Sulfur

CHARLES W. MANDEVILLE, Guest Editor

A Useful Tracer

Sulfur in Magmas

Sensing of Volcanic Emissions

Ancient Sulfur Cycling

Tour the Biogeochemical Landscape

Sulfur on Mars
Light Isotope Capability

- Pioneer of high resolution SIMS for sulfur
- Positive and Negative Ion Modes, changed over in minutes with only three switches
- Caesium source and electron gun charge neutralization system
- Advanced 5-channel multi-collector option with simultaneous operation of Faraday cups and electron multipliers
- Ability to rapidly reconfigure multi-collector under computer control, without breaking vacuum
- Highly stable magnetic field control for both high and low fields

Light Isotope Applications

- Two isotope sulfur in positive and negative ion mode
- Three isotope sulfur in negative ion mode
- Oxygen isotope ratios in biogenic and inorganic materials
- Isotope anomalies in refractory meteoritic minerals
- Search for Solar wind isotopes in lunar soil
- Sulfur isotopes in diamond inclusions, hydrothermal systems and massive sulfide deposits

Oxygen isotope compositions of Ordovician to Early Silurian conodonts and brachiopods. Coloured band is SHRIMP II-derived data from condont bioapatite, compared to earlier calcite brachiopod and conodont data.


Pioneering the Technique > Perfecting the Technology
Sulfur
Guest Editor: Charles W. Mandeville

Sulfur: A Ubiquitous and Useful Tracer in Earth and Planetary Sciences
Charles W. Mandeville

Sulfur in Magma
Nicole Métrich and Charles W. Mandeville

Ultraviolet Sensing of Volcanic Sulfur Emissions
Clive Oppenheimer

Ancient Sulfur Cycling and Oxygenation of the Early Biosphere
Timothy W. Lyons and Benjamin C. Gill

Touring the Biogeochemical Landscape of a Sulfur-Fueled World
David T. Johnston

Sulfur on Mars
Penelope L. King and Scott M. McLennan

About the Cover:
Sulfur miners earn a living the hard way in the crater of Ijen volcano in Java, Indonesia. Miners work amidst dense sulfurous clouds emitted by nearby fumaroles and the acid crater lake. Each miner hauls 70 kg of native sulfur on each trip. Read more about this “hell on Earth” on page 67. PHOTO COURTESY OF CLIVE OPPENHEIMER

Departments
Editorial – Hell on Earth ........................................ 67
From the Editors – New Advisory Board Members .......... 68
Triple Point – Fostering Integrated Science .................. 69
People in the News – On the Cutting Edge, Morel, Morgan .. 70
Meet the Authors .................................................... 72
Society News
Società Italiana di Mineralogia e Petrologia .................. 113
Mineralogical Society of Great Britain and Ireland ........ 114
Swiss Society of Mineralogy and Petrology ................ 115
European Association of Geochemistry ..................... 115
The Clay Minerals Society ...................................... 116
Mineralogical Society of America ................................ 118
Association of Applied Geochemists ......................... 120
Société Française de Minéralogie et de Cristallographie .... 121
Geochemical Society .............................................. 122
Mineralogical Association of Canada ......................... 124
Deutsche Mineralogische Gesellschaft ......................... 126
Mineral Matters – New Apatite Nomenclature ............... 127
Meeting Reports – EMU School, IYPE, Astromaterials Meeting .. 128
Book Reviews – SIMS in the Earth Sciences ................ 130
Outreach – On the Road to Energy Solutions ................. 132
Calendar ............................................................... 133
Parting Shots – Magma Mingling and Mixing ............... 135
Advertisers in This Issue ......................................... 136
The Mineralogical Society of America (MSA) was incorporated in 1919, the Society promotes, through education and research, the understanding and application of mineralogy by industry, universities, government, and the public. Membership benefits include special subscription rates for American Mineralogist as well as other journals, 25% discount on Reviews in Mineralogy & Geochemistry series and Monographs, Elements, reduced registration fees for MSA meetings and short courses, and participation in a series of workshops and conferences that supports the many facets of mineralogy. For additional information, contact the MSA business office.

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The Clay Minerals Society (CMS) was founded in 1952, incorporated with the primary purpose of stimulating research and disseminating information about clay and related aspects of clay science and technology. The CMS holds an annual meeting, workshop, and field trips, and publishes Clays and Clay Minerals and the CMS Workshop Lectures series. Membership benefits include reduced registration fees to the annual meeting, access to the CMS Workshop Lectures, and Elements.

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The Geochemical Society (GS) is an international organization with members from 54 countries, founded in 1955 for students and scientists involved in the practice, study and teaching of geochemistry. Our programs include co-hosting the annual Geochemical Society Conference™, editorial oversight of Geochimica et Cosmochimica Acta (GCA) supporting geochemical symposia through our Meeting Assistance Program, and supporting student development through our Student Travel Grant Program. Additionally, GS annually recognizes excellence in geochemistry through its medals, lectures and awards. Members receive a subscription to Elements magazine, special rate membership for GCA and Geo-Canada publication discounts, and conference discounts.

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The European Association of Geochemistry was founded in 1985 to promote geochemistry in all its subspecialties, teaching and research as well as the personal relationships among all members. Its major activities include the publication of its journal, GeoRes, and its main conference, GeoSymposium. Please visit the website www.eaag.org for more information.

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The International Association of Geochemistry (IAGC) has been a pre-eminent international geochemical organization for over 40 years. Its major activities are to foster cooperation in, and advancement of, applied geochemistry, by sponsoring specialist symposia and the activities organized by its working groups and by supporting its journal, Applied Geochemistry. The administration and activities of IAGC are conducted by its Council, comprising an Executive and ten ordinary members. Day-to-day administration is performed through the IAGC business office.

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The Societé Française de Mineralogie et de Cristallographie, the French Mineralogy and Crystallography Society, was founded on March 21, 1878. The purpose of the Society is to promote mineralogy and crystallography. Membership benefits include the "bulletin de liaison" (in French), the European journal Chemistry, Minerals, and Elements, reduced registration fees for SMFC meetings.

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The Association of Applied Geochemists is an international organization founded in 1970 that specializes in the field of applied geochemistry. Its aims are to advance the science of geochemistry as it relates to exploration and the environment, further the common interests of exploration geochemists, facilitate the acquisition and distribution of scientific knowledge, undertake the exchange of information, and encourage research and development. AAG membership includes the AAG journal, GeoExploration, Exploration, Environment, the AAG newsletter, EXPLORE, and Elements.

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The Deutsche Gesellschaft für Mineralogie (German Mineralogical Society) was founded in 1919 to “promote mineralogy and all its subspecialties in teaching and research as well as the personal relationships among all members.” Its great tradition is reflected in the list of honorary fellows, who include M. v. Laue, G. v. Tschermak, P. Eskola, C.W. Correns, P. Rendich, and H. Stuinz, to name a few. Today, the Society especially tries to support young researchers, e.g. to attend conferences and courses. Membership benefits include the European Journal of Mineralogy, the DMG Forum, GMMt, and Elements.

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The Società Italiana di Mineralogia e Petrologia (Italian Society of Mineralogy and Petrology), established in 1940, is the national body representing all researchers dealing with mineralogy, petrology and related disciplines. Membership benefits include receiving the European Journal of Mineralogy, Minium, and Elements, and discounted registration fee for the annual meeting.

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The International Association of Geoanalysts is a worldwide organization supporting the professional interests of those involved in the analysis of geological and environmental materials. Major activities include the management of proficiency testing programmes for bulk rock and micro-analytical methods, the promotion of a certification of reference materials and the publication of the Association’s official journal, Geostandards and Geostandards Research Letters.

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The Polskie Towarzystwo Mineralogiczne (Mineralogical Society of Poland), founded in 1919, brings together professionals and amateurs interested in mineralogy, crystallography, petrology, geochemistry, and economic geology. The Society promotes links between mineralogical science and education and technology through annual conferences, field trips, invited lectures, and publishing. There are two active groups: the Clay Minerals Group, which is affiliated with the European Clay Groups Association, and the Petrology Group. Membership benefits include subscriptions to Mineralogia and Elsevier.

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The Sociedad Española de Mineralogía y Petrología (Spanish Mineralogical Society) was founded in 1975 to promote research in mineralogy, petrology, and geochemistry. The Society organizes annual conferences and the training of young researchers via seminars and special publications. The SEM Bulletin published scientific information from 1973 to 2003, the year the Society joined the European Journal of Mineralogy and launched MS Microscopy in 2010. The Society publishes the official news, abstracts, and reviews. Membership benefits include receiving the European Journal of Mineralogy, Maculis, and Elements.

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The Swiss Society of Mineralogy and Petrology was founded in 1924 by professionals from academia and industry and by amateurs to promote knowledge in the fields of mineralogy, petrology and geochemistry and to encourage fruitful interactions between the scientific and public communities. The Society coorganizes the annual Swiss Geoscience Meeting and publishes the Swiss Journal of Geosciences jointly with the national geological and paleontological societies.

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PARTICIPATING SOCIETIES

The Mineralogical Society of Great Britain and Ireland, also known as the MinSoc, is an international society for all those working in the mineral sciences. The Society aims to advance the knowledge of the science of mineralogy and its application to other subjects, including crystallography, geochemistry, petrology, environmental science and economic geology. The Society further secures its aims through scientific meetings and the publication of scientific journals, books and monographs. The Society publishes Mineralogical Magazine (print and online) and Clay Minerals (print and online). Members receive the first year of membership free of charge. All members receive Elements.

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Sulfur was known to the alchemists as brimstone. The etymology of brimstone probably derives from the medieval English words *birnen* (to burn) and *ston* (stone). “Fire and brimstone” appears repeatedly in the Bible and Koran, denoting agents of divine wrath—witness the fate of the sinful residents of Sodom and Gomorrah. The Book of Revelations associates brimstone with hell. During the eighteenth century, preachers invoked the sulfurious imagery of hell so effectively that their messages about the final judgment came to be known as fire-and-brimstone sermons. It’s no wonder that sulfur has a bad image.

The properties of sulfur and some of its compounds do little to dispel the notion that this is nasty stuff. Sulfur’s myriad allotropes come in many colors, but the vivid red of hot, molten sulfur is most remembered as the hue of hell in art. (Interestingly, the viscosity of liquid sulfur, unlike most substances, increases at high temperatures, due to the formation of polymers. The rubber industry takes advantage of this behavior, using polysulfides to crosslink organic polymers in the vulcanization process.) The pungent stench of sulfur dioxide and hydrogen sulfide announces the presence of sulfur in even small quantities. And sulfuric acid is among the most corrosive chemicals known, capable of dissolving stone and searing skin. It’s no wonder that sulfur has a bad image.

Brimstone has many industrial uses in modern society, and as a consequence, it is mined in many places. No sulfur deposit, though, so epitomizes its hellish image as does that mine at Kawah Ijen, a 2600-meter-tall stratovolcano in western Java, Indonesia. This volcano contains a caldera lake 1 kilometer wide and 200 meters deep. Dip your hand into its 34°C water, and the burning sensation you feel demonstrates that the turquoise-colored liquid is a mixture of sulfuric and hydrochloric acid with pH about 0.5 (similar to car battery acid). This body of water is the largest acid lake in the world. Along the lake’s edges, continuous fumarole activity discharges 4 tons of sulfur gases each day. In 1976, eleven people died from asphyxiation when an enormous bubble of SO₂ erupted unexpectedly from the lake.

Kawah Ijen houses a thriving, if hellish, enterprise—an elemental sulfur mine. Fumarole SO₂ gas is channeled through stone or ceramic pipes, channel and condense sulfur gas into molten sulfur and use iron bars to hack the newly hardened sulfur into large chunks. These are then loaded into baskets. Two baskets, together weighing 50 to 90 kilograms, are balanced on bamboo poles and carried on workers’ shoulders up the steep crater walls and then several kilometers down the mountainside to the collection point. Each miner may make two or three such trips each day. The take-home pay for a day of this dangerous, backbreaking labor is about $5.

Nowhere else, to my mind, comes as close to epitomizing hell on Earth, from the perspective of both the natural geologic environment and the human exploitation at this mine. Sulfur mining at Kawah Ijen is featured on a number of websites, and the pictures reprinted here (courtesy of French photographer Fred Relaix) are part of a larger collection that you can view at www.pbase.com/frelaix/kawah_ijen. These images provide a fascinating glimpse of a world where brimstone reigns, and perhaps they will sensitize us to the high price paid for a critical natural resource—one that we all use in many forms, without a second thought.

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* Hap McSween was the principal editor in charge of this issue.
**Pardee Keynote Symposium, 2010 GSA Annual Meeting – Denver**

The Geological Society of America (GSA) has accepted a proposal by the Mineralogical Society of America and the Geochemical Society to hold a Pardee Keynote Symposium, “Mineral Evolution: The Coevolution of the Geo- and Biospheres,” during its 2010 annual meeting. This symposium will highlight *Elements*’ Mineral Evolution issue (volume 6, number 1, February 2010) and is scheduled for Monday, 1 November 2010. Guest Editor Robert W. Hazen will act as convenor, and several of the authors who contributed to the Mineral Evolution issue will be invited speakers. The primary goals of the Pardee Keynote Symposia are to highlight significant new research that has an impact on our science and to appeal to a wide, multidisciplinary audience, and only a handful are offered at each GSA meeting.

**Elements Fifth Anniversary**

*Elements*’ fifth anniversary will be highlighted at the three upcoming meetings mentioned below. Organizers have taken different tacks, and each venue will offer a unique approach.

**Goldschmidt 2010 – Knoxville, Tennessee**

Bruce Watson and Mike Hochella are convening a symposium entitled “Geochemistry Far from Equilibrium (A Session Celebrating the 5th Anniversary of *Elements* Magazine).” It will explore Earth’s chemical processes occurring far from equilibrium at scales ranging from nanometers to kilometers. The keynote speaker will be Reid Cooper (Brown University).

**IMA Conference, August 2010 – Budapest**

At the International Mineralogical Association (IMA) meeting, an *Elements* plenary lecture is scheduled on each day of the conference. Each lecture will be delivered by an author in a previous issue of *Elements*. These presentations were orchestrated by Ian Parsons and David Vaughan.

**SUNDAY, AUGUST 22 – Eva Valsami-Jones**

Phosphates and global sustainability

**AUGUST 23 – Rod Ewing**

“Back-end” of the nuclear fuel cycle: Role of mineralogy in the safe management of radioactive waste

**AUGUST 24 – Nigel Kelly**

Zircon – More than just a chronometer

**AUGUST 25 – Miháli Pósfai**

Biomineral attractions: Magnets in organisms

**AUGUST 26 – Nita Sahai**

Mechanisms of cellular and biomacromolecular interactions with minerals in humans and animals

**AUGUST 27 – Glenn Waychunas**

Mineralogy and geochemistry at lower dimensionality: Mineral–water interfaces and nanoparticles

**WELCOMING NEW ADVISORY BOARD MEMBERS**

At the end of 2009, the following advisory board members ended their three-year terms: Roberto Compagnoni, Tim Drever, Maggi Loubser, and Eric Oelkers. We acknowledge their contribution to the life of *Elements* and thank them. We welcome the following new members (current advisory board members are listed on the editorial page in every issue of *Elements*).

**Mauro Rosi** is a professor of volcanology at the University of Pisa, where he currently serves as director of the Department of Earth Sciences. He uses quantitative field studies of volcanic explosive deposits to elucidate past eruptive activity and analyze fundamental processes in volcanology. His research focuses on active volcanism, physical volcanology of eruptions, and volcanic hazards assessment. He has acted as an associate editor of the *Bulletin of Volcanology*. He has gained broad experience in the management of volcanic crises around the world and currently serves as a scientific advisor to the national Department of Civil Protection of Italy in volcanic crisis management.

**Barbara Sherwood Lollar**, F.R.S.C., is a Canada Research Chair professor at the University of Toronto and director of the Stable Isotope Laboratory. Her research interests include contaminant hydrogeology, the source and fate of CO₂ in sedimentary basins and natural carbon sequestration analog settings, and the biogeochemical cycling of carbon by deep subsurface microbial communities. She has been awarded the NGWA Darcy Distinguished Lectureship, the Canada Council Killam Fellowship, the E.W.R. Steacie Fellowship, and the NSERC Accelerator Award for research.

**Torsten W. Vennemann** received his BSc and BSc (Hons) degrees in geology and geochemistry, and his PhD degree (1989) on fluid–rock interactions during high-grade metamorphism from the University of Cape Town, South Africa. Thereafter, he worked at the University of Michigan, USA (until 1995), focusing on the development of analytical methods and applications of stable isotope geochemistry to ore deposits. At the University of Tübingen, Germany, he became interested in paleoclimate and paleoceanography. At the end of 2002, he was appointed full professor of geochemistry at the University of Lausanne.

**Bernard Wood** is a research professor in the Department of Earth Sciences, University of Oxford, UK. His research interests are in the application of high-pressure, high-temperature experiments to understanding the structure and evolution of the Earth. He has applied experiments to problems such as the thermodynamic properties of minerals, geobarometry and geothermometry, the nature of the seismic discontinuities in the mantle, and the factors controlling crystal–melt partitioning of trace elements. Currently his principal interest is the accretion and differentiation of the Earth. He has served as president of the VGP section of the American Geophysical Union and as president of the Mineralogical Society of Great Britain and Ireland.

**Jon Woodhead** completed his BA and DPhil studies at the University of Oxford before moving to Australia in 1988 to take up a postdoctoral research position at the Australian National University. In 1996 he moved to the University of Melbourne and has been a research fellow in the School of Earth Sciences since. His interests encompass the broad application of isotope and trace element geochemistry to problems in the Earth and environmental sciences, with emphasis on technique development and innovation in MC-ICPMS and laser ablation technologies. He is currently co-editor-in-chief of *GeoStandards and Geospatial Research*.

**David Vaughan, Hap McSween, Tim Drever, Susan Stipp,** and **Pierre Tremblay**
The Nobel Prize–winning atmospheric chemist Paul Crutzen suggested the term “Anthropocene” for the period we live in, because of the profound impact humanity has on the planet. The more we learn about human impacts, the more appropriate that designation seems. In fact, the Stratigraphy Commission of the Geological Society of London proposed that the Anthropocene be considered a true geological epoch—one that began at about the time of the industrial revolution and in which humanity has come to dominate Earth-surface geologic processes. An abbreviated list of the grounds for such a designation is disquieting:

- Humans have already transformed 40–50 percent of the ice-free land surface of the Earth.
- Humans now use 54 percent of the available fresh water on the globe.
- Humans are now an order of magnitude more important in moving sediment than the sum of all natural processes operating on the surface of the planet.
- Humans now fix more atmospheric nitrogen than all terrestrial sources combined.

Such impacts speak to the extent of our footprint on the planet. These and other planetary-scale changes are driving extensive modifications to the ecosystems that support life on Earth (see, for example, the reports of the Millennium Ecosystem Assessment, www.millenniumassessment.org/en/index.aspx). Understanding and mitigating humankind’s impacts on nature and their profound feedbacks to society are what Rittel and Webber called “wicked problems.” They are wicked because of their complexity—they always occur in a social context with a diversity of stakeholders. These wicked problems are coming our way. They transcend the scale and scope of any one scientific discipline. Characterizing and mitigating the impacts of planetary change or adapting to them goes beyond requiring input from many disciplines (multidisciplinary science), and even beyond interdisciplinary science (i.e. a cumulative approach that synthesizes the perspectives of the individual disciplines). These wicked problems also require integrated science, in which issues are framed in entirely new ways that transcend disciplinary boundaries.

Most of us who read this magazine have research careers focused on aspects of mineralogy and geochemistry. In other words, we are engaged in disciplinary research. Though a disciplinary effort may involve many scientists and the scope of the analysis may be broad, the research still employs the methods and theories of a single discipline. Over my 35-year career, as our understanding of the planet has grown, I’ve observed a dramatic increase in the number of subfields comprising Earth science. Of course, this process has not been limited to Earth science—a more general fragmentation of science has taken place. For most researchers, just keeping up with the literature in our own corner of the scientific world is a real challenge. A number of other forces are driving us towards specialization, including the disciplinary nature of academic departments that grant doctoral degrees and the way research recognition and funding are organized. We certainly realize that our scientific contributions represent important but minute pieces within the enormous mosaic of human knowledge. Our disciplinary focus as scientists can take us away from thinking about integrated Earth science. But sometimes, in viewing an impressionist painting, we need to step back to see the larger image. The reason is planetary change.

Now is a particularly important time to take in this larger perspective. Earth scientists, including those of us who work in disciplines lying outside the arena of environmental science, have a deep understanding of natural processes. Given our expertise, we have a special responsibility to contribute to the scientific and public understanding of environmental change. Jane Lubchenco considered the issue of responsibility of scientists to society in her presidential address to the American Association of Science. She stressed that because the needs of society are changing rapidly and dramatically, it may require a new social contract for science, one that takes into account the human domination of the planet. “The contract should be predicated upon the assumptions that scientists will address the most urgent needs of society in proportion to their importance.” She was certainly not advocating abandoning fundamental research. Indeed, she stressed that “new knowledge is urgently needed.” This new contract should (and will) become an increasingly important ingredient of the scientific enterprise.

As a practicing Earth scientist, if this idea of a new contract resonates with you but your research is not directly related to the planetary change issues, what should you do? There are many things, but one that perhaps has received less attention than others is our opportunity to take ownership of the importance of, and foster, integrated science. One of the first steps is simply by staying informed. Certainly, there is an abundance of literature on the natural and social science of planetary change. A real opportunity is to participate in broad-based Earth or general science meetings. At these meetings, the number of sessions focused on aspects of planetary change is increasing rapidly and they represent an outstanding educational opportunity. For example, over 50 sessions at the 2009 American Geophysical Union Fall Meeting were devoted to climate, and many others focused on other broad aspects of planetary change. One of these summarized climate impacts on the U.S. as reported in the 2009 report of the U.S. Global Change Research Program. It was held in a huge ballroom packed to overflowing. Judging from its program, the 2010 European Geosciences Union meeting will also present a rich set of opportunities for peering across disciplinary boundaries. And the Goldschmidt Conference programs, including the upcoming meeting in Knoxville, Tennessee, have a number of sessions relevant to the Anthropocene. Even with an understanding and appreciation of integrated science, facilitating its implementation is a challenge. Opportunities for funding research that crosses traditional discipline boundaries are increasing, but it still takes a reviewer who has a wide background and scope to react favorably to a proposal generated by an interdisciplinary scientific team, particularly one that may have contributions from social scientists. It’s my hope that as we further educate ourselves on the complexities of integrated science in the Anthropocene, we might be better equipped to judge such proposals. But a real key is how we guide students who are preparing for the future. We need scientists who are capable of working in the new integrated areas of environmental science. Encouraging students to take courses in other departments is a step in the right direction, but as several authors in a recent publication argue, “If it is to nurture interdisciplinary research, graduate education must be reshaped, not just tweaked around the edges.” The idea of reshaping graduate science education takes many of us out of our comfort zone, but such changes are coming and should be fostered.

E. O. Wilson, one of the United States’ leading scientists and environmental thinkers, called this the Century of the Environment. As Earth scientists, we have an opportunity, and perhaps even an obligation, to contribute to the fostering of integrated science in ways that benefit the planet.

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ON THE CUTTING EDGE WINS SPORE PRIZE

The On the Cutting Edge website (http://serc.carleton.edu/NAGTWorkshops/index.html) has been awarded the Science Prize for Online Resources in Education (SPORE) from Science. The prize honors the work of On the Cutting Edge principal investigators Heather Macdonald (College of William and Mary, Virginia), Dave Mogk (Montana State University, Montana), Barb Tewksbury (Hamilton College, New York), and Cathy Manduca (Carleton College, Minnesota); the contributions of hundreds of geoscience faculty to the site content; and the efforts of the Science Education Resource Center staff at Carleton College, Sean Fox, Karin Kirk, John McDaris, Carol Ormand, Monica Bruckner, and Ellen Iverson, in developing and evaluating the site.

SPORE was designed to honor and promote the originators of the best online materials available to science educators. The contest bears the acronym SPORE—meaning a reproductive element adapted to develop, often in inhospitable conditions, into something new—with the idea that these winning projects may be the seed for valuable progress, despite widespread challenges to educational innovation. This year, there were 12 winners from nearly 100 entries. An essay in the February 26 issue of Science outlines how On the Cutting Edge is transforming the culture of geoscience education by promoting the sharing of scientific content and teaching methods (www.sciencemag.org/cgi/content/short/327/5969/1095).

On the Cutting Edge was launched in 2002 and provides an important mechanism for geoscience faculty to learn from one another and from other experts in teaching and learning. In 2009, visitors numbered more than 700,000. They visited the site’s 3000 pages a total of 850,000 times. The site contains more than 1200 classroom activities contributed by the teaching community and includes step-by-step instructions for putting new techniques into place. The website also includes a wide variety of visual tools for use in the classroom, such as artistic renderings, visually represented data, and videos and models of Earth processes.

The On the Cutting Edge professional development project for geoscience faculty is sponsored by the National Association of Geoscience Teachers, is funded by the National Science Foundation Course, Curriculum and Laboratory Improvement Program, and contributes to the National Science Digital Library.

