves, Brazil)

The presentations will be collected in a book (AES, AIP EA Educational Series, vol. II), which will be published next year.

Four plenary lectures opened the daily scientific sessions at the 15th ICC:

- **“The First X-ray Diffraction Results from the Mars Science Laboratory: Clay Minerals, Amorphous Materials, Sulfates”** – Prof. David L. Bish (Indiana University, USA)
- **“Functional Hybrid Clay Mineral Films”** – Prof. Robert A. Schoonheydt (KU Leuven, Belgium)
- **“Complex Physics in Clays”** – Prof. Jon Otto Fossum (Norwegian University of Science, Norway, and PUC Rio de Janeiro, Brazil)

As is usual for International Clay Conferences, the contributions covered an extremely wide variety of fields related to micro- and nanomaterials. The 15th ICC featured 433 contributions (173 oral presentations and 260 posters) distributed among 8 symposia and 11 technical sessions. The symposia titles were: Clay Minerals in Petroleum Systems; LDH Layered Double Hydroxides; Structural Characterization of Lamellar Compounds; Remote Sensing and Spectroscopy of Clays and Associated Minerals; Water Mobility Studies in Reference and Real Clays; Clays in Geology; Vectors for Resources; Soil Mineralogy; and Self-Organization from Clay Particles: From Nano to Macro. The technical sessions were: Applications of Clay Minerals in Earth Sciences; Clay Minerals in Ceramic, Archaeological and Archaeometric Investigations; Geotechnics and Clay Minerals; Waste Disposal and Clay Minerals; Medical Geology and Clay Minerals; Interaction of Microorganisms, Biominerallization and Clay Minerals; Nanocomposites and Clay Minerals; Organo-modifications of Clays; and Qualitative and Quantitative Analysis of Clay Minerals.

A number of recognitions and awards were made during the conference. Professor **Robert Schoonheydt** (Katholieke Universiteit of Leuven, Belgium) was named AIP EA Fellow for his contribution to industrial applications of clay minerals.

The prestigious AIP EA Bradley Award for a young scientist was given to Dr **Ana Clecia Santos Alcântara** (Materials Science Institute of Madrid, Spain) for her contribution “Polysaccharide-fibrous clay bionanocomposites.”

Another international award, the Novelli Prize, supported by the Italian Association for the Study of Clays (AISA), was given to **Marek Szczersba** (Polish Academy of Sciences, Cracow, Poland) for his contribution to industrial applications of clay minerals.

The AIP EA Student Best Speaker Award was given to **Robert Koch** (University of Trento, Italy); **Eliana Satiko Mano** (São Paulo University, Brazil) and **Sirle Liivamagi** (University of Tartu, Estonia) were runners-up. The AIP EA Student Best Poster Award went to **Syafina Binti Mohol Ghazi** (Hokkaido University, Japan); runners-up were **Gabriella Fazio** (University of Brasilia, Brazil) and **Aleksandra Deregowska** (University of Natural Resources and Life Sciences, Austria).

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Robert Schoonheydt, AIP EA Fellow 2013 (right), and David Bish, AIP EA past president

Marek Szczersba (right) receives the Novelli Prize from Saverio Fiore, incoming AIP EA president

Student Best Speaker Award: (from left) Jeanne B. Percival (AIP EA treasurer), Robert Koch (award winner), Eliana Satiko Mano and Sirle Liivamagi (runners-up)
The level of the competition was very high, testifying to the increased interest in the world of microminerals. The Clays & Arts Award (sponsored by the Organizing Committee) was given to Dr. Ailton Luis da Silva de Souza (Petroleo Brasileiro S.A., Brazil).

The Association also helped students to participate in the conference through the Student Travel Awards programme. The following students received support to attend the conference and present their work: Dayse Mirella Oliveira Timóteo (Federal University of Rio de Janeiro, Brazil), Gabriel G. Machado Álvarez (Technical University of Crete, Greece, and Federal University of Rio Grande do Sul, Brazil), and Valentin Robin (University of Poitiers, France).