A Teaching Geochemistry workshop will be held in conjunction with the Goldschmidt Conference in Knoxville, Tennessee (http://serc.carleton.edu/NAGTWorkshops/geochemistry10/index.html), one of the many workshops held every year for geoscience faculty across the United States (http://serc.carleton.edu/NAGTWorkshops/workshops.html). David Mogk was guest editor of a thematic issue of Elements on the topic of teaching mineralogy, petrology, and geochemistry (volume 3, number 2, April 2007).

ENI PRIZE TO FRANÇOIS MOREL

François Morel was awarded the Eni Protection of the Environment Prize for his discovery of a new class of enzymes that play a crucial role in CO₂ transport and fixation. The finding is particularly important for understanding the biochemical mechanisms of CO₂ absorption into oceans, which is one of the key processes in global carbon recycling. François is the Albert G. Blanke, Jr., Professor of Geosciences at Princeton University.

The annual Eni prize was officially launched in July 2007 to encourage better use of energy sources, promote environmental research, and recognize new generations of researchers. The award demonstrates the critical importance that has been recently assigned by Eni to scientific research and to issues of sustainability. Eni is an integrated energy company headquartered in Italy. It is active in more than 70 countries, with 79,000 employees working in oil and gas, electricity generation and sales, petrochemicals, and oilfield services.

3M NATIONAL TEACHING FELLOWSHIP TO ALAN MORGAN

Alan V. Morgan, professor in the Department of Earth and Environmental Sciences at the University of Waterloo, Canada, since 1971, has received a 3M National Teaching Fellowship, considered Canada’s most prestigious award for excellence in teaching. The award is given by the Society for Teaching and Learning in Higher Education in partnership with 3M Canada. His research interests lie in Quaternary stratigraphy and climate change.

Alan Morgan has taught Earth 121, an introductory course at Waterloo, over nearly four decades. He has also energetically promoted public awareness of science, especially geology, outside the university. Morgan previously received Waterloo’s Distinguished Teacher Award in 1991; the Royal Society of Canada’s Bancroft Award in 1994 for promoting public awareness of science; the National Association of Geology Teachers John H. Moss Award for Excellence in Geology Teaching in 1995; and the Royal Society of Canada’s McNeil Medal in 2008, recognizing his outstanding ability to communicate science to students and the public.
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Moving science forward
Benjamin C. Gill is currently a postdoctoral fellow at Harvard University. He received a BSc and PhD in geological sciences from the University of Missouri and the University of California–Riverside, respectively. His research interests involve reconstructing past ocean chemistry and relating this to the history of life on Earth, particularly during the Cambrian and Jurassic periods. He utilizes several geochemical proxies and numerical modeling techniques to help constrain past cycles of biologically important elements, such as sulfur, carbon, and molybdenum.

David T. Johnston is an assistant professor of biogeochemistry at Harvard University. An isotope geochemist by training, David’s research now falls more in line with the emerging discipline of geobiology. Johnston uses isotopic techniques to bridge microbial ecology with Earth history and chemostatigraphy. His group is currently working on problems concerning Earth-surface evolution (on geological timescales), Neoproterozoic ecosystems and energy budgets, and cellular-level processing of sulfate and sulfide for metabolic energy gain.

Timothy W. Lyons, a professor of biogeochemistry at the University of California–Riverside, began cultivating his passion for anoxic marine environments during his doctoral research on the Black Sea. Exploration of the Cariaco Basin and other celebrities of oxygen deficiency followed, and soon Lyons was applying the lessons gained from his modern vantage point to major redox-dependent questions of the geologic past. Now, he and his research group split their time equally between the development of geochemical proxies in modern settings—including the sulfur isotope system and all flavors of Fe and Mo geochemistry—and the pursuit of answering big questions about the ancient ocean. Their favorite targets encompass the timing of atmospheric oxygenation, the persistence of deep-ocean anoxia, and the coevolution of seawater chemistry and life.

Penelope L. (Penny) King is a senior research scientist at the Institute of Meteoritics at the University of New Mexico. After graduating from the Australian National University, she received her PhD from Arizona State University for research in experimental petrology and microanalysis. She was on the faculty of the University of Western Ontario for seven years (where she is an adjunct research professor) before joining the University of New Mexico. Her current research focuses on the origin and evolution of planetary interiors and surfaces, and on the roles of volatiles, pH, volatile activities, and oxygen fugacity on minerals and melts at high and low temperatures. King has served on the councils of the Mineralogical Association of Canada and the Mineralogical Society of America (MSA), and was an MSA Distinguished Lecturer in 2005.

Charles W. Mandeville is a senior research scientist at the American Museum of Natural History in New York and conducts research in volcanology and geochemistry. His PhD research focused on the 1883 eruption of Krakatau. He utilizes stable isotope data (S, O, H), combined with infrared spectroscopic and petrologic data, to delineate the sources of magmatic volatiles, the extents and styles of degassing, and initial isotopic signatures. He currently conducts NSF-supported research on recycling of sulfur in subduction zone magmatism. He uses secondary ion mass spectrometry (SIMS) and X-ray absorption near edge structure spectroscopy (XANES) to measure sulfur isotope ratios and speciation in mafic melt inclusions from arc volcanoes and experimental glasses produced in high-temperature sulfur isotope fractionation experiments.

Scott M. McLennan is a professor of geochemistry in the Department of Geosciences at the State University of New York at Stony Brook. His current research deals primarily with surficial processes, sedimentary geochemistry, and crustal evolution on Mars. He uses a combination of laboratory experiments and geochemical/mineralogical data returned from the various orbital and landed missions. He is a participating scientist on the Mars Exploration Rover (MER) and Mars Odyssey Gamma Ray Spectrometer science teams.

Nicole Métrich is a senior scientist at the Laboratoire Pierre-Süé (Saclay, France). She is an associate researcher at the Istituto Nazionale di Geofisica e Vulcanologia (Pisa, Italy) and will soon join the Institut de Physique du Globe de Paris (France). Her major interest is the behavior of volatiles in magmas and degassing processes, which she studies using melt inclusions trapped during crystal growth. She was introduced to the world of melt inclusions working with R. Clocchiatti and A. Sobolev. Since then, she has concentrated her work on the role of water in magmatic processes and more broadly on the evolution of volatiles during magma decomposition, ascent, and eruption.

Clive Oppenheimer is a reader in volcanology and remote sensing at the University of Cambridge, and a research associate of “Le Studium” based at the Institut des Sciences de la Terre d’Orléans. His main research interests are how magma transport and degassing control eruptive style at active volcanoes; the atmospheric chemistry of volcanic plumes; the environmental, climatic, and human impacts of volcanism in antiquity; and development of environmental sensing techniques and applications. His favorite field location is Erebus volcano in Antarctica where he has carried out research as part of the US Antarctic Program since 2003.
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Sulfur is a widely distributed element on Earth and in the solar system. Its multiple valence states (S\(^2-\) to S\(^6+\)) allow it to participate in numerous geochemical and biochemical processes. It may be one of the light elements in the Earth's core and may have been crucial in core formation. Sulfur is an essential component in all life on Earth and likely supported earliest life. Sulfur geochemistry is used to understand the early evolution of Earth's atmosphere and hydrosphere, and serves as a monitor of volcanic \(\text{SO}_2\) and \(\text{H}_2\text{S}\) and as a tracer of anthropogenic sources of sulfur. Recent advances in the use of multiple sulfur isotopes (\(^{32}\text{S}, \, ^{33}\text{S}, \, ^{34}\text{S}, \, \text{and} \, ^{36}\text{S}\)) and in situ isotopic measurements will help to develop sulfur stable isotopes as a vital tracer in the Earth and planetary sciences and will provide applications for understanding inorganic and biogenic processes.

**Keywords:** sulfur, stable isotopes, fractionation, sulfides, sulfates, aerosol, tracer

**SOME BASIC FACTS ABOUT SULFUR**

The word “sulfur” is derived from the Sanskrit sulvere or the Latin sulphurium. Sulfur was known to the ancients, and in Genesis it was referred to as brimstone. Sulfur belongs to Group 16 (more traditionally Group VI), period 3, of the periodic table of the elements. The Group 16 elements, including oxygen, selenium, tellurium, and polonium, are referred to as chalcogens, from the Greek words chalcos (ore) and gen (formation). So the chalcogens, including sulfur, are ore formers. Sulfur’s classification as an element probably dates back to the late eighteenth century and the work of Antoine Lavoisier, though the Chinese knew in the ninth century that sulfur is a key element in the use of multiple sulfur isotopes (\(^{32}\text{S}, \, ^{33}\text{S}, \, ^{34}\text{S}, \, \text{and} \, ^{36}\text{S}\)) and in situ isotopic measurements will help to develop sulfur stable isotopes as a vital tracer in the Earth and planetary sciences and will provide applications for understanding inorganic and biogenic processes.

There are three allotropic forms of native sulfur: two are crystalline, while one is amorphous and commonly referred to as plastic sulfur. Sulfur crystals belong either to the orthorhombic or monoclinic crystal systems. They are constructed from \(\text{S}_6\) molecules that form puckered, eight-member rings of \(\text{S}\) atoms. In these rings, the \(\text{S}\) atoms are bonded to each other by single covalent bonds, and the \(\text{S}–\text{S}\) bond angle is approximately 105° (Mortimer 1977). The orthorhombic allotrope of native sulfur is rare in nature. Pertinent physical data for native sulfur are presented in Table 1. When sulfur is heated to 200°C and poured into cold water, a rubbery red-brown mass called plastic sulfur is produced. X-ray analysis of plastic sulfur indicates that it has a molecular structure characteristic of fibers formed from long chains of sulfur atoms. When plastic sulfur—a supercooled liquid—is left at room temperature, it slowly crystallizes and the \(\text{S}_6\) rings re-form. Sulfur is a poor conductor of thermal energy, so when you hold crystals of native sulfur near your ear, you can hear faint cracking noises.

Sulfur is everywhere. It occurs as sulfide minerals in the Earth’s mantle, as sulfide or sulfate minerals in crustal rocks, as native sulfur near active or dormant volcanoes, as dissolved sulfate or dimethyl sulfide in ocean water, and as a trace gas in the atmosphere. Sulfur is likely one of the light elements present in the Earth’s Fe–Ni core. It may have played a key role in the formation of the core because the melting temperatures of Fe–S mixtures are several hundred degrees below the melting temperatures of pure Fe or Fe–Ni alloys, thus facilitating the early differentiation of Earth into an Fe–Ni core and a largely silicate mantle and crust. In fact, sulfur is the sixth most abundant element in the whole Earth (~1.9%) by weight and is exceeded only by iron, oxygen, silicon, magnesium, and nickel. We also know, from the presence of sulfide minerals like troilite (FeS) in iron meteorites and of oldhamite [(Ca,Mg,Fe)S] and niningerite [(Mg,Fe,Mn)S] in enstatite chondrite and achondrite meteorites, that sulfur is present in some of the oldest materials in our solar system—materials that comprised the building blocks of the terrestrial planets (Mercury, Venus, Earth, and Mars). Going back in time even further, sulfur was formed by nucleosynthesis during explosive oxygen burning in the supernova phase of stellar evolution (Truran 1973; Clark 1979). \(^{33}\text{S}\), the most common isotope of sulfur (about 95% of total sulfur), has in its nucleus the equivalent of eight alpha particles or two \(^{16}\text{O}\) nuclei. We also know from the Voyager, Galileo, and New Horizons spacecraft missions that Jupiter’s moon Io has active, tidally driven volcanism that discharges...
Most of the sulfur produced worldwide is now recovered as a by-product from petroleum refineries that minimize \( \text{SO}_2 \) emissions and remove poisonous \( \text{H}_2\text{S} \) from natural gas supplies. In 2006, the United States was the world’s leading producer of elemental sulfur, supplying over 9.06 million metric tons (1 metric ton = 10^3 kilograms). Canada ranked second with 9.05 million metric tons. Other major producers of elemental sulfur, in descending order, include Russia, Saudi Arabia, United Arab Emirates, Japan, Kazakhstan, Iran, Germany, and Mexico (Ober 2003, 2007). Countries producing elemental sulfur as a metallurgical by-product, in order of decreasing production, are China, Japan, Canada, Chile, Australia, Korea, Mexico, United States, Russia, Germany, India, and Spain (Ober 2007).

The most important end use of recovered elemental sulfur is as a chemical reagent in the manufacture of sulfuric acid. As a raw material, it is important in all sectors of the world’s fertilizer and industrial manufacturing processes (Ober 2007). Approximately 50% of consumed sulfur in 2007 was used in the manufacture of phosphatic, nitrogenous, and sulfur fertilizers. The remaining 50% was distributed among a wide variety of industrial uses and processes, including the manufacture of pulp and paper products, inorganic pigments, paints and allied products, industrial organic chemicals, synthetic rubber and other plastic materials and synthetics, rubber and plastic products, cellulose fibers including rayon, water-treatment compounds, and steel pickling. Other uses include the processing of copper, zinc, lead, and molybdenum ore; the manufacture of soaps, detergents, pesticides, and leather goods; petroleum refining; and the manufacture of petroleum and coal products.

### SOURCES, USES, AND PRODUCERS

Anyone who’s been near the rim of an active or extinct volcano has probably come across native sulfur as veins or as encrustations formed either as a direct sublimation product or from the incomplete oxidation of \( \text{H}_2\text{S} \) (sour gas). Native sulfur can also be formed from sulfates by sulfur-reducing bacteria. Furthermore, it can be associated with sulfide minerals resulting from oxidation of the sulfides. Sulfur is often associated with anhydrite, gypsum, and calcite in the cap rocks of salt domes, for example, in Texas and Louisiana.

In the years prior to 1974, much of the production of sulfur in the United States came from the Gulf Coast region where sulfur was recovered from the tops of salt domes using the Frasch process. This method consists of injecting hot water into the sulfur-containing region in the subsurface, thus melting the sulfur in place; simultaneously air is injected, lifting the molten sulfur to the surface. This method of recovery accounted for approximately 75% of US production with the remaining 25% recovered as a by-product from smelters and petroleum refining. However, the Frasch process requires significant energy consumption, and the last processing plant in the United States ceased operation in 2000 (Ober 2003).

### Table 1: PROPERTIES OF SULFUR

<table>
<thead>
<tr>
<th>Property</th>
<th>Value</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sulfur</td>
<td>symbol S</td>
</tr>
<tr>
<td>Atomic number (Z)</td>
<td>16</td>
</tr>
<tr>
<td>Atomic weight</td>
<td>32.065</td>
</tr>
<tr>
<td>Melting point</td>
<td>112.8°C (orthorhombic)</td>
</tr>
<tr>
<td>Boiling point</td>
<td>444.674°C</td>
</tr>
<tr>
<td>Crystallography</td>
<td>orthorhombic, ( \text{2/m2/m2/m} )</td>
</tr>
<tr>
<td>Fracture</td>
<td>conchoidal to uneven</td>
</tr>
<tr>
<td>Hardness</td>
<td>1 ½ to 2 ½</td>
</tr>
<tr>
<td>Specific gravity</td>
<td>2.05–2.09</td>
</tr>
<tr>
<td>Luster</td>
<td>resinous</td>
</tr>
<tr>
<td>Color</td>
<td>yellow but varies with amount of impurities to yellowish shades of green, gray, and red; transparent to translucent</td>
</tr>
<tr>
<td>Diagnostic features</td>
<td>yellow color and burns easily</td>
</tr>
</tbody>
</table>

Data from Klein and Hurlbut (2002), De Laeter et al. (2003), and CRC Handbook of Chemistry and Physics (1978).
Sulfur’s role in the commodities markets is also significant because many of the world’s important industrial, strategic, and precious metals are found as sulfide ores, associated with sulfide ores, or as sulfosalts and sulfates (Table 2). Although metal recycling is increasingly used to recover high-purity metals in the developed world (as it should be), future worldwide demand for these metals will continue to grow, and exploration and extraction of naturally concentrated ores will be of prime importance in meeting that demand. Such ore deposits include hydrothermal deposits associated with active or extinct volcanoes and their ancient metamorphosed equivalents, evaporite deposits, and sediment-hosted deposits. For comprehensive descriptions of sulfide and sulfate mineralogy, see Vaughan (2006) and Alpers et al. (2000), respectively.

It is and will continue to be of paramount importance to explore more efficiently, extract sulfur-bearing ores with minimal impact on local ecosystems and water supplies, and ensure the application of adequate containment and acid-neutralization measures. In cases where past extraction processes have impacted the environment, it is necessary to base remediation measures on research-based studies that evaluate the reactivity of the minerals in question with the fluids that they are now in contact with and the likely reaction products.

### Table 2 Some Sulfides, Sulfosalts, and Sulfates

<table>
<thead>
<tr>
<th>Formula</th>
<th>Name</th>
<th>Use/Importance</th>
<th>Sources</th>
<th>Price/ton*</th>
</tr>
</thead>
<tbody>
<tr>
<td><strong>SULFIDES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>AgS</td>
<td>Acanthite</td>
<td>Important silver ore</td>
<td>Peru</td>
<td></td>
</tr>
<tr>
<td>Cu₂S₄</td>
<td>Chalcoste</td>
<td>Important copper ore</td>
<td>Chile</td>
<td>$5496⁺</td>
</tr>
<tr>
<td>Cu₃Fe₇S₈</td>
<td>Bornite</td>
<td>Copper ore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuFe₂S₄</td>
<td>Chalcopyrite</td>
<td>Important copper ore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>CuS</td>
<td>Covellite</td>
<td>Minor copper ore</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PbS</td>
<td>Galena</td>
<td>Lead and silver ore</td>
<td>China</td>
<td>$1774⁺</td>
</tr>
<tr>
<td>ZnS</td>
<td>Sphalerite</td>
<td>Most important zinc ore</td>
<td>China</td>
<td>$1669⁺</td>
</tr>
<tr>
<td>Fe₅S₄</td>
<td>Pyrrhotite</td>
<td>Mined in association with Ni, Cu, Pt</td>
<td></td>
<td></td>
</tr>
<tr>
<td>NiS</td>
<td>Millerite</td>
<td>Minor nickel ore</td>
<td></td>
<td>$16,845⁺</td>
</tr>
<tr>
<td>(Ni,Fe)S₄</td>
<td>Pentlandite</td>
<td>Principal nickel ore</td>
<td>Russia</td>
<td></td>
</tr>
<tr>
<td>HgS</td>
<td>Cinnabar</td>
<td>Important mercury ore</td>
<td>China</td>
<td>$15,789⁺</td>
</tr>
<tr>
<td>Sb₂S₃</td>
<td>Stibnite</td>
<td>Chief antimony ore</td>
<td>China</td>
<td>$5680⁺</td>
</tr>
<tr>
<td>FeS₂</td>
<td>Pyrite/marcasite</td>
<td>Mined for the Au and Cu often associated with it</td>
<td></td>
<td></td>
</tr>
<tr>
<td>MoS₂</td>
<td>Molybdenite</td>
<td>Principal molybdenum ore</td>
<td>China</td>
<td>$66,363⁺</td>
</tr>
<tr>
<td>Co₆S₇</td>
<td>Cobaltite</td>
<td>Cobalt ore</td>
<td>Congo</td>
<td>$80,800⁺</td>
</tr>
<tr>
<td>FeAs₂</td>
<td>Arsenopyrite</td>
<td>Principal source of arsenic</td>
<td>China</td>
<td>$1960⁺</td>
</tr>
<tr>
<td><strong>SULFOSALTS</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Ag₂S₅</td>
<td>Pyrrargyrite</td>
<td>Silver ore</td>
<td>Peru</td>
<td></td>
</tr>
<tr>
<td>Cu₃S₈</td>
<td>Tetrahedrite</td>
<td>Copper and silver ore</td>
<td>Chile</td>
<td></td>
</tr>
<tr>
<td><strong>SULFATES</strong></td>
<td></td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>BaSO₄</td>
<td>Barite</td>
<td>Density agent of drilling mud</td>
<td>China</td>
<td>$49⁺</td>
</tr>
<tr>
<td>CaSO₄·2H₂O</td>
<td>Gypsum</td>
<td>Plaster of Paris</td>
<td>China</td>
<td>$7.25⁺</td>
</tr>
<tr>
<td>Na₂SO₄</td>
<td>Thénardite</td>
<td>Powdered detergents</td>
<td>USA</td>
<td>$134⁺</td>
</tr>
</tbody>
</table>

Data from Klein and Hurlbut (2002)

* Prices from (a) USGS 2009 Mineral commodity summaries, 195 pp
  (b) London Metal Exchange

**SULFUR IN THE ATMOSPHERE AND OCEANS**

The amount of sulfur as SO₂ in the atmosphere depends on both natural and anthropogenic inputs. Natural inputs include volcanic SO₂ and H₂S, sulfate dust, sea sulfate, native sulfur, and organic sulfur compounds, the most important of which is dimethyl sulfide (DMS). DMS is formed in the oceans as a result of biological interactions among phytoplankton, microscopic algae, zooplankton, and bacteria. The phytoplankton and marine algae produce dimethylsulfiniopropionate (DMSP), which may have several vital functions. When phytoplankton and macroscopic algae are damaged because of zooplankton predation or viral attack, their DMSP is released into the upper ocean where it is degraded by phytoplankton and bacteria into DMS. DMS diffuses from the ocean water into the atmosphere where it is oxidized and converted into sulfate. Other reduced sulfur gases, such as H₂S, also are oxidized in the atmosphere. Sulfur is removed from the atmosphere through precipitation as rain or snow and as dry fallout in the form of sulfate. Anthropogenic emission of SO₂ is a result of fossil fuel combustion and ore smelting (Smith et al. 2004). Reaction of SO₂ with moisture in the atmosphere produces sulfuric acid aerosol, and the dissociation of this acid in water is the primary cause of acid rain in many industrialized regions (Doney et al. 2007). Nitrogen oxides, NOₓ, resulting from fossil fuel combustion also contribute to acid rain by reacting with moisture in the atmosphere to form nitric acid. Preventative measures that minimize acid rain include removing sulfur efficiently from fossil fuels, installing SO₂ scrubbers on industrial smokestacks, and equipping automobiles with catalytic converters to remove NOₓ emissions. With most sulfur now recovered as a by-product in petroleum and natural gas refining, global anthropogenic S emissions have decreased from a high of approximately 7.4 × 10¹⁵ g in 1980 to 6.2 × 10¹⁵ g in 2000 (Smith et al. 2004).

Sulfur derived from weathering of land-based sulfate and sulfate minerals dissolves in fresh water as sulfate ion. Sulfate concentration in fresh water ranges from less than 1 ppm to a few hundred ppm, and the global riverine flux to the oceans has been estimated at 10¹⁵ g of S per year. Sulfate is among the most abundant anionic complexes in seawater (second only to Cl⁻), with an average concentration of 2649 ppm and a total mass of 1.3 × 10¹⁳ g. Removal of sulfate from the oceans is largely through bacterial sulfate reduction to form sulfide, formation of organosulfur compounds, incorporation of trace amounts of sulfate into marine carbonate rocks, and generation of evaporite deposits (Bottrell and Newton 2006). Sulfur’s residence time in the oceans is approximately 10 million years.

**A MESSAGE IN THE FINGERPRINTS**

The abundances of the four naturally occurring stable isotopes of sulfur, ³²S, ³⁴S, ³³S, ³⁶S, are 95.04%, 4.20%, 0.75%, and 0.01%, respectively (De Laeter et al. 2003). In stable isotope studies, the ratio of the less abundant isotope (e.g. ³⁴S or ³³S) to the more abundant isotope (e.g. ³²S) in a sample is expressed in delta notation as the deviation in parts per thousand (per mil, ‰) relative to the same ratio in a reference standard; for example:

\[ \delta^{34}S = \frac{(^{34}S/^{32}S)_{\text{sample}}}{(^{34}S/^{32}S)_{\text{ref. std.}}} - 1 \times 1000 \text{‰} \]

In earlier studies of sulfur isotope ratios in terrestrial samples and meteorites, the reference standard was troilite (FeS) from the Canyon Diablo meteorite, whose ³⁴S/³²S ratio is 0.0450045. Samples with positive δ³⁴S have a higher ³⁴S/³²S ratio than the reference standard, while those with negative δ³⁴S have a lower ³⁴S/³²S ratio than the standard.
For Canyon Diablo (meteorite) FeS, $\delta^{34}S = 0\%o$, $\delta^{36}S = 0\%o$, and $\delta^{35}S = 0\%o$, by definition. The choice of Canyon Diablo meteoritic sulfur as a reference standard had to do with its homogeneity resulting from quenching from high temperature and the fact that its $34S/32S$ ratio lies at the midpoint of observed $35S$ values in terrestrial samples.

In their study of sulfur isotope ratios in a variety of meteorites, Hulston and Thode (1965) determined that the $33S/32S$, $34S/32S$, and $36S/32S$ ratios measured in some meteorites differed from Canyon Diablo troilite ratios, though even in samples with a deviation of a few per mil in $32S$, $33S$, and $36S$, there were always linear relationships between the various delta values. The reason for this will soon become obvious. In chemical and physical processes, the sulfur isotopes can become fractionated, resulting in one sulfur compound or species attaining a higher $32S/33S$ ratio than another sulfur compound or species also participating in the reaction or process. For instance, in the case of biological processes, sulfur is used by cells to produce amino acids and other sulfur-containing compounds. In this case, the sulfur isotope fractionation factor, $\alpha_{A,B}$, is by definition $R_A/R_B$, where $R_A$ is $34S/32S$ in compound A and $R_B$ is $34S/32S$ in compound B. In equilibrium chemical processes, $\alpha_{A,B}$ is proportional to $1/T^2$, where $T$ is temperature in Kelvin, and

$$1000 \ln \alpha_{A,B} = \delta^{34}S_A - \delta^{34}S_B.$$

Consequently, fractionations between sulfur-bearing species decrease with increasing temperature.

Theory also predicts that the fractionation of the isotopes $32S$, $33S$, and $34S$ with respect to $32S$ will be approximately proportional to the relative percent mass difference. For instance, $33S$ is 1 atomic mass unit (amu) higher in mass than $32S$, and $34S$ is 2 amu higher in mass than $32S$. Thus, the fractionation of $33S$ will be approximately 0.5 times the fractionation of $34S$. In the case of $36S$, whose mass exceeds that of $32S$ by 4 amu, the fractionation will be approximately 2 times the fractionation of $34S$. Hulston and Thode (1965) demonstrated this by plotting their $33S$ and $34S$ data versus $32S$ from several types of meteorites. They obtained the following relationships (within the limits of precision): $\delta^{33}S = 0.51 \delta^{32}S$, and $\delta^{36}S = 1.9 \delta^{34}S$. More recent data indicate that for equilibrium isotope exchange processes, $\delta^{32}S = 0.515 \delta^{34}S \pm$ a few percent, and $\delta^{36}S = 1.90 \delta^{34}S$ (Farquhar and Wing 2003; Ono 2008). In the case of irreversible kinetic processes that may involve a few intermediate steps (such as in biogenic processes), the relationship remains more widely, from $\delta^{35}S = 0.510 \delta^{34}S$ to $0.517 \delta^{34}S$ (Farquhar and Wing 2003; Johnston et al. 2005), and sufficient precision in $S$ isotope measurements is now possible for discrimination to the third decimal place (Farquhar and Wing 2003; Ono 2008). For most equilibrium processes on a time scale of the past 2 billion years, $\delta^{34}S = 0.515 \delta^{32}S$, and the fractionation of sulfur isotopes exhibits mass-dependent behavior as predicted by the relative differences in the masses of the isotopes.

Capital delta notation ($\Delta$) is used to express the deviation of a sample's $\delta^{34}S$ value from that predicted by the mass-dependent relationship listed above:

$$\Delta^{33}S = \delta^{33}S - 0.515 \delta^{34}S.$$

With similar reasoning, the deviation of a sample's $\delta^{36}S$ from that predicted by the mass-dependent relationship can be expressed as:

$$\Delta^{35}S = \delta^{35}S - 1.90 \delta^{34}S.$$

Samples that have nonzero values of $\Delta^{33}S$ and $\Delta^{36}S$ likely contain sulfur that was fractionated by either mass-independent or kinetic (nonequilibrium) processes (Farquhar and Wing 2003; Ono 2008). For example, nonzero $\Delta^{33}S$ values have been measured on Archean crustal and sedimentary rocks (Farquhar et al. 2000) and Archean (2.9 Ga) sulhide inclusions in diamonds (Farquhar et al. 2002). These arise from atmospheric photochemistry involving $SO_2$ and possibly $S_8$ in the early atmosphere, whose oxygen and ozone concentrations were significantly lower and UV transparency was higher than today. The sulfur isotope data of Farquhar et al. (2000, 2002) indicate recycling of surface sulfur as far back as 2.9 Ga.

Most sulfur isotope work over the past 50 years has been based on the most abundant isotopes, $32S$ and $34S$. However, the strength of the multiple sulfur isotope technique lies in its ability to discriminate mass-dependent fractionations, which likely arose from equilibrium processes, from those arising from kinetic (including biogenic processes) and mass-independent processes, such as photolysis reactions in Earth's early atmosphere and photooxidation in the present-day stratosphere. Particularly diagnostic are plots of $\Delta^{34}S$ versus $\Delta^{32}S$, $\Delta^{36}S$ versus $\Delta^{34}S$, and $\Delta^{38}S$ versus $\Delta^{36}S$ (Farquhar et al. 2000; Ono 2008), which allow discriminating of mass-independent and biogenic fractionation processes from equilibrium, mass-dependent processes. More importantly, through new laboratory experiments, it is now possible to determine both the effectiveness of a particular inorganic process (e.g. Farquhar and Wing 2003) and, in the case of biogeochemical fractionations, the identity of the S-utilizing species responsible for the fractionation (Johnston et al. 2005; Johnson 2010 this issue).

Other factors also control isotope fractionation in equilibrium processes. For example, speciation of sulfur in various S compounds controls the retention of $34S$ in the order $SO_2 > SO_3 > SO_4 > S^2- > H_2S > S^0$ (Ohmoto and Rye 1979). Where fluids are involved, pH and $O_2$ exert strong control on the magnitude of the fractionation because they control the types of $S$ species present.

**HOW LARGE IS THE BIOSPHERE IN THE OCEANIC CRUST?**

In the late 1970s, some of the first manned submersible dives to the hydrothermal vents in the Galápagos Rift (Corliss and Ballard 1977; Corliss et al. 1979) revealed a previously unknown world of organisms and ecosystems thriving in total darkness at 2.5 km water depth. The absence of light at such depths prevents primary production (the base of the food chain) by photosynthetic means, and low dissolved $O_2$ concentrations in deep ocean water precludes communities of organisms utilizing oxygen as an electron acceptor in their metabolic activity. We now know that primary production in this deep, dark world is provided by sulfide-oxidizing bacteria that oxidize $H_2S$ present in the vent fluids. This $H_2S$ originates from leaching of magmatic sulfide minerals contained in basaltic rocks by seawater heated to 350–400°C as it percolates deeper and deeper into the ocean crust. The seawater then becomes buoyant because of its higher temperature and rises towards the seafloor, where it is discharged as a plume known as a "black smoker." This sulfide-laden fluid often forms spectacular chimney-like structures, several to tens of meters high, made of Cu, Zn, and Fe sulfides (Kelley et al. 2002: Fig. 2). Sulfide-oxidizing bacteria are the base of the food chain for the larger organisms, such as tube worms, crabs, starfish, and shrimp. These fauna survive by feeding directly on the bacteria, or they may host them in specialized organs as symbionts. The sulfide-oxidizing bacteria in this case are chemotrophic life-forms because they derive their sustenance from the raw $H_2S$ of the vent fluids and take bicarbonate from the fluids to produce organic matter.
Another important group of chemautotrophic organisms that can thrive under the high-temperature, light-absent, low-oxygen conditions at seafloor hydrothermal-vent sites are methanogenic bacteria, or Archeabacteria, which may be some of the oldest life-forms on Earth. Methanogenic bacteria use H₂ and CO₂ as raw materials and generate methane gas as a by-product of their metabolic activity. H₂ is generated by the serpentinization of ultramafic rocks, and CO₂ may be dissolved in deep water or come from degassing magmas. Even more importantly, the methane they generate can be utilized by sulfate-reducing bacteria as a source of organic carbon in areas where organic carbon from sediments is unavailable.

New sulfur stable isotope results from secondary sulfide minerals in altered oceanic crustal rocks indicate the involvement of sulfate-reducing bacteria in sections of the ocean floor quite distant from active hydrothermal-vent sites and sources of organic carbon–rich sediments. Quite possibly, much of the off-axis microbial activity can be sustained by communities of chemautotrophic bacteria. The use of multiple sulfur isotopes to determine the role of biogenic activity in the alteration of the oceanic crust and to evaluate the extent of the deep-ocean crust biosphere will be of paramount importance, and we have only started looking.

A RECORD OF PAST VOLCANISM IN ICE SHEETS

A valuable record of Earth’s past explosive volcanic eruptions extending back several thousand years is preserved in the Antarctic and Greenland ice sheets. Studies of ice cores obtained from drilling into the ice caps have documented acidity layers formed by deposition of sulfuric acid (H₂SO₄) aerosol particles on snow that later was transformed into ice through compaction (Zdanowicz et al. 1999; Cole-Dai et al. 2000). Large explosive eruptions can inject SO₂ directly into the stratosphere, where it reacts with OH and H₂O and is converted into submicron-sized sulfuric acid aerosol particles. These can have a long residence time in the stratosphere (months to years following large eruptions) and are distributed globally (Zdanowicz et al. 1999; Robock 2000). Because of their small size, it takes a long time for the aerosol particles to settle out of the stratosphere. As they are long-wavelength radiation absorbers, they absorb some of the incoming solar radiation. This diminishes the amount reaching the troposphere (the lower 10–14 km of the atmosphere) and produces a global cooling effect. On the other hand, the aerosol particles cause heating in the stratosphere because they absorb incoming solar radiation as well as the longer-wavelength radiation radiated from the Earth to space. Volcanic aerosol particles also provide surfaces on which heterogeneous chemical reactions that destroy ozone can take place. Because they backscatter solar radiation, they also change the planetary albedo, or reflectivity of the upper atmosphere, thus reducing the solar radiation reaching the surface (Robock 2000). Less powerful eruptions with plumes confined to the troposphere can contribute to H₂SO₄ aerosol deposition, but the particles are not globally distributed because precipitation efficiently removes them after a period of 1–3 weeks. By studying ice cores from the Greenland and Antarctic ice caps, large volcanic eruptions that deposited H₂SO₄ globally can be discerned. It is of course necessary to discriminate volcanic sulfate from background sulfate and from other sulfur species. The latter include sea sulfate, which can be identified by its Na⁺ concentration (or Na/Cl ratio); dust, distinguished by its Ca concentration; and dimethyl sulfide (DMS) and its oxidation products, characterized by their sulfur isotope composition (Cole-Dai et al. 2000; Arimoto et al. 2001; Savarino et al. 2003). In most cases, sulfate records preserved in ice cores do not distinguish acidity layers that were deposited from stratospheric plumes from those deposited by tropospheric plumes; for example, a large high-latitude, southern-hemisphere eruption plume might result in only a small acidity spike in a Greenland ice sheet core, and a smaller, northern-hemisphere eruption plume of tropospheric height may locally record a large acidity signal. Recent use of multiple sulfur isotopes (Savarino et al. 2003) has shown new potential for discriminating between sulfate derived from stratospheric and tropospheric plumes. SO₂ injected directly into the stratosphere can undergo ultraviolet photooxidation, which produces a mass-independent sulfur isotope signature in Δ³³S and Δ³⁴S in the sulfate deposited from stratospheric plumes; on the other hand, no Δ³³S and Δ³⁴S anomalies are measured in H₂SO₄ arising from plumes confined to the troposphere. The reason for this is that the stratospheric ozone layer absorbs UV radiation of 248 nm wavelength and precludes photooxidation of SO₂ in the troposphere. The potential of multiple sulfur isotope analyses to discriminate stratosphere-penetrating eruptions from those affecting only the troposphere has been supported by laboratory experiments on photooxidation of SO₂ using UV radiation of 248 nm wavelength (Farquhar et al. 2001).

IN THIS ISSUE

In the articles that follow, the geochemistry of sulfur over a wide range of scales, environments, and time intervals is explored. Nicole Métrich and I describe the factors that control sulfur concentration and speciation in primitive and evolved magmas. We also show how new analytical and experimental techniques will allow us to more accurately assess the ultimate source of dissolved sulfur in magmas, the effects of degassing on isotope signatures, and the possible fate of sulfur gases exsolving from magmas during ascent (Métrich and ManDeville 2010). The measurement of volcanic gas emissions, in addition to seismic and deformational studies, has been an integral tool in monitoring volcanoes posing a hazard to human populations. Clive Oppenheimer highlights the importance of SO₂ and H₂S monitoring using state-of-the-art techniques and

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Figure 2 Photomosaic of the Mothra hydrothermal field located within the Endeavor Segment of the Juan de Fuca Ridge. This field contains clusters of sulfide chimneys billowing hydrothermal fluids. Some of these chimneys reach 24 meters in height. Photomosaic courtesy of J.R. Delaney, University of Washington; constructed by M. Ellen.
explains how we are refining our list of eruption precursors vital to eruption forecasting (Oppenheimer 2010). Tim Lyons and Ben Gill present the picture of Earth’s earliest sulfur cycling and coupled biospheric oxygenation, as recorded by pyrite and carbonate-associated sulfate. The latter reflects the sulfate concentration and isotopic composition of seawater sulfate, as well as the Great Oxygen Event affecting Earth’s atmosphere (Lyons and Gill 2010).

David Johnston highlights how sulfur is used in place of oxygen as the key oxidant in the anaerobic marine and subterranean biosphere, the large isotope fractionations that arise from metabolic activity, and sulfur’s role as an essential constituent in all life on Earth (Johnston 2010). Penny King and Scott McLennan bring us up to date on the distribution, forms, and probable origins of sulfur on Mars, from its core to its surface, and on the emerging picture of the hydrologic and sulfur cycles provided by the Mars Exploration Rovers (King and McLaren 2010).

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REFERENCES


Sulfur in Magmas

Sulfur is a ubiquitous element whose variable valence states (S²⁻, S⁰, S⁴⁺, S⁶⁺) allow it to participate in a wide variety of geochemical and biogeochemical processes. Depending on its redox state and controlling species, sulfur dissolved in magma may be fractionated into a water-rich phase and sulfur-bearing minerals. Retrieving information on the original sulfur abundance and isotopic signature of a magma is challenging and requires deciphering the different processes that may have operated during its evolution en route to the surface. Advances made in thermodynamic modeling, experimentation on sulfur solubility and diffusion in silicate melts, and microanalytical techniques for probing sulfur’s speciation and isotopic signature at the micrometer scale are providing an outstanding picture of sulfur evolution in magmas.

Keywords: sulfur, volatiles, magma degassing, stable isotopes, XANES, explosive eruption

INTRODUCTION

Sulfur is a minor element in magmas. Recycled by hydrothermal alteration of mid-ocean ridge basalts, sulfur fuels life in the ocean. Because immiscible sulfide liquid segregated from magma is able to mobilize transition metals and platinum-group elements, sulfur generates ore deposits. Anhydrite-bearing, hydrous, silicic magmas are also closely associated with porphyry-copper deposits (Luhr 2008). A large part of the sulfur released during explosive volcanic eruptions, as SO₂ and H₂S, forms sulfate aerosols, inducing atmospheric cooling that may persist for months, years, or even longer. Explosive eruptions of silicic magma (Wallace 2001) and large effusions of flood basalt (Self et al. 2008) have both had an impact on the atmosphere, even though the solubility of sulfur in the melt and the mechanism of its extraction during magma evolution and ascent strongly differ in these two types of magma.

The solubility of sulfur in silicate melts depends strongly on redox conditions and the resulting S oxidation state, which are key parameters in modeling volcanic degassing. Sulfur dissolves in silicate melt as two main species, sulfide (S²⁻) and sulfate (S⁴⁺) (Fincham and Richardson 1954). Oxidized and water-rich basaltic magmas, particularly in volcanic arcs, can carry a large quantity of sulfur (up to 1.5 wt%) dissolved as sulfate until very low pressure (Jugo et al. 2005). Conversely, in reduced basalts, sulfur saturation is controlled by an immiscible Fe–S–O liquid phase, and its concentration (0.22 wt%; Jugo et al. 2005) as S²⁻ depends strongly on the Fe content of the melt and temperature.

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isotopic evidence of this loss exists within erupted samples? (4) What is the ultimate source of the volatiles? Answering these questions through research is essential, because measurements of the flux of sulfur gas (SO\textsubscript{2} and H\textsubscript{2}S) at active volcanoes is a primary tool for eruption forecasting and monitoring (see Oppenheimer 2010 this issue).

The sulfur abundance in magmas and its evolution during magma ascent must be known in order to determine the degassing budget of sulfur during volcanic eruptions. However, probing sulfur in magma is challenging because more than 90% of the sulfur initially dissolved is released at the time of eruption (for example, lavas and volcanic products usually retain less than 100 ppm sulfur). The solubility of sulfur in silicate melts as a function of pressure, composition, and oxygen fugacity has been determined in high-pressure and high-temperature experiments. In parallel, studies of sulfur in crystal-hosted melt inclusions have constrained the initial sulfur abundance in magmas and helped understand how the abundance changes during ascent, degassing, and eruption. Tracking the abundance and source of sulfur in an erupted magma based on sulfur’s isotope signature is even more challenging because of isotope fractionation by sulfide and sulfate-bearing phases, possible exchange between the magma and its surroundings, and gas exsolution as the magma rises towards the surface. Here we highlight recent advances that have improved our knowledge of sulfur in magmas.

PROBING THE ELEMENTARY AND ISOTOPIC COMPOSITION OF SULFUR IN MAGMAS AND SILICATE GLASSES

Melt inclusions trapped during crystal growth are useful for determining the sulfur content of magmas. Indeed, sulfur concentrations as low as a few tens of ppm can be accurately determined in melt inclusions at the micrometer scale using an electron microprobe. However, probing sulfur speciation in silicate melt and glass, which is crucial to understanding the behavior and isotope fractionation of sulfur during magma ascent and degassing, is not easy. With recent developments in X-ray absorption spectroscopy, we can now get direct information on sulfur species in S-bearing minerals and silicate glasses at the micrometer scale and at low S concentrations (e.g. Fleet 2005). Examples of X-ray absorption spectra of experimental reduced and oxidized silicate glasses of variable compositions are illustrated in Figure 2. The spectra for Fe-free and Fe-bearing glasses, synthesized under reducing conditions, show an absorption edge peak at 2476.4 eV (Fig. 2a, b), typical of sulfur dissolved as sulfide (S\textsuperscript{2–}). The spectra are essentially identical despite significant compositional variability within each group of experimental samples. Based on these glass spectra, Métrich et al. (2009) proposed that S preferentially coordinates to Fe in the melt, presumably replacing O in the silicate framework, but does not form FeS- or Fe\textsubscript{2}S\textsubscript{3}– like species. The spectra of oxidized samples exhibit a well-defined peak at higher energy (2482.1 eV), characteristic of the SO\textsubscript{4}\textsuperscript{2–} group (Fig. 2c), a well-established feature. Thus, sulfur species dissolved as S\textsuperscript{2–} and S\textsuperscript{6+} in silicate glasses are now decipherable. A question that has emerged is whether the oxidation state of S in glasses at room temperature reflects the oxidation state of S at magmatic temperatures, because electron exchange reactions with Fe\textsuperscript{2+} and/or Fe\textsuperscript{3+} are possible. In situ probing of sulfur species at high temperature and pressure is not yet technically feasible. The S\textsuperscript{2–} and S\textsuperscript{6+} species are expected to coexist within a narrow range of oxygen fugacities (\textit{f}O\textsubscript{2}, near the Ni–NiO solid buffer), so the presence of small amounts of sulfate observed in natural, reduced basaltic glasses and glass inclusions is possibly explained by a rapid electron exchange reaction that occurred during cooling: S\textsuperscript{2–} + 8Fe\textsuperscript{3+} \rightleftharpoons S\textsuperscript{6+} + 8Fe\textsuperscript{2+}. This reaction is expected to proceed strongly to the right with decreasing temperature. However, the sulfur spectra of water-rich basaltic melt inclusions (i.e. Etna samples; Fig. 2d) suggest that nearly all S may be dissolved as sulfate, the most soluble species in oxidized magmas.

In addition to its multiple valence states, sulfur has four naturally occurring stable isotopes. These are, in order of decreasing abundance, \textsuperscript{34}S (95.04%), \textsuperscript{33}S (4.20%), \textsuperscript{32}S (0.75%), \textsuperscript{36}S (0.01%) (De Laeter et al. 2003). Most prior studies of sulfur isotopes in volcanic rocks and/or their enclosed mineral and glass components measured \textsuperscript{34}S/\textsuperscript{32}S, the ratio of the two most abundant isotopes, where the deviation of a sample’s \textsuperscript{34}S/\textsuperscript{32}S from a designated reference standard is reported in conventional delta (δ) notation in units of per mil (‰):

$$\delta^{34}S = \left[ \frac{\text{\textsuperscript{34}S_{\text{sample}}}}{\text{\textsuperscript{32}S_{\text{standard}}}} \right] - 1 \times 1000.$$
In earlier studies, the sulfur isotope reference standard was Canyon Diablo ( meteorite) Troilite (CDT), with an assigned $^{32}$S/$^{34}$S ratio of 22.220 (Ault and Jensen 1962; Jensen and Nakai 1962). Most earlier studies of sulfur isotope composition in volcanic rocks measured the $^{34}$S/$^{32}$S ratio of cryogenically purified SO$_2$ gas produced from bulk extraction techniques utilizing a couple of different protocols (e.g. Thode et al. 1961; Sasaki et al. 1979). However, subsequent studies of Canyon Diablo troilite based on analyses of SF$_2$ gas produced with laser fluorination extraction techniques revealed 0.4% heterogeneities within the troilite that far exceeded the analytical uncertainty of ±0.05‰ (Beaudoin et al. 1994). To improve upon consistency in reported sulfur isotope data, a new sulfur isotope reference standard, called Vienna Canyon Diablo Troilite (V-CDT), has been adopted worldwide (Coplen and Krouse 1998). Despite the high precision attainable by laser fluorination techniques for studies of sulfur in sulfides, this technique cannot be utilized for in situ extraction of sulfur from silicate glasses because fluorine reacts strongly with oxygen in the glass. Application of sulfur isotopes as a tracer in high-temperature magmatic processes requires the development of an in situ analytical technique with high spatial resolution (10 to 100 microns) for isotope measurements of silicate glass. For example, many newer, continuous-flow elemental analyzer (EA), gas chromatograph (GC), and isotope ratio mass spectrometer (IRMS) systems currently in use worldwide are not capable of completely extracting bulk sulfur from silicate glasses. Consequently, bulk extraction of sulfur from glasses for isotopic analysis had to rely on the Kiba reagent (concentrated phosphoric acid with tin(II)-chloride dihydrate as a catalyst) technique developed by Sasaki et al. (1979). This technique, however, requires several grams of sample (Mandeville et al. 2009), which precludes its application to the in situ analysis of melt inclusions and the glass component in small-scale, high-pressure, high-temperature fractionation experiments.

A promising new method utilizing secondary ion mass spectrometry (SIMS) has recently been developed for in situ microanalysis of $^{33}$S/$^{32}$S and $^{34}$S in silicate glasses (Mandeville et al. 2008). Earlier in situ SIMS measurements of sulfur isotopes were limited to condensed sulfur phases, such as sulfides and anhydrite, in igneous rocks and hydrothermal ore minerals (Eldridge et al. 1987; Chaussidon and Lorand 1990; McBibbon et al. 1996). Analyzing the sulfur concentration and isotope composition of silicate glasses requires measuring the secondary ion intensities of $^{32}$Si, $^{34}$S, and $^{32}$Si. Sulfur isotope studies conducted with earlier generations of secondary ion mass spectrometers lacked sufficient mass resolution to avoid interferences from $^{29}$SiH and $^{31}$PH, which interfere with $^{30}$Si and $^{32}$S in glass, respectively. Mandeville et al. (2008) demonstrated that by operating the ion microprobe at mass resolution power (MRP) of 5000, it is possible to avoid the above interferences and obtain in situ $^{34}$S measurements with a precision of ±0.4–0.6‰ from a 15 x 15 micron area in glasses containing 520–1630 ppm S. Additionally, matrix effects related to bulk composition or the oxidation state of sulfur are negligible. The advantages of extending $^{34}$S measurements down to the melt inclusion scale are that such inclusions are minimally to non-degassed and the temperature of crystallization of the host phenocrysts is sufficiently high that sulfur isotope fractionations between sulfur species dissolved in the melt ± vapor are small in magnitude. The equilibrium fractionation factor, $\alpha_{\text{A-B}}$, between two phases (A and B) can be expressed, in the case of the two most abundant isotopes of sulfur, as $\alpha_{\text{A-B}} = (^{34}\text{S}/^{32}\text{S})_{A}/(^{34}\text{S}/^{32}\text{S})_{B}$.

The natural log of $\alpha_{\text{A-B}}$ is proportional to 1/T$^2$, where T is temperature (Faure 1986). Measuring $^{34}$S in melt inclusions using the new SIMS analytical technique places important constraints on the initial $^{34}$S/$^{32}$S ratio (and $^{34}$S) of primitive magmas. Equally important, we can now analyze the products generated in sulfur isotope fractionation experiments conducted at high temperature and pressure under controlled $f$O$_2$ conditions utilizing real silicate melts saturated with one or more sulfur phases (e.g. anhydrite and pyrrhotite). Determining the ultimate source of dissolved sulfur in magmas requires constraints on the following: initial sulfur isotope composition, pressure, temperature, $f$O$_2$, and speciation of dissolved sulfur in the melt. We must also be able to quantify the amount of sulfur lost in the gas phase, assess whether sulfur loss from the
melt was under closed-system (i.e. exsolved sulfur remains in equilibrium with the melt) or open-system (i.e. exsolved sulfur is immediately removed from the melt + vapor system) conditions, and determine the magnitudes of fractionations occurring between all relevant sulfur species (e.g. $\text{SO}_4^2-, \text{SO}_2, \text{H}_2\text{S}, \text{S}^2-\)).