The AIPEA General Assembly elected its 15th Council. AIPEA officers for 2013–2017 are: Dr. Saverio Fiore (Consiglio Nazionale delle Ricerche, Italy), president; Prof. Joseph Stucki (University of Illinois, USA), vice president; Prof. Christopher Breen (Sheffield Hallam University, UK), past president; Dr. Daisy Barbosa Alves (Petrobras, Brazil), secretary general; and Dr. Jeanne B. Percival (Petrobras, Brazil), secretary general; and Dr. Jeanne B. Percival (Petrobras, Brazil), secretary general; and Dr. Jeanne B. Percival (Petrobras, Brazil), secretary general; and Dr. Jeanne B. Percival (Petrobras, Brazil), secretary general; and Dr. Jeanne B. Percival (Petrobras, Brazil), secretary general; and Dr. Jeanne B. Percival (Petrobras, Brazil), secretary general; and Dr. Jeanne B. Percival (Petrobras, Brazil), secretary general. AIPEA councilors are Prof. Balwant Singh (The University of Sidney, Australia), Dr. F. Javier Huertas (Consejo Superior de Investigaciones Científicas, Spain), Prof. Helge Stanjek (RWTH Aachen University, Germany), Dr. Victoria Krupskaya (Russian Academy of Science, Russian Federation), Dr. George Christidis (Technical University of Crete, Greece), and Prof. Makoto Ogawa (Waseda University, Japan). Prof. Stephen Guggenheim (University of Illinois at Chicago, USA) is the chair of the Nomenclature Committee, and Dr. Sabine Petit (Centre National de la Recherche Scientifique, France) is the chair of the Teaching Committee. The representative of the next ICC is Dr. Alberto Lopez Galindo.

This year’s Petrology Subgroup meeting was held at the Institute for Mineralogy in Bonn on June 7 and 8. Over 80 participants met for dinner on Friday night at the gates of the Poppelsdorfer Schloss, which was the host site for the scientific program. People from all over Germany and some international guests were in attendance, and students made numerous contributions. The next day, the scientific program was introduced by Chris Ballhaus (University of Bonn) and was highlighted by lively and contentious discussions. Nine posters were presented in the library, and nineteen talks covering field work, theoretical approaches, and experimental studies were given. Presentations focused on the influence of halogens and water on magmatic processes, element partitioning, mantle processes, and meteorites. After running out of water in terms of rain and discussions, this successful meeting culminated with a barbeque on the terrace of the Schloss, accompanied by live music.

The next AIPEA meeting, the 16th International Clay Conference, will be organized by the Sociedad Española de Arcillas (Spanish Clay Society), under the chairmanship of Dr. Alberto Lopez Galindo. The 16th ICC will take place at the Science Park in Granada, in July 2017. With the theme “Clays, from the Oceans to Space,” the conference will embrace the universe of micro- and nanominerals, confirming, once again, the central role of AIPEA in promoting multidisciplinary activities in theoretical and applied clay science. Information will be available after 1 January 2015 at the website www.16icc.org. The meeting will be an excellent occasion for sharing ideas and knowledge with scientists working in the diverse scientific fields of microminerals. It will also be a great opportunity to meet old and new friends, and to see Granada... to quote the poet Francisco de Icaza: “Give him alms, woman, for there is nothing sadder in life than being blind in Granada.”

Saverio Fiore (president@aipea.org)
President, AIPEA

Alberto Lopez Galindo, ready to carry the AIPEA flag to Granada, Spain, which will host the 16th ICC in July 2017

MEETING REPORTS

DMG PETROLOGY SUBGROUP MEETING, 7–8 JUNE 2013, Bonn, Germany

Student Best Poster Award: (from left) Jeanne Percival (AIPEA treasurer), Franz Ottner (in lieu of Aleksandra Deregowska, runner-up), Syafina Binti Mohol Ghazi (award winner), and Gabriella Fazio (runner-up)
URANIUM – CRADLE TO GRAVE

Uranium – Cradle to Grave, the newest volume in the Mineralogical Association of Canada Short Course Series, was developed for a short course held in Winnipeg, Canada, in May 2013. The volume provides a wide-angle snapshot of the ever-growing field of uranium research. Examining the intersection between the nuclear fuel cycle and the geochemical cycle of uranium, the volume expertly covers uranium mineralogy and geochemistry, but also provides access to topics less commonly found in the mineralogical and geochemical literature, notably nuclear nonproliferation and nuclear forensic science.