Results from fractionation experiments will allow us to more accurately evaluate open-system versus closed-system behavior of magmas stored in the crust because we will be able to generate $\delta^{34}\text{S}$ data from melt inclusions that best constrain the initial isotopic composition and $S$ concentration and fill the current data gap between extensively degassed samples collected at the surface and samples measured by conventional bulk extraction techniques. In particular, it is important to measure the $\delta^{34}\text{S}/32\text{S}$ ratio of matrix glass in these erupted samples because this is the one magmatic component that degasses on the timescale of an eruption (Mandeville et al. 2009). Finally, sulfur isotope data from melt inclusions and matrix glasses could also be reconciled with those of high-temperature gas emissions, allowing us to constrain the amount of sulfur lost prior to and during eruption and the magnitude of $S$ isotope fractionation between gas and melt. Through better constraints on initial $\delta^{34}\text{S}$, new high-temperature experimental constraints on sulfur isotope fractionations at magmatic temperatures, and refinement of sulfur speciation data in the melt and vapor phases, we will be able to identify the most likely source of dissolved sulfur in magmas and develop a more complete understanding of volatile degassing.

**SULFUR BEHAVIOR AND EVOLUTION DURING MAGMA ASCENT**

Sulfur plays a central role in the monitoring of active volcanoes because remote sensing tools measuring the $\text{SO}_2$ flux have been developed (see Oppenheimer 2010). These routine measurements have provided important insights into the magma-degassing process. Modeling the composition of gas released at surface requires a robust thermodynamic treatment and good estimates of the pressure-related behavior of sulfur and other volatile components. Crystal-hosted melt inclusions are useful, particularly when they are representative of the magmatic system, for constraining these values. As an example, Spilliaert et al. (2006) studied volatiles ($\text{CO}_2, \text{H}_2\text{O}, S, \text{Cl}$) in olivine-hosted melt inclusions and concluded that sulfur was exsolved into the vapor phase at high pressure (~140 MPa) during the closed-system ascent of basaltic magma erupted during the 2001 and 2002 flank eruptions of Mt. Etna. Such a process could be common in volcanoes producing oxidized, water-rich basaltic magmas in which sulfur is dominantly dissolved as sulfate. In contrast, $S$ is inferred to degas at low pressure from sulfide-saturated basaltic magma emplaced on the seafloor (i.e. MORB). Sulfur and water contents were found to decrease simultaneously during closed-system ascent of Etna basaltic magma, whereas Cl remained dissolved in the melt up to very shallow depths. Following this line of reasoning, Burton et al. (2007) interpreted high $S/\text{Cl}$ ratios (up to 4.7 molar) in gas emissions at Stromboli volcano as indicating a deep derivation, possibly from the volcano-crust interface, for gas bubble pockets (slugs) driving Strombolian explosions.

However, changes in the redox conditions, melt composition, and temperature of slowly ascending magmas, linked with processes of crystallization, degassing, or magma mingling/mixing, may provoke a drastic change in sulfur solubility. The low solubility of sulfur in silicic melts erupted during explosive eruptions leads to the question of the ultimate source of sulfur. This problem has been widely discussed (for example, concerning the 1991 eruption of Mt. Pinatubo, Philippines), in particular the role of underplating basaltic magma and recharge episodes on the sulfur budget (Wallace 2001). Di Muro et al. (2008) proposed a rather complex mechanism of sulfur transfer during recharge events at Mt. Pinatubo, during which sulfide-saturated, mafic magma intruded and mingled with resident, water-rich, oxidized dacitic magma. They suggest that hydrous flushing and subsequent cooling and oxidation of the basaltic andesite magma resulted in (1) the partial breakdown of the primary sulfide phase (Ni-bearing pyrrhotite), (2) the release of sulfur into the gas phase ($\text{H}_2\text{O}–\text{Cl}–\text{S}$), and (3) the formation of low-temperature Cu-sulfides. In this interpretation, Cu-rich sulfide globules are related to the fluxing of the injected mafic magma batches by hydrous, Cu-bearing fluids coexisting with the dacitic magma. Ultimately, sulfur released by Cu-sulfide breakdown during magma ascent contributed to the $S$ degassing budget. This study provides a detailed picture of the drastic effects of magma oxidation on sulfur speciation, melt $S$ concentration, and mineral stability (Fig. 3).
Assessing the source of magmatic volatiles through isotope characterization requires careful evaluation of potential modifications to the initial isotopic signature that could occur as a result of degassing. Therefore, isotope fractionation between relevant species must be evaluated at the temperature, pressure, and $f_{O_2}$ conditions that control the speciation of sulfur in the melt and gas phases. Crucial to this evaluation is determining whether gas loss from the magma took place under closed-system or open-system conditions. This is important, because under closed-system conditions at the temperature of most magmas, the magnitude of isotopic shifts accompanying complete (100%) degassing will be limited to a few ppm because of the buffering capacity of the exsolved vapor to limit further changes to the isotopic composition of the melt. In contrast, open-system gas loss from magma, even at a temperature of 885–975°C, can produce significant shifts in initial isotopic composition, particularly in oxidized arc magmas (Mandeville et al. 2009).

Scaillet et al. (1998) gathered experimental data on sulfur partitioning between dacitic to rhyolitic melts and fluid at temperatures, pressures, and $f_{O_2}$ spanning the ranges observed in most arc magmas. Their data indicate that the S concentration of the fluid in equilibrium with the melt will be 1 (at low $f_{O_2}$) to 1564 (at high $f_{O_2}$) times greater than that of the melt. These experiments demonstrate the strong partitioning of sulfur into the exsolved fluid phase in evolved, oxidized melts, which are common in convergent-margin settings. These authors also conducted experiments at conditions relevant to rhyodacitic magma erupted during the large explosive eruption of Mt. Mazama. The experimental conditions were $T = 899°C$, $P = 225$ MPa, and $f_{O_2} = +1.2$ log units above the Ni–NiO buffer, and the partition coefficient of sulfur between the fluid and the melt was 72. Measurements of the Kx X-ray wavelength for sulfur in melt inclusions from this eruption using an electron microprobe indicated that 80% of dissolved sulfur in the rhyodacitic magma was present as $SO_3$ (Mandeville et al. 2009).

Oxidized compounds of sulfur have a greater tendency to retain $^{34}S$ in equilibrium processes, in the order $SO_3 > SO_2 > S^2$ (Ohimoto and Rye 1979). The predominance of $SO_3$ species in dissolved sulfur in Mt. Mazama magmas suggested an enrichment of $^{34}S$ in the sulfur remaining in the melt after removal of some $SO_2$ and $H_2S$ during degassing. Most importantly, calculation of the equilibrium fractionation factor between gas and melt, $\epsilon_{gas-melt}$, for conditions relevant to degassing of Mazama magma yielded values of 0.996 to 0.998 and predicted a change in $^{34}S$ of residual sulfur in the melt of +2 to +4‰ with complete (100%) degassing under closed-system conditions, with an initial $^{34}S$ of the magma reservoir near that of the most primitive pyrrhotite $^{34}S$ values of 0.6 to 0.8‰.

Mandeville et al. (2009) obtained new sulfur stable isotope data on a suite of rhyodacitic pumice, vitrophyre, whole-rock, and glass separate samples spanning the stratigraphy of the climactic eruption and the preclimactic Cleetwood eruption at Mt. Mazama. The pumice and vitrophyre samples had $^{34}S$ values ranging from 2.4 to 18.2‰, far exceeding the range predicted by closed-system degassing (Fig. 4). The elevated $^{34}S$ values of Mazama whole-rock and corresponding matrix-glass samples could have been achieved only through open-system degassing. In addition, the elevated $^{34}S$ values of >9‰ cannot be attributed to contamination from local groundwaters, as these have $^{34}S$ values of 8 to 9‰ and S concentrations of 2 ppm. Ion microprobe analyses of pyrrhotite in Mazama rhyodacitic samples exhibit a range of $^{34}S$ values, from near 0‰ to 5.8‰ (Mandeville et al. 2009). This range in pyrrhotite $^{34}S$ indicates that open-system degassing took place in the Mazama magma chamber. This conclusion is in agreement with melt-inclusion data, which span a wide range in sulfur concentrations, from 80 to 330 ppm, and indicate that up to 50% of initial dissolved sulfur may have been lost through pre eruptive degassing of the magma + vapor system. Many melt inclusions with ~80 ppm S still retain >4.0 wt% H$_2$O, indicating S loss at depths of 4–5 km. Magma bodies can undergo volatile exsolution events associated with decompression and buoyant rise in the crust, heating from recharge magmas, and crystallization of volatile-poor minerals. Stresses induced by overpressurization of the magma chamber may lead to tensile failure of the surrounding wall rock, resulting in loss of gas-charged melt collected at the roof. Though the volume of gas-charged melt lost may be only a few tenths of a percent to a few percent of the initial volume, the number of events might be large during the hundreds to thousands of years of magma storage in the crust. The sulfur isotope data from the climactic and Cleetwood eruptions of Mt. Mazama illustrate the significant changes (12 to 16‰) to the initial isotopic composition (which was most likely equal to 0 ± 1‰, i.e. the value for mantle sulfur) that are possible when sulfur is degassed from oxidized arc magmas under open-system conditions and prolonged storage in the shallow

**Figure 4** $^{34}S$ values for rhyodacitic whole-rock and matrix glass separates from the climactic and preclimactic Cleetwood eruptions at Mt. Mazama versus the fraction of S remaining (F). The graphs are based on a maximum sulfur concentration of 330 ppm, as measured in rhyodacitic melt inclusions. The solid curves show $^{34}S$ evolution in the magma under open-system conditions, for $\epsilon_{gas-melt}$ values of 0.998, 0.996, and 0.995. The straight dashed lines illustrate $^{34}S$ evolution during closed-system degassing for the same $\epsilon_{gas-melt}$ values. The initial $^{34}S$ for rhyodacitic magma is constrained by the $^{34}S$ of the most primitive pyrrhotite grains (Po) in pyrrhotite from the climactic eruption, as measured using SIMS. These Mt. Mazama data illustrate the large changes in initial S isotope composition that result from open-system degassing of uncontaminated, oxidized arc magma. PCRD = post-caldera rhyodacitic dome whole-rock sample; WWT = Wineglass Welded Tuff. DATA FROM MANDEVILLE ET AL. (2009)
crust. One implication of the S isotope results from Mt. Mazama is that more mantle sulfur may have degassed at this arc volcano (and possibly others) than previously thought, due to the mistaken belief that elevated δ34S values indicate slab-derived or crustal sources of sulfur.

**CONCLUSIONS**

We are now better able to quantify dissolved sulfur species in silicate glasses by utilizing the micro-XANES technique, and we can carry out sulfur isotope measurements in silicate glasses at the 10–100-micron scale. These new capabilities are necessary for studying melt inclusions as well as the glass component in new isotope-fractionation experiments. They will lead to significant improvements in modeling sulfur degassing in magmas. New experiments on sulfur isotope fractionations between the various sulfur species will give us a better understanding of the ultimate source of sulfur dissolved in magmas and the recycling of sulfur among Earth’s major reservoirs.

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Ultraviolet Sensing of Volcanic Sulfur Emissions

Clive Oppenheimer*

While other volcanic gas species are more abundant than sulfur, it is the measurement of sulfur dioxide emissions that has played the key geochemical role in volcano monitoring for decades. Recently, this sphere of volcano surveillance has undergone a revolution: the instruments suitable for the task have become cheaper, more compact, less power hungry, and more capable than their predecessors. It is now possible to measure multiple gas species simultaneously, at high time resolution, and even to image volcanic clouds remotely. This technological explosion is leading to the installation of a global network of volcanic-emission sensors. This network will underpin the geochemical surveillance and hazard assessment at volcano observatories worldwide and will yield new insights into the degassing and eruptive style of volcanoes and the impact of volcanic clouds on the atmosphere.

**WHY SULFUR?**

Gas emissions from volcanoes are sourced from deep within magmatic plumbing systems and their associated hydrothermal systems (Fig. 1). Their vigour and chemical and isotopic composition can thereby reveal much about subterranean processes, especially concerning the chemistry, storage and transport of magmas and the relationships between degassing and eruptive style. The importance of gas emissions was recognized by early pioneers of volcanology, including Frank Perret, who, in the early 1900s, bubbled fumarolic gases into bottles of alkaline solution to trap the acidic species for subsequent analysis. The kind of field apparatus employed by Perret remains in use today, a century later. Of course, since then, analytical capabilities have developed enormously, and this manner of direct observation continues to yield the most detailed analyses of the chemical and isotopic composition of volcanic gas emissions. However, such sampling is challenging for sustained geochemical surveillance, especially when fumaroles are inaccessible except to the most daring and agile breed of volcanologist. The motivation for applying remote sensing techniques to volcanic gas measurements is readily appreciated by anyone who has blanched at the sight, or even the thought, of colleagues rappelling into active craters.

What is striking in reviewing the history of remote sensing applied to volcanic emission measurements is the prominence of observations of sulfur dioxide (SO₂). Considering that the most abundant volcanic vapours are water and carbon dioxide and that sulfur species (including hydrogen sulfide) typically account for less than 5% or so of the cocktail of gases emitted, it is not obvious why sulfur has been such a focus of study. The reason has much to do with pragmatism. Water and carbon dioxide are both abundant in air, and the comparatively small enhancements in abundances of these molecules in volcanic plumes can be difficult to detect against the background. This is especially true of genuinely remote methods, where the volcanic cloud is sensed against the sky such that ‘column amounts’ of gases are measured rather than their mixing ratios.

Imagine sensing across 1 km of open atmosphere, whose background carbon dioxide abundance is 390 parts per million (ppm), in which a volcanic plume 100 m across is drifting. Downwind of the emission source, after the volcanic emissions have mixed well into the air, the enhanced carbon dioxide abundance in the plume might bring the total to around 395 ppm. A simple calculation shows that the ‘column amount’ of carbon dioxide (i.e. the product of the path length and the abundance) increases by only 0.13% when the plume is present. It would be very challenging to resolve such a small difference given atmospheric and instrumental variability. The goal becomes even more challenging if the plume is to be measured against the whole sky (i.e. a path greatly exceeding 1 km). In contrast, the abundance of SO₂ in the atmosphere is generally very low – hundreds of thousands of times less than carbon dioxide; thus it is much easier to detect SO₂ in a plume from a volcano (or industrial smokestack, for that matter). Fortunately, SO₂ is a very informative constituent of volcanic emissions, and in the next section we explore how it is measured by means of ultraviolet remote sensing.

**THE HERITAGE OF VOLCANIC SO₂ SENSING: ‘COSPEC’**

Sulfur dioxide absorbs electromagnetic radiation in several wave-bands: in the microwave region due to rotations of the molecule; in the infrared due to vibrations and distortions of the S–O bonds; and in the ultraviolet as a result of electrons jumping between orbits. The key to recording these spectral fingerprints of the molecule is to obtain a geometry that places the volcanic cloud between the sensor (spectrometer) and the source of radiation (Box 1). For this reason, ultraviolet sensing has proved particularly valuable...
for SO₂-emission measurements because, by day, there is an abundant source of natural ultraviolet radiation – the sky. The light source, of course, is the Sun, but the sky acts as a diffuser thanks to Rayleigh scattering in the atmosphere. Thus, one typical problem with optical spectroscopy is avoided – the need to align precisely the spectrometer with a light source. All that is necessary is to collimate some of this sky light through a telescope and direct it into the spectrometer. The flux of SO₂ can be measured by recording all the SO₂ molecules that pass through a vertical section of the whole plume. In practice, the plume may be traversed, roughly perpendicularly to the wind direction and looking up from the ground, or scanned from a fixed position. Thanks to the diffuse sky ultraviolet source, the pointing direction of the telescope is not critical.

The first remote instrument to become widely used for volcanic-plume monitoring was the Barringer Research ‘COSPEC’, or Correlation Spectrometer. The instrument was even featured in the 1997 volcano disaster movie Dante’s Peak, in which the volcanologists deployed it from a helicopter to survey the sulfur emission from the restive, fictional volcano (the part was played admirably by Mt. St. Helens). The COSPEC was introduced four decades ago to measure industrial sulfur dioxide and nitrogen dioxide sources, but its value for measuring volcanic emissions was quickly recognized (Stoiber et al. 1983). Early volcanological interest addressed the question of whether changes in SO₂ flux could be associated with magma migration and eruptive style. For instance, Malinconico (1979) reported a positive correlation between increasing SO₂ flux and eruptive vigour at Mt. Etna. Of particular note, COSPEC played a vital role in civil emergency planning during the unrest of Mt. Pinatubo in 1991. As seismic unrest increased two weeks before the magmatic denouement, so did the SO₂ flux, confirming shallow intrusion of magma. This interpretation prompted the civil evacuation credited with saving tens of thousands of lives (Daag et al. 1996).

COSPEC measurements have also been influential in recognizing the importance of magma convection, permeability and gas separation in volcanic conduits. And, as COSPEC observations were made at more and more volcanoes around the world, the compiled data provided another very important result for our understanding of the effects of volcanoes on the atmosphere, namely the first estimate of the global emission of volcanic SO₂ (about 20 Tg yr⁻¹; Stoiber et al. 1987).

**‘DOAS’ AND THE ERA OF PLUG-AND-PLAY SPECTROSCOPY**

A drawback of the COSPEC was its ‘black box’ nature and the fact that it did not actually record the ultraviolet spectrum. Its design was very much engineering oriented, in that the goal was to build a system capable of minimizing all ‘noise’ (such as arises from other atmospheric absorptions) in order to measure a single species (e.g. SO₂). The result was an instrument that yields an estimate of the column amount of SO₂ in the field of view. While this greatly simplifies data retrieval and processing, it makes it difficult to assess potential errors that arise from wavelength shifts, scattering and solar-elevation effects, thermal and mechanical distortions, and so on. Also, the COSPEC response depends on the correlation mask used and the abundance of gases present. An alternative approach is to measure wide-band spectra with sufficient spectral resolution to be able to model trace-gas abundances.

The most common approach to recording a spectrum in the ultraviolet region is to use a diffraction grating to disperse the light received by an optical telescope coupled to the spectrometer. Spectra are nowadays typically collected using a CCD detector array onto which the dispersed light is focused. Analysis of the spectra and determination of trace-gas abundances is routinely practised using a methodology known as differential optical absorption spectroscopy, or DOAS. For the most recent exposition on this approach, see the definitive and eponymous book by Platt and Stutz (2008). A key trick of DOAS is the discrimination of fluctuations in the recorded spectrum that are not due to gas absorptions. These fluctuations arise, for example, from molecular and aerosol scattering in the atmosphere. Because their spectral dependence is of lower frequency than that associated with the electronic structure of absorbing molecules, appropriate signal processing yields absorption spectra that may then be modelled. Another trick widely used in DOAS practice is to obtain atmospheric spectra with and without the emissions of interest present. In the case of volcanic emissions, this can be achieved simply by collecting ‘background’ or ‘clear sky’ spectra from either side of the plume.

All the plume spectra are then divided by the out-of-plume background spectrum. This reduces interferences caused by background atmospheric absorption and the solar spectral structure (Fraunhofer lines). Following the Beer-Lambert law (see Box), the logarithm of the resulting spectrum is computed, and then SO₂ (and other gas) amounts can be calculated by scaling reference spectra of the gases of interest (freely available thanks to meticulous laboratory experiments) until they match the observed spectrum. The scaling factors thus identified, along with the known abundances for the laboratory reference spectra, determine the gas column amounts in the plume.

The first volcanological DOAS observations were made in 1992 from a scientific vessel cruising the Mediterranean – more specifically, downwind of the steaming craters of Etna, Stromboli and Vulcano (Edner et al. 1994). A rather bulky ultraviolet spectrometer was employed, and it was operated alongside a COSPEC and a laser system (so large it was housed in a truck manoeuvred onto the ship) that was also capable of SO₂ measurements. At that time, COSPEC represented the state of the art for remote
geochemical surveillance of volcanoes, and its pre-eminence was not challenged by the expensive and more operationally complex DOAS and laser-based systems. But this picture changed in what can, perhaps, be viewed as a revolution in volcano remote sensing that took place early in the 2000s. This came about thanks to the commercial availability of a new kind of ultraviolet spectrometer, vastly cheaper, smaller and less power hungry than anything else on the market and operating with USB, plug-and-play simplicity. The death knell of the COSPEC, which had served volcanology so admirably for three decades, was sounded.

The first volcanological measurements with this new generation of spectrometer were made at Masaya (Nicaragua) in 2001 as part of a European-funded project (‘MULTIMO’, http://earth.leeds.ac.uk/Multimo), reported by Galle et al. (2003). Several competing spectrometers are now available, and there has been tremendous innovation in the application of the new technology as volcanologists have been quick to seize on the potential of such cheap, adaptable and capable devices.

One of the first tasks required was to confirm good agreement between DOAS-based estimates of SO$_2$ emissions and those obtained by COSPEC. This was particularly important for volcano observatories switching to the new technology (Elias et al. 2006). The next development was the more imaginative deployment of the miniature ultraviolet spectrometers. Observational platforms for traverse-style measurements have included pedestrians (Mc Gonigle et al. 2002; Mori et al. 2006), ultralight aircraft (Guttridge et al. 2008) and even a remote-controlled helicopter (Mc Gonigle et al. 2008).

**MORE GASES, MORE VOLCANOES**

In contrast with the COSPEC, wide-band ultraviolet spectrometry enables the detection and quantification of multiple gas species (see Box). Hydrogen sulfide is a gas of some chemical and hydrothermal interest that can be measured in the ultraviolet region. Its measurement alongside that of SO$_2$ is instructive since the proportion of the two species is influenced by several factors, including the degree of interaction between magmatic and hydrothermal fluids, the oxidizing capacity of the degassing magma and the depth at which gas is effectively extracted from the magma. Some of these processes can be appreciated from the redox equilibrium that exists between the two species:

$$\text{SO}_2 + 3\text{H}_2\text{S} = 2\text{H}_2\text{O} + \text{H}_2\text{S}$$

More reducing conditions and lower temperatures will shift the equilibrium to the right (higher H$_2$S/ SO$_2$), while decompression (through magma/gas ascent) will shift the equilibrium to the left in favour of SO$_2$ (readily appreciated from the stoichiometry of the equation and consideration of the ideal gas law).

Another important process, especially in hydrothermal environments, is the disproportionation reaction:

$$\text{SO}_2 + 2\text{H}_2\text{S} = 1.5\text{S}_2 + 2\text{H}_2\text{O}$$

Unfortunately, while there is an ultraviolet spectrum for hydrogen sulfide, it is of short wavelength (below 250 nm) and in the so-called ‘solar-blind’ region, where there is effectively no sunlight reaching the Earth’s surface (due primarily to absorption by stratospheric ozone). This means it cannot be measured in the same way as SO$_2$ can (above 300 nm). However, it is possible to measure both SO$_2$ and H$_2$S simultaneously using compact spectrometers but with an ultraviolet lamp, as demonstrated by O’Dwyer et al. (2003) at the fumarole fields of Vulcano and Solfatara.

Although not directly pertinent to this review of sulfur gas monitoring, it is nevertheless worth mentioning that several other volcanogenic gas species can be measured by ultraviolet spectroscopy using scattered sunlight as a light source. Of particular significance was the detection of bromine monoxide (BrO) in the plume emitted by Soufrière Hills Volcano (Montserrat) (Bobrowski et al. 2003). This finding opened up an entire field of enquiry into the generation and atmospheric impact of reactive halogens in volcanic plumes. A further halogen species, chlorine dioxide (OCIO) has been identified more recently (Bobrowski et al. 2007), confirming chemical schemes outlined for the generation of reactive halogens by heterogeneous chemical processes in the atmosphere (Oppenheimer et al. 2006). A further reactive trace gas, nitrogen dioxide, was detected (along with SO$_2$) in the plume emitted by Erebus volcano (Antarctica); the NO$_2$ was thought to form via thermal fixation of atmospheric nitrogen at the surface of the volcano’s incandescent lava lake (Oppenheimer et al. 2005). Where both reactive bromine and nitrogen species are present, further chemical interaction is likely.

Thanks in part to the mobility and operability of the new generation of compact spectrometers, there have been many new measurements of SO$_2$ emissions from seldom-monitored volcanoes. These observations are leading to arc-scale compilations of SO$_2$ flux data, e.g. for Papua New Guinea (Mc Gonigle et al. 2004), Hokkaido (Mori et al. 2006) and Central America (Mather et al. 2006). Elsewhere, new measurements have revealed that some volcanoes emit vast quantities of SO$_2$, of the order of 200 kg s$^{-1}$, including Nyiragongo (Sawyer et al. 2008), Anatahan (Hilton et al. 2007) and Ambrym (Bani et al. 2009). Such amounts challenge our (possibly low) estimates for global volcanic sulfur degassing. As the inventory improves, we shall gain a deeper understanding of the atmospheric and climatic implications of the spatial and temporal distribution of emissions by sustained degassing, which will complement the knowledge we have of the global change induced by individual sulfur-rich explosive eruptions, such as at Mount Pinatubo in 1991.

**RAPID, ROUTINE AND RELIABLE OBSERVATIONS**

The sustained surveillance carried out by volcano observatories demands a high degree of automation of monitoring systems. This saves the time, cost and expense of manned fieldwork, enables networks of sensors to be developed, protects staff from prolonged exposure in hazardous areas, and permits more time to be spent on data analysis, synthesis and interpretation. The low power requirements and cost of the new generation of ultraviolet spectrometers have spurred development of autonomous SO$_2$ monitoring stations. However, to measure SO$_2$ degassing rates, fixed installations must mimic the traverse method of flux estimation by scanning the sky sequentially in a plane that intersects the plume. This can be readily achieved by rotating the field of view of the spectrometer around the sky by use of a stepper motor to which a plane mirror is attached. Combined with a telemetry system and powered by solar energy, such a station may operate autonomously and transmit spectra back to the volcano observatory. The first scanner development applied to volcanic-plume measurements was reported by McGonigle et al. (2002). This was a portable system designed for rapid, campaign installation, but it was soon superseded by Montserrat Volcano Observatory’s autonomous ultraviolet DOAS stations (Edmonds et al. 2003). Subsequently, scanner networks were installed at Tungurahua volcano, Ecuador.
(Arellano et al. 2008), Stromboli (Burton et al. 2009) and Etna (Salerno et al. 2009). Two European projects (DORSIVA and NOVAC; www.novac-project.eu/) have taken this concept even further through the development of a scanning system that has now been installed at seventeen volcanoes around the world.

One complication in obtaining a flux measurement with a scanning instrument is that uncertainty in the plume height corresponds directly to uncertainty in the flux estimation. Since the measurements are made radially within a plane that intersects the plume, the measurement from a single instrument cannot discriminate between a high, wide plume and a low, narrow plume (with correspondingly lower SO$_2$ flux), even if the two have identical SO$_2$ mixing ratios and thicknesses. Thus, plume height must be determined accurately if the scanner is to yield a reliable measurement of flux. This can be achieved through simple scaling between wind speed and plume height, through more sophisticated dispersion modelling, or, ideally, from the observations themselves. Arguably the most robust procedure is the tomographic reconstruction of the plume’s SO$_2$ cross section (Fig. 2), recently demonstrated by Wright et al. (2008).

A further important benefit of scanning systems is their capability for rapid measurements of flux. In practice, plume scans may be made within a few minutes, providing a high time resolution. This can reveal rapid variability in source emissions, which might, for instance, relate to fluctuating magma flow to the surface. When two-dimensional CCD detectors are used (one dimension representing the spectral information), it is possible to build an image with a scanning system, yielding valuable information on gas distribution within a plume (e.g. Louban et al. 2009). But even higher time resolution is possible with UV cameras (the use of which, however, entails sacrificing much spectral information) since an entire plume can be captured in a single frame, obviating the need for the more time-consuming scanning procedure (Fig. 3; Mori and Burton 2006; Bluth et al. 2007).

A variation on this approach is the use of telescopes with distorted optical fields of view. Boichu et al. (2010) designed a device with two spectrometers attached to telescopes with cylindrical lenses, whose ‘footprints’ projected onto the plume were equivalent to two long thin strips. The two fields of view were parallel but offset by a small angle, achieved with a goniometer. The instrument was trained on the base of the plume rising from Erebus volcano on a still day. The advantage of the system is that the stretched field of view ‘sees’ all the SO$_2$ rising out of the crater simultaneously (without recourse to scanning). Further, the angular offset between the two telescopes permits calculation of the plume speed by correlating the time series of SO$_2$ obtained from the two spectrometers. (The two records are offset by a small lag time corresponding to the passage of puffs of plume between the two fields of view, whose vertical separation projected to the plume is known from the goniometer reading and the distance between the spectrometer and the plume.) This approach can provide SO$_2$ flux measurements every second and could, in principle, provide a real-time SO$_2$ flux meter. At Erebus volcano, it revealed a cyclic degassing that is probably related to the fluid dynamics of bubbly magma in the shallow conduit feeding the volcano’s lava lake.

Reliable measurements are the cornerstone of volcano monitoring and are vital if hazard evaluation is to be meaningful and effective. These new spectroscopic approaches, which provide good constraints on plume speed and height, are essential for obtaining accurate, high-time-resolution, SO$_2$ flux measurements. Work remains to be done to establish the extent to which atmospheric radiative transfer effects (such as multiple scattering in dense plumes and in-scattering of light in front of plumes when observed from long distances) affect measurements (Kern et al. 2010), but undoubtedly, SO$_2$ observations will increasingly contribute to routine observatory work and, more generally, to a deeper understanding of magma degassing and volcano behaviour.

**SUMMARY**

Since 2001, when the first measurements were made with compact UV spectrometers at Masaya volcano, there has been rapid technological and methodological innovation in the application of UV sensing to volcanology. Some of the key results are:

1. The capability to make very high-time-resolution measurements (suited to studies of dynamic degassing phenomena related to magma flow instability, volcanic conduit geometry and gas segregation, and explosive degassing);
Box 1 BACKGROUND TO UV SPECTROSCOPY AND SULFUR DIOXIDE FLUX MEASUREMENTS

The sensing methods described here are based on the spectroscopic observation of molecular species of interest from their distinctive rotational, vibrational and electronic transitions, seen in absorption (i.e. the attenuation of a source of radiation crossing the gas cloud). Specific gases can be identified by their characteristic absorption spectra, and their abundances can be derived from the strength of the absorption, following the Beer-Lambert formula:

\[ I(\lambda) = I_0(\lambda) \exp[-\sigma(\lambda)NL], \]  

where \( I(\lambda) \) is the observed intensity of radiation at wavelength \( \lambda \); \( I_0(\lambda) \) is the original intensity of radiation, before interaction with the sample; \( \sigma(\lambda) \) is the absorption cross section of the absorbing molecule at wavelength \( \lambda \); and \( N \) is the mean mixing ratio of the species over the path length \( L \) of the sample. Measurements of more than one species provide gas ratios, in an analogous manner to direct sampling; traverses or scans of volcanic clouds, combined with plume transport speeds, can be used to derive fluxes of gases.

In the ultraviolet region of the spectrum, which is concerned with electronic transitions in atoms and molecules, the light source may be natural (diffuse sky radiation or direct solar radiation) or artificial (often a deuterium or xenon lamp). ‘Passive’ measurements that use natural ultraviolet light are invariably based on ‘open-path’ observing geometries through the free atmosphere. Active measurements may be ‘open-path’ or ‘closed-path’; in the latter, the gas sample is admitted to a cell of known path length, through which the beam is passed. Multi-path cells of modest dimensions (e.g. <1 m) can simulate substantial atmospheric paths (e.g. >100 m) via multiple internal reflection.

For quantitative applications, it is usually necessary to separate out the spectral features of the volcanic gas species of interest from other signals, which may arise from absorptions by air molecules and scattering of light in the atmosphere. This can be achieved by modelling the total atmospheric path (e.g. using a radiative transfer code, atmospheric and meteorological data, and known absorption coefficients for all relevant species), or from the ratio of spectral observations acquired for the same path with and without the volcanic plume present \( (I_0, I_{0,0}) \) respectively. The latter approach is generally referred to as differential optical absorption spectroscopy, or DOAS (Platt and Stutz 2008). From inspection of equation (1), it can be seen that the column amount of a given species [i.e. the product of mixing ratio \( (N) \) and path length \( (L) \)] can be obtained if \( \sigma(\lambda) \) is known (Fig. 4).

Volcanic sulfur dioxide fluxes are most readily obtained by transporting a zenith-viewing ultraviolet spectrometer beneath the plume, approximately perpendicular to its transport axis (the instrument is usually carried in a road vehicle, boat or aircraft), and recording sulfur dioxide abundance as a function of position (recorded with a GPS receiver). The product of the plume’s drift speed and the sulfur dioxide amount integrated across the plume yields the sulfur dioxide flux (typically expressed in kg s\(^{-1}\); Galle et al. 2003). When other measurement geometries are used, for instance using scanners that view multiple (non-vertical) axes through the plume from a fixed location on the ground, retrieval of the sulfur dioxide flux is somewhat more complex and potentially ambiguous if the plume height is not well constrained (Wright et al. 2008).

2. The provision of more accurate \( \text{SO}_2 \) flux estimates, thanks to more robust spectroscopy (arising from better constrained spectral evaluations, including fitting for scattering effects in the atmosphere, absorption by other atmospheric species, and so on) and direct measurements of plume speed (rather than reliance on infrequent, distant meteorological measurements and/or poorly constrained modelling of air flow around complex topography).

3. In parallel with (2), more robust estimates of measurement uncertainty through modelling of error propagation.

4. The measurement of other gas species along with \( \text{SO}_2 \), including \( \text{H}_2\text{S}, \text{NO}_2, \text{BrO} \) and \( \text{OCIO} \). The identification of the reactive halogens has, in particular, led to a new appreciation of the potential for volcanic degassing to perturb the ozone abundance and oxidizing capacity of the troposphere on at least local spatial scales around degassing volcanoes.

Future developments in software and hardware will include improved telemetry systems; proliferation of unmanned aerial vehicle technology; detailed intercomparison and integration of spaceborne and ground-based ultraviolet observations of plumes; deployment of distributed sensor networks; and improved techniques for signal processing of multiple geochemical, geophysical and geodetic data streams. Thus, the next decade promises major advances in our understanding of volcanoes and the evaluation of their hazards through the application of geochemical surveillance.

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Ancient Sulfur Cycling and Oxygenation of the Early Biosphere

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The amount of sulfate in the early ocean was tied directly to oxygen levels in the atmosphere and the deep ocean. These concentrations and other environmentally diagnostic biogeochemical pathways of the sulfur cycle can be expressed through isotope fractionation between sulfate and pyrite. The balance between rising oxygen and sulfate concentrations and varying hydrothermal iron inputs led to a pattern of iron, oxygen, and sulfide domination that varied in time and space in the early deep ocean and was more complex than previously recognized. Through all this change, no element played a bigger role than sulfur as a recorder of early oxygenation of the biosphere and the coevolution of life.

Keywords: sulfur, biogeochemistry, isotopes, early ocean, oxygen

BACKGROUND

Coupled C–S Cycling and Implications for Atmospheric Oxygen

The formation of sedimentary pyrite (FeS$_2$), the principal sink for reduced sulfur in marine systems, begins with the activity of prokaryotic microorganisms (Bacteria and Archaea) that reduce sulfate (SO$_4^{2-}$) while oxidizing organic substrates and, less commonly, hydrogen. Sulfate reduction requires biological mediation, except at temperatures much higher than those typical of most surficial marine settings (thermochemical reduction prevails at temperatures above 100°C). This anaerobic pathway of organic degradation dominates in modern oxygen-free marine sediments and water columns, as in the deep Black Sea. Because sulfate is so abundant in modern seawater—its 28 mM concentration ranks second only to chloride’s among the anions—sulfate reduction takes a back seat only to aerobic respiration in terms of the quantity of organic matter remineralized (recycled) in the modern ocean.

The hydrogen sulfide (H$_2$S) formed as a waste product during sulfate reduction is highly reactive with iron oxides delivered to the ocean by rivers principally as coatings on detrital sedimentary grains. Reaction of H$_2$S with these oxides and other iron phases yields pyrite (Fig. 1) by way of metastable iron “monosulfide” precursors with stoichiometries closer to FeS. Because the organic matter oxidized during sulfate reduction comes mostly from oxygen-producing photosynthesis, the net result of pyrite formation and its subsequent burial is an increase in atmospheric oxygen. These multiple steps of sedimentary pyrite formation and the consequent impact on O$_2$ levels can be simplified in a net reaction:

$$2\text{Fe}_2\text{O}_3 + 16\text{Ca}^{2+} + 16\text{HCO}_3^- + 8\text{SO}_4^{2-} \rightarrow 4\text{FeS}_2 + 16\text{CaCO}_3 + 8\text{H}_2\text{O} + 15\text{SO}_2.$$ 

Similarly, burial of organic matter equates to net photosynthesis, with a corresponding gain in atmospheric O$_2$. This burial and, to a lesser degree, that of pyrite account for essentially all the oxygen released to the atmosphere. Together with O$_2$-consuming oxidation of pyrite and organic matter, these processes modulate concentrations of atmospheric O$_2$ on geologic timescales. [Pathways of anoxygenic primary production during the Precambrian via iron and H$_2$S oxidation in the photic zone may have tempered these effects (Johnston et al. 2009).]

Isotopic Fingerprints

Given that the O$_2$ content of the atmosphere reflects the net burial versus oxidation of pyrite and organic matter on geologic timescales, the question becomes how to deduce this balance over millions to billions of years of Earth history through proxies captured and preserved in the rock record. It is our good fortune that sulfate-reducing prokaryotes and O$_2$-producing photosynthesis by diverse CO$_2$-fixing (photoautotrophic) organisms favor the light isotopes of sulfur ($^{32}$S) and carbon ($^{12}$C), respectively, relative to their heavier cousins ($^{34}$S and $^{13}$C). The simple explanation is that the S–O and C–O bonds of $^{32}$S and $^{12}$C are more easily broken during heterotrophic sulfate reduction and autotrophic oxygenic photosynthesis.

The extent of isotopic discrimination, or fractionation, is large during these processes, which is true for light stable isotope systems in general (e.g. hydrogen in the extreme case), since the relative mass differences among the isotopes are far greater than those of heavier elements (e.g. iron and molybdenum). Typical isotopic signatures of photosynthesis are seen in product organic matter. These light-isotope enrichments are expressed as $^{13}$C/$^{12}$C ratios that are on average 25 parts per thousand (‰) depleted in the heavy isotope relative to the parent CO$_2$. Similarly, experiments yield H$_2$S during sulfate reduction that can be up to 45‰ depleted in $^{34}$S relative to the sulfate. Sulfur fractionations seen in nature are often much larger, commonly ranging up to 1.5 times the maximum known from experiments. The roughly 60‰ offset seen between H$_2$S and SO$_4^{2-}$ in the water column of the Black Sea is a good example.

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The apparent discrepancy between natural and experimental systems is a subject of vigorous debate and ongoing research; for example, it is possible that the extent of fractionation in the laboratory, under the right experimental conditions, could be greater than that now observed. Other models have suggested that single-step sulfate reduction alone is not enough to explain the large fractions seen in nature. Such models require additional S cycling by disproportionating prokaryotes that convert intermediate sulfur species, such as elemental sulfur and thiosulfate, into H$_2$S and SO$_2$$^-$$^-$ (Johnston 2010 this issue). With this recycling comes added isotope discrimination, further depleting the H$_2$S in $^{34}$S and more than adequately explaining the apparent disparity between laboratory results and nature (Canfield and Thamdrup 1994). Another school of thought asserts instead that single-step fractionations in nature by sulfate-reducing prokaryotic microbes can exceed those now known from the lab. Regardless, disproportionation pathways are unquestionably an important part of the sulfur cycle. They have also factored prominently in interpretations of the Precambrian isotope record and will resurface in discussions below.

Most relevant to our focus here, and independent of these mechanistic details, is that microbial cycling of S results in H$_2$S and subsequently pyrite that are typically $^{34}$S depleted, and the burial of this pyrite leaves the ocean enriched in $^{34}$S (by ~21 parts per thousand in modern seawater, although this enrichment has varied through geologic time). From these relationships, we can surmise that secular trends in the C and S isotope compositions of CO$_2$ and SO$_2$$^-$$^-$ in seawater track the balance between the burial of pyrite and organic matter beneath the ocean and their oxidative recycling on land. When marine sediments are exposed on the continents, the isotope effects of burial can be offset by the return of dissolved CO$_2$ and SO$_2$$^-$$^-$-produced, with little isotopic fractionation, during weathering of organic matter and pyrite. These isotopic systemsatics must be coupled, for reasons outlined above, to the varying O$_2$ content of the atmosphere. If we can extract the changing isotopic compositions of carbon and sulfur dissolved in the ocean, we should be able to estimate varying atmospheric O$_2$ levels using straightforward numerical models tied to the burial/weathering mass balances of pyrite and organic matter. Such models are well established and now buttress our understanding of the evolving O$_2$ content of the atmosphere, particularly in the Phanerozoic where isotope data are comparatively continuous across the last 500+ million years (Berner 2006). Past studies have most often relied on data extracted from sulfate-containing evaporites (gypsum and anhydrite) and, for carbon, well-preserved calcitic fossils (brachiopods in particular) or bulk fine-grained lithologies, when fossils are sparse or absent.

**THE EARLY HISTORY OF SULFUR CYCLING**

**Before the Great Oxidation Event**

Connections linking the amount of sulfate in ancient seawater, its S isotope ratio, and the amount of O$_2$ in the atmosphere did not escape the vigilant eyes of Precambrian workers decades ago (Schidlowski 1979). Sulfate in the ocean is supplied mostly by the weathering of pyrite and other sulfide minerals on the continents beneath an O$_2$-containing atmosphere. Given this connection between sulfate and O$_2$, we might expect the diagnostic sulfur fingerprints of sulfate reduction and their relationship to sulfate concentration to be expressed in the geologic record at the transition from an O$_2$-poor to an O$_2$-containing atmosphere. Not surprisingly, the first clear, persistent record of large sulfur isotope fractionation is seen in pyrite deposited 2.3 to 2.4 billion years ago, roughly coincident with independent signals marking the first great transition in biospheric oxygenation (the so-called “Great Oxidation Event,” or GOE) (Fig. 2).

Among the independent fingerprints of atmospheric oxygenation are the disappearance of the reduced detrital minerals (pyrite, siderite, and uraninite) from ancient fluvial sediments and the first evidence for oxidation in ancient soil horizons (as reviewed in Canfield 2005 and Swerjensky and Lee 2010). But the true “smoking gun” for this fundamental shift from dominantly reducing to oxidizing Earth-surface conditions is another sulfur story, now well known: the disappearance of mass-independent fractionation (MIF) of sulfur isotopes in sulfate- and sulfide-bearing minerals about 2.4 billion years ago. The loss of these MIF signals points convincingly to the first accumulation of free O$_2$ in the atmosphere beyond the minute, trace levels of the earlier atmosphere (Farquhar and Wing 2003). Oxygen contents never again dropped low enough to yield MIF in the rock record, although dramatic post-GOE dips in atmospheric oxygen have been proposed (Canfield 2005; Frei et al. 2009). Theoretical constraints on the magnitude of oxygenation required for the loss of MIF demand only a small increase in O$_2$ to values still much less than 1% of present atmospheric levels. The rise was likely higher. Yet despite what may have still been a relatively small O$_2$ increase, many proxies point similarly to a fundamental shift in Earth-surface oxidation at the GOE.

One explanation for an assumed lack of mass-dependent sulfur isotope fractionation in rocks deposited before the GOE (Fig. 2) is that bacterial sulfate reduction had not yet evolved because of the near-absence of sulfate in early seawater. Another idea, now more widely held, is that sulfate reduction is much older, dating back to the earliest well-preserved sedimentary rocks in Western Australia.
latter hypothesis is based on appreciable isotope offsets between co-occurring, 3.5-billion-year-old pyrite and barite (BaSO₄; Shen et al. 2001). If sulfate reduction was indeed such an ancient pathway, we are forced to explain why the isotopic fingerprint of a metabolism that evolved so long ago is otherwise expressed infrequently in rocks that predate the GOE. One possibility is that the arguments for active sulfate reduction 3.5 billion years ago are wrong. To some, for example, the data from 3.5-billion-year-old rocks reflect abiotic thermochemical processes.

If, however, you accept the arguments for the early onset of bacterial sulfate reduction, you are left with a fairly straightforward view of the pre-GOE (Archean) ocean: the predominance of small sulfur isotope fractionations in sedimentary pyrite must reflect very low levels of sulfate in an ocean beneath an oxygen-lean atmosphere. For this claim to stand, there must be a tight relationship between the magnitude of fractionation and the amount of sulfate in the ocean. In fact, experimental calibrations show this to be the case at very low sulfate concentrations and place the threshold at less than 1% of today’s level, below which fractionations are negligible (Habicht et al. 2002). Whether this value from a few laboratory cultures provides the precise limits for the early ocean is hard to know, but the basic story of very low Archean sulfate concentrations is certain to remain intact apart from any future refinements. Consistent with low concentrations of sulfate, abundant banded iron formations (BIFs) suggest an anoxic ocean dominated by iron rather than sulfur (Fig. 3), although emerging evidence is indicating very early episodes of euxinia as well (e.g. 2.5 billion years ago; Reinhard et al. 2009). Euxinic waters are O₂-free (anoxic) or (3) anoxic and H₂S-containing (euxinic) (Canfield 2005; Scott et al. 2008). The BIF gap in this interval argues against persistently ferruginous (Fe²⁺-containing) anoxic waters, and, truth be told, the limited available data point to the presence of euxinia (Scott et al. 2008) long before the emergence of the “Canfield Ocean” (Canfield 1998) later in the Proterozoic. This earlier euxinia could reflect an increased flux of sulfate to an ocean still lacking oxygen in the deep waters, given higher but still relatively low O₂ in the atmosphere. The interval between ~2.2 and 2.0 billion years ago contains the largest positive carbon isotope excursion in Earth history (the so-called Lomagundi event). Any relationship between the implied high levels of organic-carbon burial and increased O₂ in the atmosphere might have favored either oxic deep waters or greater sulfate delivery to still O₂-lean conditions at depth (Fig. 4), yielding euxinia. BIFs reappear in a big way between ~2.0 and 1.8 billion years ago, recording, perhaps, reinvigorated hydrothermal inputs of iron to the ocean from submarine volcanism. Another possibility, assuming the deep ocean and atmosphere were previously oxygenated, is a return to very low oxygen levels (Canfield 2005), with decreased sulfate delivery to the ocean (Frei et al. 2009).

By ~1.8 billion years ago, the BIF-favoring conditions were gone, with iron solubility waning in the ocean through enhanced deep-water oxygenation (Holland 2006), decreasing iron inputs, or increasingly prevalent deep euxinia as a result of greater sulfate delivery (Canfield 1998; Poulton et al. 2004; Frei et al. 2009; reviewed in Lyons et al. 2009a, b). Both oxic and euxinic conditions promote low iron solubility. The atmosphere had long since stopped favoring the mass-independent S isotope behavior of the Archean, but O₂ remained a very long way from the ~20% levels present today. The possibility of euxinia for more than a billion years of Proterozoic history (Canfield 1998)
and the predicted biological implications (e.g., Anbar and Knoll 2002) are hot topics in current Precambrian research (Fig. 3) (as reviewed by Lyons et al. 2009a, b).

One thing is clear: although sulfate delivery to the ocean increased across the GOE, the evidence points to still low concentrations in seawater throughout most of the Proterozoic (Fig. 4). We can imagine that comparatively low levels of oxygen in the atmosphere might have limited oxidative weathering. However, it is unlikely that the breakdown of pyrite was particularly sensitive to atmospheric $O_2$ concentrations greater than the threshold levels already exceeded at the GOE. (Another frontier in research is the scaling between oxidation of pyrite and other metal sulfides and atmospheric $O_2$, which is not well known on global and geologic scales.)

Instead, we can argue that the abundance of pyrite formed within sulfidic sediments and water columns and subsequently buried beneath the Proterozoic ocean acted as a buffer against appreciable sulfate rise. Voluminous pyrite burial in the deep ocean may have exacerbated this buffering through subsequent seafloor subduction, which prevented later sulfur recycling and its return to the ocean via uplift and weathering (Canfield 2004). When the deep ocean is oxygenated, as has been the case over much of the last 500 million years, the formation of pyrite is restricted to organic-rich sediments along the ocean margin and is unlikely to be subducted. This shift allows for recycling and maintenance of steady-state sulfate concentrations at mostly higher levels.

The evidence that sulfate was low in the mid-Proterozoic comes in diverse forms. For example, despite a few notable exceptions, there is a general lack of bedded gypsum and anhydrite. Some of this scarcity must reflect the poor preservation of soluble calcium sulfate evaporites, but the difficulty of achieving gypsum saturation in a low-sulfate ocean was certainly a factor. The mid-Proterozoic is also known for abundant $^{34}$S-enriched pyrite (Fig. 2), in contrast to the $^{34}$S depletions that typify bacterial sulfate reduction.

Although exceptions abound, the abundance of $^{34}$S-enriched pyrite is consistent with a limited sulfate pool. Such a sulfate reservoir would yield isotopic discrimination that was correspondingly muted on the cellular level during sulfate reduction and/or during the complete or near-complete consumption of the sulfate pool on a larger scale as a consequence of pyrite burial (Lyons et al. 2009a). As a note of caution, deficiencies in seawater sulfate were likely exacerbated in restricted marginal marine basins that had limited exchange with the open ocean. Preferential preservation of these settings, as controlled by large-scale tectonics, may skew our data toward $^{34}$S-enriched pyrite and bias our interpretations, in general, away from conditions in the open ocean. The deeper open ocean, which is not well preserved in the geologic record due to subduction, may have been the burial locus of much of the $^{34}$S-depleted pyrite and the primary cause of the $^{34}$S enrichments seen in sulfate of the same age.