The past two decades have seen remarkable advances in uranium chemistry. Much of this progress derives from environmental research, including radioactive-waste disposal and remediation of contaminated sites. To a large extent, technology has propelled this knowledge growth, including the exponential growth in computing power. This latter factor has dramatically expanded the field of theoretical actinide science, including crystal chemistry, aqueous chemistry, and surface complexation. Advances in absorption and emission spectroscopies have also contributed greatly, proving especially powerful when combined with computational chemistry. There seems every reason to expect such progress to continue. And while Uranium – Cradle to Grave does not explicitly address analytical techniques, many chapters bear testament to these advances.

The volume opens with a brief historical sketch, sprightly written, though not carefully enough (for example, the author states that natural fission reactors are characterized by being abnormally enriched in $^{235}$U; they are, of course, anomalously depleted in that fissile isotope). The second chapter introduces the volume’s contents and provides context, including current issues related to the complex legacy of the nuclear fuel cycle for production of energy and weapons.

Krivovichev and Plášil (chapter 3) provide an excellent, well-organized review of $^{6+}$ mineralogy, including crystal chemistry and bonding, mineral occurrences, and structures ($^{4+}$ minerals are not discussed in any detail). Sections describing structural topologies, polytypism, and topological isomers, especially among uranyl phosphates, sulfates, and molybdates, are illuminated through the graphical use of anion topologies and cation nodes, bringing clarity to some otherwise complex structural features and relationships. The authors also provide links between cation coordination in the solid state and solution complexes, a good primer for chapters 6–8. Though minor, the omission of simple uranyl (hydr)oxides neglects a few new minerals: paulscherite, heisenbergite, and vorlanite [(CaU$_6$)$_2$O$_4$], with its apparently singular paragenesis.

Fayek (chapter 4) provides a well-written and succinct review of uranium ore deposits, including three classification schemes based on (1) host rocks (lithology and morphology); (2) ore genesis and the geologic cycle; and (3) fluid type and mineralizing system, with magmatic, metamorphic, and meteooric end-members. The diagrams are especially clear. Somewhat buried at the end is a discussion about using trace elements and stable isotopes to help identify the provenance of uranium ores. This has applications to nuclear forensic science, also discussed in chapter 13. Unfortunately, the two chapters don’t refer to each other.

Navrotsky and coauthors (chapter 5) review thermodynamic studies of uranium-bearing solids, with considerable attention paid to compounds unknown in nature. The important but small number of studies on uranium minerals help emphasize the need for continued work. The authors confute fission products and decay products, a surprising mistake.

Surface-mediated controls on geochemical transport of uranium form a common theme for chapters 6 through 8. Indeed, there is considerable overlap among these chapters (especially 6 and 8), all of which address sorption to some degree. Chapters 6 and 8 both review aqueous speciation and solution chemistry, surface-complex modeling, mineral-specific sorption, and sorption in natural sediments. Fein and Powell (chapter 6) review uranium sorption on bacteria, while Zachara and coauthors (chapter 8) describe uranium minerals in contaminated sediments. Zachara and coauthors culminate their thorough review with a case study about uranium migration at Hanford (USA). Their cautionary notes about challenges in interpreting and modeling data for experimental and complex natural systems are worthwhile reading for anyone interested in reactive-transport modeling. Schindler and Ilton (chapter 7) focus on abiotic surface-mediated reduction of $^{6+}$ by Fe$^{2+}$, followed by uranium-mineral precipitation and dissolution reactions, including coprecipitation of uranium with silica, calcite, and gypsum. These authors note that reactions at interfaces may not reflect expectations based on bulk solution chemistry, a point also mentioned in chapter 8. Schindler and Ilton end each section with a helpful summary of questions for further research.

Spent nuclear fuel and other radioactive wastes are inevitable products of the nuclear fuel cycle, and actinide-bearing waste forms destined for eventual disposal are discussed in chapters 9–12. The first three of these chapters review the most commonly considered waste forms: borosilicate glass, crystalline ceramics, and spent UO$_2$ fuel from nuclear power reactors. These three chapters expertly cover the most pertinent aspects of waste forms, including actinide loading, radiation stability, chemical durability, and actinide release during corrosion/dissolution. Polinski and coauthors (chapter 12) focus narrowly on structural studies of a few synthetic actinide-bearing compounds, without clear relevance to waste disposal or natural environments.