Perhaps most notably, the mid-Proterozoic is also known for large isotopic variability in seawater sulfate on timescales that were much shorter than those observed for similar amplitudes of variability over the last 500 million years (Kah et al. 2004; Gill et al. 2007). Under these lower concentrations, the residence time of sulfate in the ocean would have been short (compared to roughly 25 million years in the modern ocean), and the isotopic sensitivity of the reservoir to the quantity and isotopic composition of the fluxes would have been correspondingly high. These sulfur fluxes were dominated by inputs resulting from weathering and hydrothermal processes and by outputs through pyrite burial; the latter was likely enhanced by widespread euxinia during this time period, thus keeping sulfate concentrations low.

Earlier, we described the expanded range of sulfur isotope fractionations across the GOE as evidence for increasing sulfate content of the ocean. It is important to keep in mind, however, that these greater values need only reflect an increase in sulfate concentration to values greater than...
1% of the modern seawater, just as the loss of MIF need only signify an increase in atmospheric O₂ to concentrations that were still only a small fraction of today’s. In other words, this was a defining, yet still small, step in biopsheric oxygenation that nonetheless crossed critical thresholds in global redox chemistry. The precise sizes of the steps in atmospheric oxygenation are poorly known within the resolution of our proxies—yet the unambiguous sulfur signpost across the GOE, confirming that oxygenic photosynthesis had taken hold, heralds one of the great steps in the history of life on Earth.

By the late Proterozoic, the oxygenation state of Earth’s surface took a second fundamental step—one that welcomed the first animals and presumably set the stage for a Phanerozoic world much more like today’s. But what do we really know about conditions in the ocean during this interval? There is little doubt that the so-called “Snowball Earth” glaciations of the late Proterozoic pulled down sulfate levels to extreme lows, yielding an anoxic ocean that once again favored ferruginous intervals (Hurtgen et al. 2002). But the possibility also exists that an iron-dominated anoxic deep ocean prevailed over much of the late Proterozoic (Fig. 3; Canfield et al. 2008; Johnston et al. 2010; Li et al. 2010) after a billion years of efficient pyrite burial and subduction beneath an H₂S-rich mid-Proterozoic ocean (Canfield 2004). Other data argue for increasing oxygenation of the deep ocean during the Ediacaran—at the tail end of the Proterozoic (Fike et al. 2006; Canfield et al. 2007; Scott et al. 2008), and estimates for sulfate concentrations during the latest Proterozoic range from vanishingly small to those approaching modern levels (Lyons et al. 2009b). During the same time period, euxinic conditions have also been recorded (Li et al. 2010, Johnston et al. 2010).

At first glance the story may seem untidy, with seemingly conflicting observations suggesting very different ocean redox conditions over the same general time interval. But a parsimonious resolution is at hand: that is, an ocean that was complexly structured in space and over narrow slices of time, including the likelihood of persistent and perhaps pervasive redox layering in the ocean and strong local controls within individual marine basins (Reinhard et al. 2009; Johnston et al. 2009, 2010; Li et al. 2010). The big message in all this detail is that end-member ocean models for vast swaths of Archean and Proterozoic time have matured into images of more-textured biogeochemical evolution, reversibility, and lateral and vertical heterogeneity in the ocean (Fig. 3).

What do the pyrite data tell us? Just as the δ isotopes show larger ranges and inferred fractionations across the GOE, the late Proterozoic is noted for a second major broadening of isotope values and inferred fractionations (Fig. 2), yielding for the first time the persistently and particularly large offsets between sulfate and pyrite that typify the last ~540 million years. This relationship could simply reflect large and rapid isotopic variability for the sulfate from which the pyrite was produced and/or greater concentrations of sulfate in seawater (although some indicators point to very low sulfate during this interval, as mentioned above). Canfield and Teske (1996) provided another model, which attributes the greater fractionation to disproportionation pathways responding to increasing oxidation of the surface ocean and concomitant production of the required intermediate sulfur species through partial oxidation of H₂S. They tied enhanced production of the intermediates to evolutionary radiation of nonphotosynthetic, marine sulfide-oxidizing bacteria in the late Proterozoic. Recent work pushes the existence of disproportionating prokaryotes to at least the mid-Proterozoic (Johnston et al. 2005), but it is reasonable to imagine that disproportionating microbes and their isotope effects became more prevalent under the increasingly oxidizing conditions of the late Proterozoic (Canfield and Teske 1996; Fike et al. 2006).

The story of sulfur in the Proterozoic ocean is also a tale of eukaryotic life. The age of the first eukaryotes is not easily agreed upon, with some work pushing the oldest records to at least 2.7 to 2.6 billion years ago (Brocks et al. 1999; compare Rasmussen et al. 2008). Independent of first appearances, the Proterozoic was undoubtedly a key time of eukaryotic diversification. As a backdrop, widespread H₂S in the sediments and water column may have reduced the availability of trace metals (e.g. molybdenum) that are key for diverse prokaryotic and eukaryotic enzymatic pathways. Such deficiencies in micronutrients would have impacted the evolutionary and ecological patterns of the early eukaryotes (Anbar and Knoll 2002; Scott et al. 2008) and the predominant prokaryotic metabolisms (reviewed in Lyons et al. 2009a, b). Then, further oxygenation in the late Proterozoic, as suggested by the sulfur isotope and trace metal data (Fike et al. 2006; Canfield et al. 2007; Scott et al. 2008; Li et al. 2010), seems to have ushered in the first animals.

In contrast to the negative impact from reduced trace metal availability, widespread sulfidic conditions in the water column may have factored positively in primary production in the Proterozoic ocean by promoting the anoxygenic photosynthetic activity of certain H₂S-oxidizing bacteria (Johnston et al. 2009). Canfield (1998) envisioned widespread and persistent euxinia for much of the mid-Proterozoic ocean. Although embraced as an overarching model, the full extent of this state remains poorly constrained, and ocean-wide euxinia at all depths below a surface oxic layer is not necessarily indicated (Scott et al. 2008; Johnston et al. 2009; Lyons et al. 2009a, b). Another hot topic is the transition from the Proterozoic to the early Phanerozoic. Suggestions that sulfate and oxygen remained low or returned to low levels during the Cambrian (Canfield 2004; Gill et al. 2007) have important implications for the explosion of animal diversity during the early Paleozoic.

**OLD PROBLEMS SEEN THROUGH NEW WINDOWS**

We have seen the value of tracking the sulfur isotope composition of seawater sulfate over time and the rewards that come with estimates of the isotope fractionation between sulfate and pyrite as a result of microbial cycling. Unfortunately, gypsum and anhydrite records of seawater sulfate composition are sparse in the Precambrian. Both
minerals have high solubilities and thus poor preservation potential, and gypsum saturation was less easily reached in the sulfate-poor early ocean. One approach growing in popularity is to extract the sulfate captured and preserved in the lattice of carbonate minerals (carbonate-associated sulfate, or CAS). In a perfect world, the sulfate is captured at the time of deposition and remains unaltered. Early workers showed that CAS can be abundant in carbonate rocks. But more importantly, Burdett et al. (1989) demonstrated in a pioneering paper that CAS can acquire and preserve the isotopic composition of seawater.

One of the primary attractions of the CAS method is the ubiquity of shallow-water carbonates over much of geologic time. Furthermore, these rocks can yield sulfur isotope data for pyrite and sulfate from the same sample, thus giving us—but not guaranteeing—the possibility of extracting the isotopic offset between SO$\textsubscript{4}^{2-}$ and H$_2$S during bacterial sulfate reduction (plus or minus any effects of disproportionation) within a single porewater or water-column reservoir.

**WHAT LIES AHEAD?**

No matter what side you take in the various debates, it is clear that sulfur has played a major, if not leading, role in our understanding of early oxygen in the atmosphere and ocean. But with this success comes added responsibility. We are still a long way from understanding the limits that diagenesis may impose on the CAS proxy, for example. Our experiences have been encouraging (e.g. Kah et al. 2004; Gill et al. 2007, 2008), but we remain keenly aware of the problems that have surfaced in other CAS studies, where local, regional, and global variability (spatial and stratigraphic) is not easily explained by primary paleoceanographic conditions. As for all proxies, those hosted by carbonates in particular, caution is the operative term.

We do not yet understand the full range of controls on isotopic fractionations tied to the sulfate biogeochemical cycle, including the role of sulfur disproportionation and the extent to which inferred fractionations unambiguously track paleoenvironmental conditions, such as seawater-sulfate concentrations. In studies of modern sediments, we can generate porewater data for co-occurring dissolved H$_2$S and SO$\textsubscript{4}^{2-}$, but determinations of fractionations from these integrated records still require oversimplifying assumptions of closed-system behavior or sophisticated reactive-transport models.

The challenge is even greater for ancient rocks, in part because continuous, robust sulfate isotope records are sparse. Given this gap, pyrite and sulfate data that only loosely represent the same age and region are often compared. Previous work has shown that rapid isotopic variability in the ocean can make such comparison risky (Kah et al. 2004). Part of the solution lies with the novel approach of generating pyrite and sulfate isotope data from single samples, using CAS for the latter (Fike et al. 2006). But even then, the offset is only an approximation of the instantaneous fractionation during microbial sulfate reduction—plus or minus any additional biological processing. Different signals can be recorded at different times in the early history of the same sediment, just as porewater data are not easily tied to instantaneous, simultaneous processes. But we have taken big steps in the right direction, and first-order relationships have emerged and are holding up well under the scrutiny of additional work.

The degree to which specific metabolic processes, such as sulfate reduction and disproportionation of sulfur intermediates, can be recognized in the ancient record from isotopic offsets between parent and product sulfur species is enhanced by recent studies emphasizing multiple S isotopes ($^{32}$S, $^{33}$S, $^{34}$S, and $^{35}$S) (Johnston et al. 2005). These challenging but rewarding measurements and interpretations, supported by rigorous experimental work, are yielding unique fingerprints of specific sulfur metabolisms. Each new step will bring us closer to a better understanding of the early ocean and the complexity of its structure in time and space over billions of years of history.

**CONCLUDING REMARKS**

Among the elements, sulfur has played the greatest role in our understanding of early biospheric oxygenation. For example, studies have shown that the loss of mass-independent sulfur isotope fractionation is a consequence of the initial rise of atmospheric oxygen and that isotopic offsets between sulfate and sulfide constrain the amount of ancient seawater sulfate. Seawater sulfate derives primarily from oxidative weathering on the continents, so its delivery to the ocean is tied intimately to the amount of oxygen in the early atmosphere. Oxygen in the atmosphere and sulfate in the ocean were both low before the Great Oxidation Event about 2.4 billion years ago. That said, before the GOE, subtle and varying oxygen and sulfate contributions, along with variability in hydrothermal iron inputs, favored at least local euxinia and even weakly oxic surface waters in an ocean traditionally assumed to have been unyieldingly anoxic and ferruginous. Following the GOE, sulfate delivery increased, although atmospheric oxygen remained sufficiently low to permit widespread accumulation of sulfide in the sediments and deep water column. The spatiotemporal extent of these conditions, including the enigmatic state of the ocean between 2.4 and 2.0 billion years ago, remains an area of particularly active research. However, well beyond any uncertainty over whether all the H$_2$S resided, its overall Proterozoic abundance and its impact on trace metal (micronutrient) solubility are certain to have influenced the patterns and rates of prokaryotic and eukaryotic evolution. These controls are an exciting area of active research.

The mix of arguments for the state of the deep ocean in the late Proterozoic seem to point in different directions, including (1) iron-dominated conditions, like those of the Archean; (2) increased oxygenation, in phase with the greater O$_2$ content of the atmosphere that spawned the advent and initial proliferation of animal life; and (3) even euxinia on at least local scales. But there is little reason for concern. The latest models are welcoming the possibility of temporal and spatial heterogeneity, particularly in an ocean operating at low, near-threshold levels of oxygen and sulfate. The likelihood of heterogeneity is not unique to the late Proterozoic, with mid-water-column euxinia and other variations of redox layering as well as localized conditions within restricted settings possible throughout the Precambrian. Sulfur has been a linchpin in our understanding of early oxygen in the atmosphere and ocean. The last two decades have seen a renaissance in studies of sulfur biogeochemistry, but the most exciting times lie ahead.

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From Lab to Field

**Elemental Analysis with XRF**

- S1 TURBO Handheld EDXRF for field surveys
- S2 PICOFOX TXRF Benchtop for ppb level effluent analysis
- S8 TIGER WDXRF for fast laboratory based analysis
- S2 RANGER EDXRF Benchtop for onsite analysis
Touring the Biogeochemical Landscape of a Sulfur-Fueled World

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Life, as recorded in almost every corner of the oceans and continents, has evolved to take advantage of chemical gradients. Organisms, both big and small, utilize reduction–oxidation (redox) reactions to gain the energy required to live and grow. Although aerobic respiration (using \( \text{O}_2 \)) is the most popular form, other modes of respiration use oxygen alternatives and drive additional element cycles (for example, nitrogen, sulfur, and metals such as iron and manganese). These alternative metabolisms, and especially those cycling sulfur, helped shape Earth’s long history and much of the world we see today. Sulfur is a fundamental constituent in macroscopic and microscopic worlds alike and is a key oxidant in the anaerobic biosphere. By reconstructed the distribution of sulfur metabolisms throughout the marine realm, we can better understand the role that sulfur plays in marine biogeochemical cycling and Earth-surface processes.

Keywords: sulfate reduction, sulfur isotopes, seawater sulfate, metabolism, electron acceptors

THE MODERN SULFUR CYCLE

Most of the biogeochemical work aimed at understanding the surface sulfur cycle has zeroed in on the oceans and the biological processes housed therein. This review will highlight a diversity of sulfur-driven metabolisms, which in turn catalyze numerous redox reactions and move materials between oxidized and reduced reservoirs. Before embarking on a tour of the biological landscape, however, we must first look at the topology of the surface sulfur cycle.

Like all other geochemical cycles, the sulfur cycle can be understood through identifying respective sources, sinks, and standing pools. Most of the sulfur in the oceans comes from the oxidative weathering of sulfides on land and is delivered to the oceans via rivers as the soluble sulfate ion (volcanic inputs represent a smaller, yet appreciable, source) (Holser et al. 1979). Sulfate (\( \text{SO}_4^{2-} \)) is one of the most abundant anions in seawater, with a present concentration of 28 millimolar (mM). Given the high concentration and long residence time, which is \(-10^7 \) years (Claypool et al. 1980), the oceanic sulfate reservoir is relatively homogeneous.

We look to the seafloor for indications of how sulfur is removed from the oceans. Prominent sulfur sinks target both sulfate and sulfide, with the latter bearing a more intimate biogeochemical link. In the case of sulfate sinks, the isolation and evaporation of shallow seas can result in the precipitation and deposition of sulfate evaporite minerals (Holser et al. 1979). Further, circulation through seafloor sediments and hydrothermal systems can also lead to the removal of sulfate via the precipitation of anhydrite, a calcium sulfate mineral (McDuff and Edmund 1982). Both of these processes rely primarily on physical, rather than biological, mechanisms. However, the most prominent mechanism for sulfur removal is the biogenic production and subsequent precipitation of sedimentary sulfide. In this process, microbes reduce seawater sulfate and produce hydrogen sulfide, which can then bind with iron and other metals to form pyrite and other sedimentary sulfide minerals. Examination of any marine sedimentary profile (an example is given in Figure 1, inset) reveals the prevalence of these biogeochemical catalysts (the microbes); in these profiles, sulfate concentrations diminish as sulfide increases. These sulfide minerals are then transported, along with the rest of the sediment package, into subduction zones and out of reach of the surface biosphere.

An additional component in the modern sulfur cycle, and one that is directly linked to Earth’s climate, is the cycling of organosulfide across the sea surface–atmosphere interface (Fig. 1). This cycling does not represent a significant long-term sulfur source or sink, but its role in surface-ocean biogeochemistry is becoming more appreciated with continued research. Prior to being liberated to the water column or atmosphere, reduced organosulfide compounds serve numerous functions within cells, including helping to control osmotic balance. These compounds are then released into surface-ocean environments during zooplankton grazing and viral attack (see an overview in Brimblecombe 2006). Once in the marine environment, they can be oxidized, metabolized, and/or exported to the deep ocean. If transported to the atmosphere, usually as dimethylsulfide (DMS), additional chemical reactions help form sulfate and the nuclei needed for cloud condensation (the climatic link). The emission of DMS from surface waters represents the greatest flux of reduced sulfur from the ocean to the atmosphere.

THE PLAYERS IN THE GAME

Given this simple schematic of the surface sulfur cycle, we can better understand the interactions of these different chemical constituents by examining the role that microbes play. Microbial activity provides a simple window into
biogeochemical cycling—if a rich energy source exists, then it will almost certainly be consumed. With this principle in mind, we first discuss the most abundant marine sulfur pool, seawater sulfate.

In anaerobic environments, such as most marine sediments, the consumption and oxidation of organic matter (termed remineralization) are driven by various oxidants in a predictable fashion, based on the energy yield for a given redox pair (that is, the oxidant and the organic matter) (Amend and Shock 2001). The predominance of a particular metabolic process is also related to the availability (concentration) of each oxidant. Though sulfate yields less energy than nitrate and certain metal oxides, its high abundance renders it a significant player in the carbon cycle. In fact, dissimilatory sulfate reduction, the microbial process that reduces seawater sulfate to sulfide, is thought to be responsible for roughly 50% of the remineralization in sediments (next only to oxic respiration) (Jørgensen 1982). These bacteria employ a suite of enzymes, working in series, to reduce seawater sulfate systematically, via intermediate oxidation state species (such as sulfite), to sulfide.

In the mid-twentieth century, researchers (e.g. Harrison and Thode 1958) delved more deeply into the mechanics of this metabolism. Early geochemical studies began with an appreciation that the sulfate ion must first be taken up into the cell and internally reduced, with hydrogen sulfide as the excretory by-product. Shortly thereafter, the physiology of sulfate reduction came to be understood as (from Rees 1973):

\[ \text{SO}_4^{2-} \leftrightarrow \text{SO}_3^{2-} \Leftrightarrow \text{APS} \Leftrightarrow \text{SO}_2^{2-} \rightarrow \text{H}_2\text{S}, \]

where the brackets represent the cell membrane. In this process, sulfate is actively transported into the cell by membrane-bound proteins, where it is activated with adenosine-5'-triphosphate (the currency of energy) to adenosine-5'-phosphosulfate (APS). APS is then enzymatically reduced to sulfite (SO_3^{2-}), which is further reduced to hydrogen sulfide (H(S)). Most of these reactions are thought to be reversible, with the net fluxes favoring the production of sulfide.

For geochemists interested in understanding the role of sulfate reducers in natural environments and over Earth history, this metabolic network on its own is interesting, but it is difficult to link it directly to marine sedimentary environments. The power of this conceptual framework is realized, however, when isotopes are included.

Researchers have demonstrated that microbial sulfate reduction can produce very large δ^{34}S fractions. In size, these fractionations far exceed those produced by most inorganic processes and, as a result, microbial sulfate reduction can be easily distinguished from nonbiological processes in natural environments. Decades of rigorous laboratory work have extended our understanding of the process and broken the sulfate reduction pathways down even further. Research suggests that the reduction of APS to sulfide and the reduction of sulfite to sulfide are each accompanied by 25‰ fractionations. The final isotopic effect arises from the cellular uptake of sulfate and is assigned a value of ~3‰. As a result of this research on the constituent fractionations, the overall fractionation limit for a sulfate-reducing bacterium is estimated at 47‰ (with sulfide being isotopically lighter than sulfate) (Harrison and Thode 1958).

This view of sulfate reduction has held for decades, with only minimal changes. However, spurred on by the finding of extremely sulfidic environments in which overwhelming fractionations (up to 70‰) have been ascribed solely to the activity of sulfate reducers (Wortmann et al. 2003), recent efforts have revisited the steps involved in sulfate reduction, in search of a more precise understanding of how these fractionations are produced and how these microbes work. Recent modeling and experimental studies have focused on the operation of sulfate reducers (e.g. Johnston et al. 2007), and the results suggest that the conventional reaction sequence should be reassessed. It will be exciting to watch in the coming years as new experimental, analytical, and theoretical approaches are applied to classic models, especially since the simple understanding

![Figure 1](image-url) Schematic representation of the surface sulfur cycle. Sulfur is sourced from the continents and atmosphere as sulfate, and is cycled within the ocean both aerobically and anaerobically. A vigorous cycle of organosulfide compounds (DMS, DMSO, DMSO) related to primary production and heterotrophy exists in the surface ocean; some of this sulfate escapes into the atmosphere, where it can contribute to cloud condensation nuclei and climate. At the sediment–water interface at the bottom of the ocean, microbes drive the degradation of organic matter using sulfate as an oxidant. This is evident by the decrease in sulfate concentration and the increase in sulfide concentration within marine sediments (see inset, from Jørgensen et al. 2004). However, when integrated globally, ~90% of sulfide produced is reoxidized. This cycle of reduction and oxidation is almost completely microbial, and the cycle shown in the inset is driven by sulfate-reducing bacteria (a), sulfide oxidizers (b and d), and elemental sulfur reducers (c), along with the inorganic formation of pyrite (e), which serves as the terminal sink for sulfur. Sulfate and sulfide (in blue) can reach appreciable concentrations, whereas intermediate species of sulfur (S_w) rarely accumulate. These intermediates are further subject to microbial disproportionation processes, which are discussed in the text.
of sulfate reduction outlined above serves as the backbone for our collective interpretation of almost all natural sulfur isotope records.

The conventional understanding of how each of the constituent steps in sulfate reduction contributes to the overall fractionation signature allows for information to be extracted about the actual operation of this metabolism and about the local environmental conditions affecting it; all this information is inferred from the magnitude of the observed net fractionation (the $\delta^{34}$S difference between sulfate and sulfide). For instance, Earth historians are interested in tracking the concentration of seawater sulfate through geological time. By performing careful experiments, they have convincingly calibrated seawater-sulfate concentrations across the Archean–Proterozoic boundary. This was possible because, under low-sulfate conditions, the transport of sulfate into the cell is the overall rate-limiting step during sulfate reduction. In keeping with a fundamental rule of isotope geochemistry (that the rate-limiting step is the most fully expressed isotopically), the overall fractionation associated with sulfate reducers is small. Similarly, small fractionations have been observed in the late Archean, with larger effects recorded in the early Paleoproterozoic. This change in observed fractionations was ascribed to a significant increase in sulfate concentrations across the boundary (Habicht et al. 2002).

Although we have a reasonable understanding of the physiology of microbial sulfate reduction, there is still a gap between what is observed using pure cultures in the laboratory and what is measured in natural populations of sulfate reducers. Natural populations consistently produce larger $\delta^{34}$S fractionations than pure cultures, though both share a similar upper limit between +45 and +50‰ (Fig. 2). Identifying the environmental conditions responsible for this difference remains elusive. Perhaps more striking than this difference is that, despite sulfate reduction being pinpointed as the dominant sulfur metabolism in marine settings, the overall range of fractionations seen in nature far exceeds that of sulfate reducers (Fig. 2): this points to additional, and significant, contributions from alternative metabolisms. In fact, closer examination reveals that ~90% of the sulfide produced in marine sediments today is ultimately reoxidized biologically or chemically by $O_2$ (Jørgensen 1982); this process has been greatly aided during the Phanerozoic by bioturbation. Thus, it is expected that wherever we find sulfate reducers and sulfide generation, we will also find sulfide oxidizers (and their associated fractionations). This reinforces the principle noted above that when there is energy to be gained (through chemical gradients), microbes will find a way to take advantage!

Unlike the reductive sulfur cycle, which is dominated by sulfate reduction alone, a wide range of different metabolic processes populates the oxidative sulfur cycle. A diverse suite of metabolic processes catalyzes the oxidation of sulfide to various intermediate species, most commonly to elemental sulfur, but not uncommonly to sulfate. In order to perform such a task, microbes need an oxidant and, as a result, they are often found living at the oxic-anoxic interface in sediments. Here, they can access $O_2$ and nitrate from overlying seawater to pair with sulfide, which is advecting upwards from depth (from the zone of sulfate reduction). For instance, the white films observed on mud in a salt marsh are often communities of Beggiatoa—sulfide oxidizers that use $O_2$ and produce elemental sulfur (the white precipitate). In the absence of $O_2$ or nitrate, sunlight can also be harnessed to drive microbial sulfide oxidation. Isotopic studies have shown that even with the diversity of strategies employed to oxidize sulfide, these microbes cannot amend the fractionation discrepancy shown in Figure 2. Sulfide-oxidizing bacteria (both photosynthetic and non-photosynthetic) have been extensively studied and shown to produce only small $\delta^{34}$S isotope effects (see review in Zerkle et al. 2009). In part because of these discrepancies (both in modern systems and in the geological record), researchers began looking more closely and found a curious metabolism that can simultaneously oxidize and reduce material, and extract energy from the net transformation (Bak and Pfennig 1987). Termed disproportionation, this metabolism performs an inorganic fermentation of intermediate-redox-state sulfur species (like SO$_3^-$, S$_2$O$_3^-$, and S$^0$). More specifically, disproportionators use these intermediates to produce both sulfide and sulfate. In most marine sediments (or modern sulfidic environments), these sulfur intermediates rarely accumulate to appreciable concentrations and, as a result, disproportionators are relegated to localized microenvironments where minimal concentrations exist (albeit only transiently). In addition to performing a unique metabolism, disproportionators possess another characteristic that is almost exclusive to this process, making them of great significance to studies of Earth history. They are capable of producing very large $\delta^{34}$S fractionations—fractionations even greater than those produced by sulfate reducers (Canfield and Thamdrup 1994). Thus, it is through coupling the fractionations produced by both sulfate reduction and sulfur disproportionation that natural records are now understood.

**AND THEN THERE WERE MATS...**

Given the implications for early Earth environments, there has been a recent resurgence of research aimed at understanding biogeochemical cycling within modern microbial mat communities. Today, microbial mats are relegated to...
atyypical environments, where they can escape grazing by benthic animals (often mats are found in evaporitic, or salty, environments as animals generally lack the osmoregulatory capabilities possessed by some microbes). In these special settings, light, sulfur, and oxygen drive an entire ecosystem on a scale of millimeters to centimeters. These communities often form weakly laminated, vertically stacked packages of microbes employing different metabolisms and relying on their upstairs and downstairs neighbors for nutrients (Jørgensen et al. 1983). It is also here that we meet another member of the biogeochemical sulfur cycle—photoautotrophic sulfide oxidizers (also known as purple and green sulfur bacteria).

The community structure within a microbial mat can frequently be differentiated by color, often revealing striking similarity between mats. For instance, in an example of a gypsum-crusted microbial mat (Fig. 3, from Canfield et al. 2004), various types of cyanobacteria dominate the bright green layer and also form a thin veneer on the mat’s uppermost surface. Generally, these cyanobacteria are the primary producers in these environments, generating the organic matter that will later drive sulfate reduction and sulfide generation. In a clever biological twist, cyanobacteria can operate as normal oxygenic photoautotrophs or as anoxygenic photoautotrophs using sulfide rather than water (Cohen et al. 1986). This flexibility may be a relic of the earliest cyanobacteria, suggesting that the filamentous cyanobacteria that populate the lower green layer in Figure 3 may in fact also be oxidizing some sulfide. Despite this flexibility in cyanobacteria, most of the sulfide oxidation is performed by the microbes comprising the bright purple layer. Appropriately named purple sulfur bacteria, these microbes harvest light and oxidize sulfide, all the while using ambient inorganic carbon to build biomass. Often, and especially in water column environments like the Black Sea where the transition from oxic to anoxic environments is more extended, green sulfur bacteria can be found directly beneath purple sulfur bacteria (Manske et al. 2005). “Greens” are similar to “purples” but survive better under lower light and higher sulfide concentrations (Vila et al. 1998). At the surface, these two phototrophic sulfide-oxidizing bacterial groups require the same food sources; however subtle differences position them in different environmental niches. This general concept permeates microbial ecology.

Continuing downward into the mat shown in Figure 3, sulfate-reducing bacteria comprise the black bottom layer at the base of the mat structure and provide the foundation of these communities (or at least the sulfide). These sulfate reducers feed off the organic matter produced by the autotrophs living above them, and in this case, as evidenced by the gypsum (CaSO₄·2H₂O) crusts, sulfate is readily available. The sulfide produced moves back towards the surface of the mat, feeding the purple sulfur bacteria and closing the geochemical loop. These crusts begin to physically isolate the microbial mats from the overlying brine (Canfield et al. 2004). This illustrates one way these systems evolve with time and demonstrates how sustainable the internal recycling of nutrients and electrons actually is.

In addition to the intellectual resurgence associated with ongoing microbial mat research, technological advances are also spurring exciting new research directions. For example, a central problem in studying microbial mats has long been one of scale, as specific microbiological horizons wax and wane over millimeters. As a result, geochemical fingerprints of these biological processes vary similarly. However, with the advent of nanoSIMS technology, this geochemical landscape is now being more fully explored.

Fike et al. (2008) employed a clever technique to obtain a 2D snapshot through a microbial mat from Guerrero Negro (Mexico); this technique simply involves fixing sulfide on a thin silver plate (silver and sulfide react very quickly to form a stable precipitate). Via nanoSIMS, these silver sheets were then analyzed at the submillimeter scale for δ²⁵³⁵ S variability (Fig. 4). The data revealed huge isotope gradients over strikingly small scales. The depth profiles and contoured color maps shown in Figure 4 demonstrates that the overall isotope composition of sulfide was progressively enriched in heavy sulfur (more positive values of δ²⁵³⁵ S) towards the surface of the mat, with an overall variability ranging from near seawater-sulfate values of ~ 20‰ down to less than −30‰—an overall range of greater than 50‰.

More interesting than the overall trends, however, are the heterogeneities and isotopic “hot spots,” where extremely depleted (negative) values were recorded. Understanding this spatial scale of variability requires that the distribution of microbial metabolisms be followed over similar length-scales. Thus, to complement these 2D geochemical maps, Fike et al. (2008) used molecular biological techniques to understand the diversity of microorganisms present within the mats, pinpointing the spatial pattern of key metabolisms as it related to geochemical and isotopic variability.

**Figure 3** Two images of gypsum-crusted microbial mats from a saltern in Israel. The mat thickness in A is 3.5 cm, and the coin in B is 2.1 cm in diameter. The mat in A has the same orientation as the original mat. Changes in color with depth reflect different microbial communities: photosynthetic populations occur near the surface, whereas sulfate-reducing heterotrophs are located at the bottom. These mats are described in detail in the text and in Canfield et al. (2004).
THE SULFUR WE ALL NEED

Sulfur is a necessary constituent for all life. In addition to being used as an energy source, it is an essential component in every living cell on Earth. In a fashion similar to dissimilatory sulfate reducers, cells most often incorporate sulfate and then reduce it to whatever form is necessary. The most common and widespread process is the intracellular reduction of sulfate for the synthesis of the amino acids cysteine and methionine. However, unlike dissimilatory sulfate reducers, this process requires energy and thus comes at an expense to the cell. There are numerous other sulfur-bearing biomolecules within cells (Bacterial, Archaeal, and Eukaryotic cells alike) that serve a wide range of functions. Some molecules are housed within membranes and tissues and play a structural role; others participate in essential metabolic processes.

CURIOSOUS COLLABORATIONS

Modern ecosystems have taken sulfur assimilation a step further. During the last decade, the discovery of new biological relationships has given rise to an emerging scientific discipline, one that combines biogeochemistry with animal physiology (see Fig. 5). In the darkness of the seafloor and around both hot and cold hydrothermal seeps are communities of deep-sea animals, the most famous of which is the tube worm Riftia. What makes these ecosystems particularly interesting, especially with regard to sulfur geochemistry, is that these tube worms extend roots into the marine sediments through which anoxic, and often seemingly toxic, seep fluid is being advected. Most animals are extremely sensitive to hydrogen sulfide (a primary seep fluid component), but the roots of tube worms house huge populations of chemoautotrophic sulfide-oxidizing bacteria, or microbes that use sulfide and inorganic carbon (also provided by vent fluid) to produce organic matter (Freytag et al. 2001; Girguis et al. 2002; Girguis and Childress 2006). In truly endosymbiotic fashion, the chemosynthetic microbes provide the host worms with a source of organic carbon and detoxify the environment by removing the sulfide. Further, the character of these tube worm “forests” is such that the organisms engineer their surroundings to ensure longevity (Cordes et al. 2003).

A NEW DIRECTION

Drawing from decades of experimental, environmental, and geological work on δ34S fractionation, recent studies have extended the applications to include the two much less abundant sulfur isotopes, δ33S and δ36S. Two exciting research directions have emerged: (1) most famously, Farquhar et al. (2000) identified evidence in the rock record for low levels of atmospheric oxygen early in Earth’s history, and (2) a growing body of evidence now indicates that δ33S and δ36S can also be used to track microbial fractionations by providing information distinct from that recorded in δ34S (Johnston et al. 2005). Basic laboratory experiments using pure cultures of prominent sulfur metabolisms (sulfate reducers, sulfur disproportionators, and sulfide oxidizers) were performed and their products analyzed. The most powerful finding, and one that will shape future research, is that although each of these processes produces overlapping signatures in δ34S, they are uniquely resolvable with the inclusion of δ33S measurements. Put simply, this work has identified metabolism-specific isotope signatures that can be used to diagnose contributions from different metabolic processes to an overall environmental signature recorded in modern and ancient environments. In addition, these signatures may prove useful in the search for extraterrestrial life (Johnston et al. 2008).

CLOSING THOUGHTS

The biogeochemistry of sulfur has long been an active field of research, and during the last decade, the field has been reinvigorated with new ideas, technologies, and questions. However, this has been made possible only with the strong and thorough context provided by decades of earlier work.
research. Perhaps most intriguing is the diversity of research topics that are emerging from the core of sulfur biogeochemical research. For instance, with our search for life on the early Earth now extending to neighboring planets, the development of new ways to fingerprint metabolic processes will remain a vibrant avenue for research, which will, almost by necessity, include sulfur. We have just begun to uncover the vast and complex ecology of seep- and vent-related seafloor environments. The study of the syntrophic and endosymbiotic interactions among different metabolisms (animal and bacterial alike) and how these relationships shield organisms from their surround-
ings, effectively generating favorable microenvironments, is in its infancy. These environments serve as a key filter to subsurface reservoirs of gases, such as methane, that may have an impact on climate. Therefore it is important to understand the efficacy and operation of these ecosystems because they are intimately related to the atmosphere we breathe.

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For every outstanding research question that approaches resolution, new and exciting ones take its place. The new directions are numerous, but the next generation of researchers will need to merge disciplines to draft a more complete environmental picture. As this picture is resolved at smaller and smaller spatial scales, we will more actively assess how biochemistry and geochemistry interact, and we will uncover the variety of ways and scales at which microbial metabolisms participate in animal physiology and sediment diagenesis.

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The sulfur cycle is arguably the most important geochemical cycle on Mars because the transfer of sulfur limits processes on Mars’s differentiation, processes, sedimentary, geomorphic and aqueous processes, past climate, and current and past habitability. The presence of sulfur-rich compositions on Mars is suggested by meteorite data, in situ bulk chemical and mineralogical analyses, remote sensing data from dust and surfaces, and geochemical models. The inferred sulfur-rich nature of Mars may have resulted in an Fe–(Ni–)S core that has been liquid throughout Mars’s history. On the surface, Mg- and Ca-sulfates are widespread and Fe$^{3+}$-sulfates are found locally. It is likely that these minerals occur in a variety of hydration states and host much of the mineral-bound hydrogen in the Martian subsurface.

**INTRODUCTION**

Sulfur is central to studies of Mars’s planetary-scale processes, surface evolution, climate history, and potential habitable environments. Mars has long been considered a “sulfur-rich planet.” Data from Martian meteorites suggest elevated sulfur concentrations in the interior, and Martian surface deposits contain high levels of sulfur (SO$_3$ up to ~37 wt%, average ~6 wt%), probably in the form of sulfate salts. These salts provide clues to unique Martian hydrologic and sulfur (S) cycles that we are just beginning to unravel. In this contribution, we highlight key mineralogical and geochemical evidence from Martian meteorites and Mars’s surface that provides insight into the S cycle on Mars.

**SULFUR IN MARTIAN METEORITES**

**Primary Phases**

Four meteorites that were observed to fall, and collected soon after (Shergotty, Zagami, Nakhla, and Chassigny), are widely accepted to come from Mars and are interpreted as being minimally affected by terrestrial processes (Leshin and Vicenzi 2006). In addition to these rare falls, ~50 additional meteorites of Martian parentage have been found, mainly in Antarctica and the northern African deserts. These “Martian” meteorites have up to ~0.2 wt% S (Meyer 2008), and this S content has been used as an upper limit for the S content of Mars’s mantle and core (see below). Most primary igneous S is concentrated in sulfides (<1%), including pyrrhotite, rare chalcopyrite and/or cubanite, pentlandite, troilite–pentlandite–chalcopyrite intergrowths, pyrite (likely hydrothermal), and some secondary marcasite (references in Meyer 2008). Most sulfides are located near rims of pyroxene (Fig. 1) or in interstitial mesostasis, indicating that the late-stage magmatic liquids were rich in S. Because sulfides are located near grain boundaries and are readily weathered, they are very susceptible to alteration by fluids (even at low fluid/rock ratios) and readily form S-bearing secondary phases. To date, Mössbauer spectrometers deployed by the Mars rovers Spirit and Opportunity have not detected Fe-sulfides in any igneous (or sedimentary) rocks or soils.

**Sulfur-Bearing Secondary Phases**

Sulfur is found in a variety of secondary phases in Martian meteorites: sulfates, impact glasses, iddingsite, and carbonates. Sulfates are especially labile due to their high solubility and the sensitivity of phase transitions to relative humidity and temperature; therefore, it is necessary to document textural features, age, and isotope signatures, which can provide evidence in support of a Martian origin.
(e.g. Leshin and Vicenzi 2006). Ca- and Mg-sulfates have been observed in the interiors of some Martian meteorites (i.e. inside fusion crusts), suggesting that these secondary minerals formed on Mars (e.g. Bridges et al. 2001; Ming et al. 2008). Iron-bearing sulfates (some with Na, K, or P) have been identified in Martian meteorites, but only a jarosite [KFe$_3$(SO$_4$)$_2$(OH)$_6$] trapped in a melt inclusion (McCubbin et al. 2009) likely formed on Mars. Na-sulfates in some meteorites found in Antarctica likely represent terrestrial contamination.

The Martian meteorite EETA79001 (an Antarctic find) contains gas-rich impact-melt glasses with substantial S contents (SO$_3$ < 22 wt%). The S contents are interpreted to be derived from secondary sulfates on the Martian surface that were incorporated into the impact melt (Rao et al. 2008). The Shergotty glasses have SO$_3$ < ~3 wt%, but some contain Ca-sulfate crystals (Rao et al. 2008). Finally, S was reported in iddingsite (<0.69 wt% SO$_3$) and carbonate (<0.26 wt% SO$_3$) (Rao et al. 2008).

**Sulfur Isotopes**

Mass-independent S-isotope anomalies in both sulfides and sulfates have been identified in Martian meteorites (summarized in Farquhar et al. 2007). A key finding is that secondary sulfides (>3.5 billion years old, Ga) from the ancient ALH84001 meteorite and sulfates from the 1.3 Ga Nakhla meteorite contain negative $^{33}$S mass-independent anomalies (Δ$^{33}$S = -0.5 to -1.25‰). In both cases these anomalies were interpreted to be indigenous to Mars and, if so, most likely resulted from photochemical reactions in the ancient Martian atmosphere. Accordingly, these data provide compelling evidence that a surficial S cycle has operated on Mars for at least 3.5 billion years. In the case of the Nakhla sulfides, the S isotope data also suggest a component of hydrothermally derived S.

**SULFUR AND SULFATES ON THE MARTIAN SURFACE**

**Bulk Sulfur Chemistry**

Almost forty years ago, X-ray fluorescence analyses from the Viking missions revealed that Mars has S- and Cl-rich surface regoliths or “soils” (Clark et al. 1976). No S-speciation data were collected, but the red color of the soils suggested that $S^{6+}$ likely predominates and that the S is hosted in sulfates. Sulfate salts were identified using telescope-based spectroscopy of Martian dust, and sulfates were proposed by various authors using geochemical models. Subsequent landed missions confirmed high S contents using APXS instruments: either an alpha-proton X-ray spectrometer (Pathfinder mission) or an alpha-particle X-ray spectrometer (Mars Exploration Rover, MER, mission). Native S has not been identified on Mars thus far.

Dust, ubiquitous on Mars’s surface and in its atmosphere, has an average SO$_3$ content of 6.8 wt% (2.7 wt% S), and soils have an average SO$_3$ content of ~6.2 wt% (2.5 wt% S) (Taylor and McLennan 2009). These values are higher than the average S content of the top few tens of centimeters of the global Martian surface (SO$_3$ = 4.4 wt%), mapped using the Gamma Ray Spectrometer (GRS) on the 2001 Mars Odyssey spacecraft (Fig. 2; McLennan et al. 2010). The lower average S value determined by the GRS, compared to average soils, constrains the relative distributions of soil and igneous bedrock exposed at the surface. Overall, these findings are consistent with the suggestion that S has been extensively transported and deposited across the Martian surface.

Remobilization of S on Mars is also supported by a strong correlation between the degree of alteration and the SO$_3$ content of Martian rock surfaces and the amount of dust and soil. The lowest SO$_3$ contents (~1.1 wt%) were found on basaltic rocks where the surface was cleaned with a Rock Abrasion Tool (RAT). However, it is possible that even those surfaces contained some S-rich debris or dust or had been altered by S-bearing fluids. Some extensively altered rocks in the Columbia Hills (Gusev Crater) have SO$_3$ contents that are higher in the rock interior than on the surface, suggesting that the rock interior is cemented by sulfates. To date, the highest SO$_3$ values measured on Mars were obtained on white-yellow soil exposed in Spirit rover’s wheel ruts and inferred to be comprised of Fe$^{3+}$-sulfates (e.g. the Arad site, SO$_3$ = 35.1 wt%; Fig. 3A).

**Sulfate Mineralogy from the Mars Exploration Rovers**

Sulfate mineralogy was inferred during the MER mission by correlating APXS-derived SO$_3$ and major cation contents (accounting for silicates and oxides), Mössbauer spectroscopy, visible and near-infrared (VNIR, PANCAM) spectra and soil. The lowest SO$_3$ contents (~1.1 wt%) were found on basaltic rocks where the surface was cleaned with a Rock Abrasion Tool (RAT). However, it is possible that even those surfaces contained some S-rich debris or dust or had been altered by S-bearing fluids. Some extensively altered rocks in the Columbia Hills (Gusev Crater) have SO$_3$ contents that are higher in the rock interior than on the surface, suggesting that the rock interior is cemented by sulfates. To date, the highest SO$_3$ values measured on Mars were obtained on white-yellow soil exposed in Spirit rover’s wheel ruts and inferred to be comprised of Fe$^{3+}$-sulfates (e.g. the Arad site, SO$_3$ = 35.1 wt%; Fig. 3A).

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Sulfate mineralogy was inferred during the MER mission by correlating APXS-derived SO$_3$ and major cation contents (accounting for silicates and oxides), Mössbauer spectroscopy, visible and near-infrared (VNIR, PANCAM) spectra and soil. The lowest SO$_3$ contents (~1.1 wt%) were found on basaltic rocks where the surface was cleaned with a Rock Abrasion Tool (RAT). However, it is possible that even those surfaces contained some S-rich debris or dust or had been altered by S-bearing fluids. Some extensively altered rocks in the Columbia Hills (Gusev Crater) have SO$_3$ contents that are higher in the rock interior than on the surface, suggesting that the rock interior is cemented by sulfates. To date, the highest SO$_3$ values measured on Mars were obtained on white-yellow soil exposed in Spirit rover’s wheel ruts and inferred to be comprised of Fe$^{3+}$-sulfates (e.g. the Arad site, SO$_3$ = 35.1 wt%; Fig. 3A).
and/or thermal emission infrared (mini-TES) spectra. Below, we highlight two important sulfate localities investigated during the mission.

Meridiano Planum The rover Opportunity discovered S-rich outcrops, informally termed the Burns formation, soon after landing on the Meridiani plains (see review in McLennan and Grotzinger 2008). These outcrops consist of a sequence of “wetting upwards” eolian sandstones, in which repeated episodes of groundwater recharge periodically breached the surface to form local, subaqueous depositional settings. Sulfates are interpreted to represent a suite of evaporative minerals and their diagenetic products. The SO\textsubscript{3} contents of these sedimentary rocks are high (18 to 25 wt%). The Mössbauer spectrometer identified about 10% jarosite—an important line of evidence for low-pH aqueous conditions during deposition. Based on geochemistry and thermal infrared spectroscopy, other sulfate minerals are inferred to consist of a mixture of ~18% Mg-sulfate and ~10% Ca-sulfate of unknown hydration states, and possibly Na-bearing sulfates (Clark et al. 2005; McLennan and Grotzinger 2008).

Paso Robles Soils, Columbia Hills, Gusev Crater S-rich soils termed “Paso Robles class” (Fig. 3a, b) are widespread in Gusev Crater’s inner basin and contain Fe\textsuperscript{3+}-, Mg-, and Ca-sulfates. The Fe\textsuperscript{3+}-sulfates dominate, based on studies using Mössbauer, VNIR (with two different data-processing methods), mini-TES, and APXS spectroscopies. Ferricopiapite [Fe\textsuperscript{3+}\textsubscript{4-x}(SO\textsubscript{4})\textsubscript{x}(OH)\textsubscript{2-x}2H\textsubscript{2}O] has been identified by all methods, and other Fe-sulfates commonly proposed include coquimbite, fibroferrite, parabutlerite, and rhomboclase (e.g. Lane et al. 2008).

Sulfate Mineralogy at the Phoenix Lander Site Evidence for sulfate phases at the Phoenix Lander site in the north polar region has been ambiguous. However, a recent reevaluation indicates that water-soluble SO\textsubscript{3}\textsuperscript{2-} contents of 1.4 ± 0.5 wt% are present in the soils and that this is likely related to a Mg-sulfate phase (Kounaves et al. 2010).

Sulfate Mineralogy from Remote Observations Sulfate minerals have been identified on the Martian near-surface using VNIR spectra collected with the Mars Express Observatoire pour la Minéralogie, l’Eau, les Glaces et l’Activité (OMEGA) and the Mars Reconnaissance Orbiter Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) instruments. OMEGA has found extensive deposits of kieserite (MgSO\textsubscript{4}•H\textsubscript{2}O) and gypsum (Gendrin et al. 2005; Bibring and Langevin 2008). These sulfates occur in the equatorial Valles Marineris canyon system and adjacent Meridiani area (Meridiani Planum, Aram Chaos, Valles Marineris, and Terra Meridiani), and gypsum deposits are prevalent in the northern circumpolar erg deposits (e.g. Bibring and Langevin 2008) but were not observed at the Phoenix Lander site. In addition, an unidentified “polyhydrated sulfate” has been identified at several locations. Ferric oxides are commonly associated with polyhydrated sulfates and may also be associated with kieserite (Bibring and Langevin 2008).

CRISM data for Mars were recently summarized by Murchie et al. (2009), who recognized five types of sulfate deposits: (1) Meridiani-type layered deposits (e.g. Terra Meridiani and Aram Chaos) consist of monohydrated or polyhydrated sulfates (probably Mg rich) superposed on cratered terrain, with some layers rich in hematite. (2) Valles-type layered deposits (in Valles Marineris) contain polyhydrated sulfates that overlie monohydrated sulfates in discrete layers. They are ill-chasmatas, form mounds, and form deeply eroded plateaus up to several kilometers in relief. These deposits may be deformed, and some have layers rich in ferric oxides, oxyhydroxides, or hydrated sulfates. (3) Intracratere clay–sulfate deposits (e.g. craters in Terra Sirenum) have hydrated sulfate layers interbedded with kaolinite layers and are exposed on crater walls. (4) Gypsum plains (north polar erg and layered deposits) are made of sandy material and reworked into dunes, probably with other hydrated minerals. (5) Silicate layered deposits (e.g. plains surrounding Valles Marineris) consist of jarosite associated with amorphous silica layers.

SULFUR IN MARTIAN RESERVOIRS

S in the Martian Mantle and Core Sulfur was delivered to Mars during accretion and by later impacts (Fig. 4a). The S content of Martian meteorites has been used to argue that Mars and its mantle are intrinsically S rich and that the core is particularly S rich. There is little direct evidence for the S content of Mars’s mantle, although enrichments compared to Earth’s mantle are expected (Gaillard and Scailliet 2009; Righter et al. 2009). Higher S contents on Mars are favored by Mars’s higher mantle FeO content and the likelihood that it had a shallower magma ocean than Earth (e.g. Righter et al. 2009). A S-rich core (~10.6–16.2 wt%); Stewart et al. 2007) is suggested by limited geophysical data indicating that the core may be completely or partially molten. Melting may occur if S is added to an Fe(Ni) core because the liquidus occurs if S is added to an Fe(Ni) core because the liquidus is lowered relative to Mars’s pressure–temperature profile (Stewart et al. 2007). If the core was liquid throughout Martian history, as implied by this hypothesis, then the thermal remnant magnetism of some Noachian southern highland rocks would be due to vigorous core convection before ~3.7 Ga. (Noachian refers to >~3.7 Ga; Hesperian ~3.7–3.0 Ga; and Amazonian, after ~3.0 Ga. Surface ages are obtained by comparing crater counts with the lunar cratering record. Boundary ages are highly uncertain, especially for the Hesperian–Amazonian boundary.) The shutdown of such a convection system and the consequent loss of the magnetic field have important implications for models of Mars’s heat production, plate tectonics, and atmosphere and climate evolution.