The attribution of certain nuclear materials using nuclear forensic science is the subject of chapters 13 and 14. Hutcheon and coauthors (chapter 13) review analytical methods used to analyze interdicted nuclear and radiological materials and describe two case studies. Analytical methods described here will be familiar to Earth scientists. Simonetti and coauthors (chapter 14) give a fascinating account of a forensic investigation of postdetonation nuclear materials: glassy residues of the first-ever nuclear explosion in New Mexico, USA, in 1945. The chapter reveals many complications related to extracting accurate information about a nuclear explosive device and details of a post-detonation scenario, complications likely to be compounded if such a scenario were to occur in an urban center. The volume closes with a look to the future: Cuney (chapter 15) reviews worldwide resources of uranium and thorium for potential energy production.

Uranium – Cradle to Grave is an excellent addition to the immense and ever-expanding literature on uranium, covering an unusually wide range. It is a bit uneven, with a few obvious errors and occasional inconsistencies. Although the book is already expansive, the editors might still have included other topics (theoretical studies or perhaps uranyl-peroxide nanoclusters, the omission of which I find a bit unfortunate). Several truly outstanding chapters make up, by far, the bulk of the volume. Chapters 3, 4, 8, 9–11, and 14 are especially well written, comprehensive, and just plain interesting (to me). This is and may long remain a valuable resource for researchers in a range of disciplines and should help inspire continued interest in this prodigious subject.

Robert J. Finch, Albuquerque, New Mexico

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When I accepted the task of reviewing this well-written, informative, well-referenced, and somewhat expanded (an additional 55 pages) and updated sequel to Environmental Mineralogy (EMU Notes in Mineralogy 2, published in 2000), I decided to explore the early history of environmental mineralogy. One source I examined was Herbert and Lou Henry Hoover’s translation of Georgius Agricola’s De Re Metallica, which was first published in Latin in 1550. This classic work by Agricola (aka Georg Bauer)—a physician, author of the first mineralogy textbook (De Natura Fossilium, 1548), and natural scientist—served as the main textbook and guide to miners and metallurgists until 1738, when Andreas Schlüter’s work on metallurgy appeared. In hindsight, the beginnings of what is now called “environmental mineralogy” were evident in Agricola’s time. For example, the miners of this period recognized that arsenic derived from naturally occurring orpiment was a “powerful poison” to humans (fast-forward to the arsenic pollution problems in Southeast Asia derived from the natural breakdown of ashen orpiment in the Himalayas, the cause of the largest mass poisoning in human history). They also knew from experience that if the mineral dust breathed by miners in dry mines “has corrosive qualities, it eats away the lungs and implants consumption in the body” (fast-forward to lung diseases common among underground coal miners today). Even earlier, in Roman times, the dangers of mineral dusts and the need for protective masks on miners were known, as pointed out by Pliny the Elder. These early examples of environmental problems caused by mining, beneficiation, and smelting of ores show a strong connection between extracting metals from minerals and their impact on the environment and human health.

Like the earlier version, this volume helps define the modern field of environmental mineralogy, which is still in its infancy, as pointed out by coeditor David Vaughan in the introductory chapter. The volume’s 11 chapters cover the same topics as the first edition by essentially the same group of authors plus several new ones. These chapters encompass various aspects of environmental mineralogy, including the modern analytical, experimental, and computational methods used to study minerals and the chemical processes occurring at mineral surfaces (Roy Wogelius and David Vaughan), the role of minerals in the development of soils (David Manning), and the types of minerals found in marine sediments (Andrew Alpin and Kevin Taylor). The important impact that microbial organisms have on the mineralogy of the environment is dealt with in a chapter by Susan Welch and Jillian Banfield, and the types of mineral aerosols that occur in Earth’s troposphere and their role in various environmental processes are the subjects of a comprehensive chapter by Mihály Pósfai and Agnes Molnar. The mineralogy of mine wastes, acid mine drainage, and strategies for remediating abandoned mine sites are covered in a chapter by David Blowers, Carol Ptacek, and John Jambor. In a chapter on the mineralogy of municipal waste deposits, Rita Hermans Stengele and Michael Plötze discuss the multibarrier approach in landfill design and the impact of waste disposal facilities on groundwater quality. The role of mineralogy in long-term nuclear waste management is summarized in a brief chapter by Charles Curtis and Katherine Morris, and the role of modern analytical methods in conservation of cultural heritage is discussed by Giacomo Chiari. The final chapter, by Catherine Skinner, focuses on the impact of biominerals on human health in both positive ways (e.g. hydroxyapatite in bones and teeth) and negative ways (e.g. pathological hydroxyapatite in human arteries).

It would be difficult to cover all the important areas that comprise modern environmental mineralogy in one manageable volume, and this is true of the current volume. For example, the discussion in chapter 2 of quantum chemical and molecular dynamics modeling of mineral structures, mineral–aqueous solution interfaces, and chemical reactions at mineral surfaces is relatively brief. However, this is offset by a very nice summary of many of the modern experimental methods used to study the geometric and electronic structures of minerals and mineral surfaces and the bulk and surface compositions of minerals, as well as by useful summaries of reaction kinetics and reaction path modeling in the same chapter. Other topics that are largely ignored in this volume include the impact of mineral dusts on human health; nanogeoscience (which focuses on minerals in the nanometer size range, i.e. 1–100 nm in at least one dimension); and important environmental areas such as CO2 sequestration through mineral carbonation, the mineralogy of fly ash, and the release of toxic metals such as mercury, arsenic, and selenium from coal combustion. However, these and other related topics are covered in detail in the recent environmental mineralogy/geochemistry publications listed in the appendix at the end of chapter 1. In spite of this minor criticism concerning coverage, I recommend this volume for a beginning-level graduate course on environmental mineralogy, supplemented by the lecturer’s own experience and material from some of these other recent publications.

Having been a player in the field of mineralogy for the past 40+ years, I have enjoyed watching its evolution from a somewhat descriptive science in the 1960s and 1970s—including the description of the crystal structures of minerals based on X-ray crystallographic studies (I used to do this)—to a more quantitative science in which mineralogists employ the principles of physical chemistry, molecular modeling, solid-state physics, and molecular geomicrobiology to focus on more fundamental issues, such as the bonding forces in minerals, the nucleation and growth of minerals, chemical and microbiological reactions at mineral–water interfaces, and the processes that transform minerals under different conditions. Major developments in computational and experimental methods and theory over the past 30 years have had a significant impact on most areas of science and engineering, including mineralogy and the related field of environmental mineralogy/geochemistry. For example, the development of synchrotron light sources that emit extremely intense beams of X-rays, the advance of density functional theory, and the continuing improvement in computers, the fastest of which now operate in the petaflop range, have revolutionized the way chemists, geochemists, mineralogists, and other scientists and engineers approach the problems in their fields. This is especially true in environmental mineralogy/geochemistry, as is evident in several chapters in Environmental Mineralogy II. My prediction is that this field will continue to benefit from applications of modern experimental and computational methods to complex environmental problems involving minerals. This new volume showcases many of these problems and methods. The good news is that there are plenty of important unanswered questions left for the next generation of environmental mineralogists/geochemists to tackle using this modern toolbox of molecular methods.

Gordon E. Brown Jr.
Stanford University, Stanford, USA

October 26–27 Short Course: Soil-mediated Drivers of Coupled Biogeochemical and Hydrological Processes across Scales, Tucson, AZ, USA. Web page: chapman.agu.org/soilmotivated


December 1–4 MRS Fall Meeting & Exhibit, Boston, MA, USA. Web page: mrs.org/fall2013


March 15–20 24th ACS National Meeting & Exposition, Dallas, TX, USA. Web page: www.acs.org


April 6–9 AAPG 2014 Annual Convention & Exhibition, Houston, TX, USA. Web page: www.aapg.org/meetings


April 27–May 2 European Geosciences Union General Assembly 2014, Vienna, Austria. Web page: www.egu2014.eu


May 4–14 6th Orogenic Lherzolite Conference, Marrakech, Morocco. Web page: www.gm.univ-montp2.fr/lherzolite


May 24–28 American Crystallographic Association Meeting, Albuquerque, NM, USA. Details forthcoming


June 30–July 4 Asteroids, Comets, Meteors, Helsinki, Finland. E-mail: acm-2014@helsinki.fi; web page: www.helsinki.fi/acm2014


August 5–12 23rd Congress and General Assembly of the International Union of Crystallography, Montréal, Canada. Website: www.iucr2014.org

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