S in the Martian Crust and Atmosphere Ultimately, the indigenous S on Mars’s surface must have come from the mantle and crust (planetary and impactor leaching in Fig. 4a) in the form of magmatic or hydrothermal S-bearing gas, immiscible sulfide fluids, and/or sulfate minerals (King and McSween 2005). Righter et al. (2009) calculated that degassing of 2400 ppm S from the
Fe-rich Martian melts over Mars’s geologic history may have produced all the S at the surface. However, they caution that any degassing model relies on knowing whether the melt is S saturated (i.e. degasses S species) or whether sulfide saturation has been reached. Thus, to fully understand the degassing history of Martian magmas, we require additional constraints, such as the initial S content, oxygen fugacity, pressure, temperature, and composition of the magma, including the concentrations of other volatile elements, like water (see Métrich and Mandeville 2010 this issue). Nonetheless, Martian meteorites indicate that S is hosted in late-stage magmatic sulfides, and it is likely that much S was transported in fluids and gases (Fig. 4a), such as magmatic gases, acid sulfate fumaroles, hot springs, and hydrothermal fluids (as evidenced by the S isotope ratios in Nakhla sulfides). Deposits resulting from these high-temperature processes might include hydrated silica–sulfate deposits and intracrater clay–sulfate deposits (Fig. 4a).

Sulfur gases have not been detected in the current Martian atmosphere, possibly because H₂S and SO₂ form sulfate minerals readily through photochemical reactions (Fig. 4a), as suggested by Δ³⁵S values in Martian meteorite sulfates (Farquhar et al. 2007). However, if residence times and fluxes were such that atmospheric sulfur gases were at significant concentrations, they may have acted as an efficient greenhouse gas and warmed the Martian climate (Johnson et al. 2008). An interesting, but yet untested, suggestion is that early in Mars’s history, sulfur was less efficiently oxidized during atmospheric processing, leading to the formation of sulfite minerals (Haley et al. 2007). In any case, sulfur species were then incorporated into sedimentary and hydrological cycles on the planet’s surface and near-surface (e.g. McLennan and Grotzinger 2008; Ming et al. 2008; Fig. 4a).

**SULFATES IN SEDIMENTARY AND HYDROLOGIC SETTINGS ON MARS**

**Sulfate Brines and Sulfate Crystallization**

Layered sulfate deposits (e.g. Meridiani-type and Valles-type) and the gypsum plains were probably derived through sedimentary, hydrologic, glacial, and diagenetic processes (Fig. 4b, c); specifically, the sulfates likely crystallized from brine. Intracrater clay–sulfate layered deposits and the Paso Robles soils may have formed through brine processes. The crystallization sequence and identity of the sulfate minerals on Mars depend on the initial bulk composition of brines (including the salt/water ratio) and intensive parameters such as pH, temperature, and partial pressure of oxygen (PO₂). Accordingly, there are several conceptual end member models for Martian fluids in which these parameters differ, but all such models may be relevant on Mars. Below we discuss the geochemical models in which brine compositions are derived from mafic-ultramafic rocks, because this is most relevant to the Martian surface (e.g. Fig. 4a, b).

**Low-fluid/rock-ratio and low-pH models**

An acidic nature for the Martian surface is suggested by the abundance of S, the occurrence of jarosite and other Fe³⁺-sulfates with amorphous silica, experiments simulating the alteration of basalt under acidic conditions, and geochemical models of rover data (Tosca et al. 2005; Tosca and McLennan 2006; Hurowitz et al. 2006). Acidic weathering on Mars under low fluid/rock ratios (e.g. Fig. 4c) would differ from typical weathering on Earth because acidic conditions promote preferential dissolution of olivine, olivine, and Fe–Ti oxides relative to pyroxene and plagioclase; slow oxidation of Fe⁴⁺; increased Al and Fe solubility; and the production of amorphous silica during alteration, whereas Al- and Fe³⁺-clays and Fe³⁺-oxides are not formed (Hurowitz et al. 2006). Brines produced by acid sulfate weathering of typical Martian crust (olivine basalt) are rich in Mg, Fe³⁺, Ca, and SO₄²⁻. Tosca and McLennan (2006) modeled acidic brines using a chemical-divide approach with varying HCO₃⁻/SO₄²⁻ ratios (i.e. initial pH) in the starting brine to generate evaporite assemblages that match those identified on Mars.

**Low-pH, variable-pO₂ models**

Extreme acidic conditions (high H₂SO₄ molality, pH ~ -2) result in Fe³⁺- and SO₄²⁻-rich solutions that are predicted to precipitate Fe³⁺-sulfates (King and McSween 2005; Tosca et al. 2005), such as szomolnokite (Fe₂SO₄·H₂O; Bishop et al. 2009). Under oxidizing conditions, Fe³⁺-sulfates then form mixed Fe³⁺–Fe²⁺-sulfates, followed by Fe³⁺-sulfates (like jarosite), and finally Fe³⁺-oxides/hydroxides/oxyhydroxides (hematite/ ferricyanide/goethite) which “age” to form hematite. This sequence may be obtained following a path of either dehydration → oxidation → neutralization (King and McSween 2005) or oxidation → aqueous diagenesis (Tosca et al. 2008).

**Near-neutral-pH models**

Neutral-pH brines may be produced on Mars through melting of ice or snow in contact with rocks or dust or through neutralization of initially acidic solutions by reaction with silicate minerals. In either case, such solutions likely would be salt rich and water poor in order for salts to form on the Martian surface. Neutral- to alkaline-pH environments on Mars are suggested by the occurrence of clays and carbonates on the Martian surface (OMEGA and CRISM data) and carbonates in Martian meteorites. Weathering of Martian basalt by a near-neutral solution results in Mg–Na–Ca–SO₄–(Cl)-rich solutions, similar in bulk composition to average Martian soil. In this case, Fe³⁺-oxides/hydroxides/oxyhydroxides precipitate early with phosphates, possibly followed by carbonates (Fe–Ca–Ca–Mg-carbonates), followed in turn by Ca-sulfates, Mg–(Na)–sulfates, and finally Na-halides (King et al. 2004). If the fluid/rock ratio was higher or the interaction time longer, then Al- and Fe³⁺-clay minerals may have formed.

**SULFATE AGE, PRESERVATION, AND RECYCLING ON MARS**

The timing of sulfate deposition is poorly constrained but most likely occurred early in Martian history. OMEGA data were used to propose three distinct alteration periods in Mars’s history: (1) early, alkaline, water-rich alteration, producing phyllosilicates (~3.7 Ga; Noachian); (2) acidic, water-rich alteration, producing sulfates (Late Noachian; Hesperian); and (3) young, anhydrous alteration, producing ferric oxides (Late Hesperian/Amazonian; Bibring et al. 2006). In this model, the acidic environment that formed the sulfates resulted from climate change, perhaps due to massive SO₂ degassing during Tharsis volcanism. Subsequent models suggested that Meridiani-type and Valles-type layered sulfate rocks formed in the Late Noachian to Early Hesperian (~3.5 Ga) as a result of large-scale groundwater recharge during the Tharsis volcanic episode (Andrews-Hanna et al. 2007; Murchie et al. 2009; Fig. 4b). Other sulfate deposit types likely formed through a range of processes (e.g. high-temperature processes or precipitation from a range of brine compositions under a variety of conditions) throughout Martian history and over a range of distances. Future orbital and rover data may allow quantitative tests of models of sulfate formation (for example, using mineral abundances and mass balance coupled with detailed stratigraphy).

Sulfate remobilization and redeposition on Mars likely occurred episodically over time (for example, as observed at Meridiani Planum). These events may have been in
response to aqueous alteration triggered by volcanic, hydrothermal, or impact events; eolian activity; outflow channels and mass flow; seasonal sublimation and dehydration events; obliquity cycles; diagenesis and thermal maturation; and the formation of solution films on mineral surfaces (Fig. 4a, c) (King et al. 2004; McLennan and Grotzinger 2008). Remobilization events may have played a role in changing the pH of solutions on Mars’s surface: rhomboclase [HFe$^{3+}$(SO$_4$)$_2$·4H$_2$O] produces acid when it breaks down, whereas jarosite consumes acid and commonly produces Fe$^{3+}$-oxides.

The preservation of large amounts of sulfates on Mars’s surface relative to Earth’s highlights some major differences in the two planets’ geologic histories and environments. Sulfate deposition requires water-limited conditions (low water activity or relative humidity, $a_{H_2O}$) because many of these minerals are very soluble. Sulfates are probably preserved on Mars because any surface solutions have largely been lost and only existed episodically on the surface, and because relatively low temperatures (at least since ~3.7 Ga) favored their preservation (King et al. 2004). Lack of plate tectonics caused S to be concentrated near the surface as it would have been derived from volcanic and fluid–rock reactions. On Earth, on the other hand, S is recycled in subduction zones and redistributed during formation and chemical fractionation of continental crust as well as in the hydrologic cycle (weathering, river input, etc.; King et al. 2004; McLennan and Grotzinger 2008). Finally, on Mars, there are no documented mechanisms for reducing sulfate, in contrast to Earth where mid-ocean-ridge hydrothermal brines deposit sulfides and biological activity commonly reduces sulfate (King et al. 2004).

### Sulfate Hydration State(s) on Mars

Mg-, Ca-, and Fe-sulfates may contain H as OH$^-$ or H$_2$O or both, with total H$_2$O contents up to ~60%. Accordingly, sulfates may host the majority of mineral-bound H on Mars. The hydration state in sulfates is controlled by $a_{H_2O}$ and temperature and is influenced by the overall chemistry of the system (e.g. Vaniman and Chipera 2006). In the case of Mg-sulfate minerals, hydration states vary from ~1 to ~7. Mercury sulfide (HgS) is a more extreme case than iron sulfides, with hydrogen sulfide (H$_2$S) released as a product of the hydration reaction. When the degree of hydration is greater than 3, the Ca$^{2+}$ and Mg$^{2+}$ cations in the interlayer space of the clay hydrates are replaced by interlayer H$_2$O molecules. This phenomenon is known as “intercalation.”

The geologic history of adjacent sulfate deposits with differing hydration states is enigmatic and may only be explained by multiple events (e.g. precipitation, diagenesis and thermal maturation, dehyration, aqueous alteration; Roach et al. 2009). Climate change associated with past variations in the planet’s obliquity has likely played a role in the formation and long-term stability of near-surface hydrated sulfates.

Dehydration of sulfate minerals is accompanied by large molar volume changes; for example, when meridannite dehydrates to form epsomite at 2°C, there is a 34% loss of the solid volume (Peterson and Wang 2006). Volume changes associated with sulfate dehyration–dehydration processes have been suggested as a possible explanation for a variety of geomorphic and textural features on Mars, including some catastrophic outflow features and gullies, secondary pores and veins in sedimentary rocks, physical properties of the soils (e.g. clods), and the formation of small-scale fracture and vein systems (e.g. Fig. 4c).

### SUMMARY: THE SULFUR CYCLE ON MARS

The sulfur cycle dominates many geologic processes on Mars. Substantial amounts of S were delivered to Mars in accretionary materials and through later impactors (Fig. 4a), resulting in a S-rich planet. Sulfur partitioned into the core to form a liquid Fe–(Ni–)S core, which may have undergone a period of rapid convection during the Noachian, causing a transient magnetic field. Transfer of S to the crust through degassing, magmatism, and hydrothermal processes resulted in substantial S at the surface (Fig. 4a, b). Photochemical reactions of S gases likely resulted in rapid sulfate formation and may have warmed the early Martian climate. Sedimentary and hydrologic processes dominated the surface S cycle, including S fractionation, recycling, and transport (Fig. 4a, c). Several plausible models exist for sulfate-brine formation and crystallization, and it is likely that multiple sedimentary and hydrologic events have affected sulfate assemblages. Impactors may have played a role in delivering and trapping S (e.g. in melts); impact events may have caused near-surface hydrothermal systems capable of transporting S phases and recycling S from sulfate-rich deposits (Fig. 4a). In summary, the Martian sulfur cycle is central to past and present aqueous, atmospheric, sedimentary, and geomorphic processes on Mars.
FUTURE DIRECTIONS

The upcoming Mars Science Laboratory mission will provide unparalleled information on the mineralogy and geochemistry of the Martian surface. The environment of sulfate formation may be determined, provided we have appropriate phase equilibria and reaction-kinetic models, and sufficient information to infer the geologic setting. Understanding Martian sulfate mineralogy and textural relations will make it possible to assess the past and current habitability of Mars and the likelihood of biomarker preservation. Samples returned from Mars in the future would greatly expand our understanding of the Martian sulfur cycle.

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INAUGURAL ADDRESS BY SIMP PRESIDENT 2010–2011

Dear friends and colleagues,

As the new president of the Italian Society of Mineralogy and Petrology (SIMP), I would like to thank past president Simona Quartieri and all members of the previous SIMP Council for their enthusiastic commitment to the Society, despite an increasingly difficult national scene. Indeed, the scientific community in Italy is facing a dramatic contraction of financial resources dedicated to fundamental and applied research. The absence of a national funding agency, comparable to the DFG in Germany, SNF in Switzerland, and NSF in the United States, is a unique situation on the international scene. The only national public funding frame (PRIN-MIUR) did not distribute grants in 2009. Most recent allotments are in the order of just a few thousand euros per year per research unit. Laboratories are forced either to shut down active scientific instrumentation or to dedicate most of their energies to fund-raising. Financial contraction is coupled to a complete absence of government policy on instrumental facilities in the Earth sciences. Such a situation contrasts with our competitive scientific production, as represented in 2009 by more than 500 articles published by Italian authors in international journals in the subject area “geochemistry and geophysics” (ISI-WoS), compared to about 700 articles by French and German authors.

This negative trend can be reversed only by promoting the common initiatives of our learned societies and increasing the influence of our scientific representatives in the political arena. The SIMP will therefore be strongly involved in reinforcing links with the Italian Geological Society, the Crystallographic Association, the Geochemical Society and the Volcanological Association. Another step toward synergy will be the organization of the 89th meeting of the SIMP, entitled “The Evolution of the Earth System, from Atoms to Volcanoes,” to be held in Ferrara in September 2010 and chaired by Massimo Coltorti.

Reinforcing relationships with European mineralogical societies will be a major pursuit of the Council. Actions include common editorial or meeting initiatives and the development of an active strategy toward the European Commission (e.g. European Strategy Forum on Research Infrastructures) for sustaining the geosciences and, more specifically, the mineralogical sciences. In parallel, the SIMP Council is committed to improving its outreach activities. The potential impact of mineralogy and petrology on society and the Italian economy is highlighted by phenomena in the public sphere such as large volcanoes and famous marble and granite quarries.

Stefano Poli, President

SIMP PRIZES FOR 2009

Bianchi Prize for Petrology – Two Winners Ex æquo

Riccardo Avanzinelli graduated from the University of Firenze in 2000, and he received a PhD from the same university in 2004 for a project developed in collaboration with the University of Bristol (UK). After a postdoc at the University of Firenze, he spent 4 years at the Bristol Isotope Group (University of Bristol), first as a Marie Curie Fellow and later as a research assistant. At present he is employed as a researcher/lecturer at the University of Firenze. His research focuses on the application of different isotope systematics to geologic and petrologic problems. His studies are aimed at understanding mantle melting and extraction processes in different geodynamic settings, timescales of magma formation and differentiation, and the recycling of crustal material into the mantle through subduction. Lately, he has been applying different isotope systems (Sr-Pb and Mo isotopes) to the study of the timescales and redox conditions during the genesis, migration and storage of petroleum.

Chiara Groppo is a research fellow at the Department of Mineralogical and Petrological Sciences, University of Torino. Her MSc thesis dealt with ultrahigh-pressure metamorphism in the western Alps. She completed her PhD at the University of Torino and the Université Joseph Fourier in Grenoble, where she studied the petrology of asbestos-bearing serpentinites in the western Alps. Currently, Chiara’s research focuses on the reconstruction of the metamorphic evolution of collisional orogens. Her interests cover a large variety of tectonometamorphic processes, from the subduction of continental and oceanic crust at high- and ultrahigh-pressure conditions to high-temperature metamorphism and crustal anatexis. She applies phase petrology and thermodynamic modelling to investigate the P–T evolution of metamorphic terranes, mainly in the Alps and Himalayas. Chiara has also been involved in several geological expeditions to the Himalaya and Karakorum ranges. The results of her work have been published in more than 15 papers in international journals.

SIMP Prizes 2009 for PhD students

Giulio Borghini “The Spinel- to Plagioclase-Facies Transition in Mantle Peridotites: Natural and Experimental Constraints”

Plagioclase peridotites are important markers of processes that characterize the petrologic and tectonic evolution of the lithospheric mantle at extensional settings. Subsolidus experiments at 0.25–1.0 GPa and 900–1200°C have been performed on fertile and depleted anhydrous lherzolites modelled in a complex chemical system, to define how the stability of plagioclase changes with varying peridotite bulk composition and to determine the chemical and modal changes in minerals within the plagioclase facies as a function of P, T and bulk composition. Results shed light on the origin of metamorphic plagioclase peridotites and can be used to constrain the geobarometric evolution of natural mantle peridotites, thus providing insight into the subsolidus exhumation of the lithospheric mantle.

Maria La Calamita “Chemical and Structural Study of Anionic and Cationic Sites in Trioctahedral Micas at Room and High Temperatures”

Volcanic trioctahedral biotites from several sources were studied at room temperature (RT) and high temperature (HT), combining EPMA, SIMS, SCXRD, Mössbauer and FTIR spectroscopy. The RT investigation showed the predominance of oxy-type substitutional mechanisms. In some micas, interlayer H2O and NH4+ occur. These features were interpreted as the likely result of post-magmatic thermal oxidation and hydrothermal alteration, respectively. The HT study provided evidence for a one-step, irreversible Fe-oxidation/deprotonation process and a phase transition with no symmetry change. The kinetics of the process followed an exponential law. The OH stretching region in the FTIR spectrum, collected before and after heating, exhibited significant changes.
FROM THE EXECUTIVE DIRECTOR

Moving Forward

This year sees the Mineralogical Society progressing on several fronts. Our membership numbers are up; we are now co-publishers of the EMU Notes in Mineralogy series (expect three new titles this year); we will publish the third edition of the mineralogical classic Rock-Forming Minerals, by Deer, Howie and Zussman; we will publish at least one more title in the Landmark Papers series (there are four on our ‘to-be-published’ list); Rockwatch, the junior arm of the UK’s Geologists’ Association, has become one of the co-organizers of our now annual Nature’s Treasures meeting, and this will lead to much increased participation by younger people; our website is being rebuilt (among other new features, our e-commerce capacity will be greatly expanded); and the collaboration with fellow European mineralogical societies that began with the 2009 MAPT conference has been extended to 2012, when we will hold a meeting in Frankfurt with the German, French, Italian, Austrian and Swiss societies. Much to keep us busy.

Future Meetings

2010 Annual Meeting – Nuclear Waste Management

28–29 September 2010
The Society’s Annual Meeting has the title “Nuclear Waste Management: Research Challenges for the Future” and is being jointly organized with the Geological Society. Prof. Rod Ewing has agreed to deliver the Hallimond Lecture, and an exciting line-up of speakers and posters is anticipated. Go to www.minersoc.org/pages/meetings/nuclear/nuclear.html for information about the event and to register.

Process Mineralogy of Metalliferous Ores: An Introduction for Geologists

22–25 June 2010 – Meeting of the Applied Mineralogy Group

Website www.minersoc.org/pages/groups/amg/amg.html
Contact J.C. Andersen (J.C.Andersen@exeter.ac.uk)
Venue University of Exeter, UK

Field Excursion to Cornwall, UK

28 June–3 July 2010 – Applied Mineralogy Group

The excursion will provide an introduction to the wide range of geology found in Cornwall and will include the tectonics of the Devonian metasediments, the granites, the Lizard Ophiolite and the classic Sn, W, Cu and kaolin mineralization.

Website www.minersoc.org/pages/groups/amg/amg.html#excursion
Contact P.W. Scott (p.w.scott@ex.ac.uk)

Nature’s Treasures 3

12 December 2010
Now in its third year, ‘Nature’s Treasures’ has become a successful regular on our calendar of events.

Venue Natural History Museum London

2011 Annual Meeting – Frontiers in Environmental Geoscience

21–24 June 2011
Make plans now to attend our 2011 Annual Meeting.

Contacts N. Pearce (nick.pearce@aber.ac.uk), Karen Hudson-Edwards (k.hudson-edwards@geology.bbk.ac.uk)
Venue University of Aberystwyth, Wales

Website

The Society’s website is to receive a much-needed face-lift. As well as rebuilding the navigation system and reorganizing the content, we will be adding new features, such as an online bookshop, educational material, integral links to social networking sites and perhaps a presidential blog. Your input is requested. What would you find useful on the site? What could we do to improve existing material? Let us know about new features that we could build in. Send your comments to Kevin Murphy (kevin@minersoc.org).

Journals

‘Publish ahead of print’ has now been fully deployed for Mineralogical Magazine, on both the GeoscienceWorld and Ingenta (now known as Publishing Technology) platforms. Papers will be published online as they are accepted, in advance of paper-version publication. The same system has now been arranged for Clay Minerals. This will further shorten the already quick submission-to-publication time for both of these journals. Remember also that colour printing is available free of charge in Mineralogical Magazine.

Sustaining Membership

We have been very successful in the first year of appeals for donations to our sustaining membership fund. Many donors have opted to remain anonymous but others’ names are listed on the website (www.minersoc.org/pages/msinfo/sustaining.html). We are very grateful to all donors. The funds will be used to create an endowment, the income from which will be used to support student activities, for example, attending conferences and doing fieldwork, and to help provide one-year free membership to students. Commercial organizations are also being solicited, and monies received from them will also be added to the fund.

Bursaries

This year saw a larger crop of applications for our bursaries than ever before. Read the list of successful applicants at www.minersoc.org/pages/awards/bursary-winners-2010.html.

Kevin Murphy
Executive Director
SEVENTH SWISS GEOSCIENCE MEETING
20–21 November 2009, Neuchâtel

The 7th edition of the Swiss Geoscience Meeting was organized by the Center for Hydrogeology at the University of Neuchâtel and focused on the contribution and importance of water in the geosciences. On November 20, a large audience was present at an interdisciplinary plenary session entitled “Water across Boundaries.” This plenary session was followed by an awards ceremony for various prizes and distinctions. On November 21, 12 parallel sessions covered a wide range of geoscience topics. Our Society sponsored the open session “Mineralogy–Petrology–Geochemistry,” which was convened by our members B. Grobéty (Fribourg) and E. Reusser (Zürich). The 16 oral presentations and the well-presented posters attracted a significant and noticeably young audience.

2009 PAUL NIGGLI MEDAL TO ALAIN BURGISER

Our Society is actively involved in the annual award of the Paul Niggli Medal, which is Switzerland’s most prestigious “young scientist award” in Earth sciences. It is given to young Swiss scientists who have made outstanding contributions to mineralogy, crystal chemistry, petrology, resource geology, or exploration physics. The medal and prize are awarded yearly at the Swiss Geoscience Meeting.

The 2009 Paul Niggli Medal went to Alain Burgisser, a CNRS researcher at the Earth Science Institute of Orléans (ISTO), France. Alain completed his PhD in 2003 at the University of Alaska Fairbanks in physical volcanology. His research focused on degassing in volcanic conduits and the mechanics of pyroclastic density currents. He is currently leading a European project (ERC–DEMONS) whose goal is to model the quantity and composition of volcanic gases as a function of the petrology of the magma at depth and the eruptive regime. The chemical kinetics of degassing in a volcanic conduit are evaluated through a combination of experimental, mathematical, field, and numerical approaches. Natural targets include convection in the lava lake at Erebos volcano (Antarctica), a conduit-flow model of Strombolian activity at Llaima volcano (Chile), and lava-dome extrusion at Soufrière Hills volcano (Montserrat). By bridging the knowledge gap between deep magmatic processes and surface emissions, Alain and his team aim to improve the application of volcanic gas analyses to the mitigation of volcanic risk.

EIGHTH SWISS GEOSCIENCE MEETING
“Hot and Cold – Extreme Climates in Time and Space”
November 19–20, 2010
University of Fribourg
http://geoscience-meeting.scnatweb.ch

LETTER FROM THE EAG PRESIDENT

The Earth’s Future

When putting together the 2009 Davos Goldschmidt Conference, Chris Ballentine and I debated at length what was missing from past meetings. Upon reflection, we concluded that although the Goldschmidt Conference provides an excellent forum for discussing the latest scientific advances among ourselves, we were doing little to bridge the gap between the academic community and society.

It is clear that society is facing a large number of challenges closely related to the management of the Earth. The carbon concentration of the atmosphere has been increasing dramatically over the past century; this increase has been linked by many to global warming. The combination of dwindling petroleum resources and higher demand led to a spike in oil prices in 2008. The twin concerns about global warming and increasing oil prices led to increasing biofuel production using land that could otherwise be used to produce food. Food prices rose, leading to increased starvation in many countries. As an alternative to expensive petroleum, nuclear energy has again become a popular option, reopening the question of the safety of radioactive waste storage. The price of many base metals has also risen dramatically as rumors of dwindling reserves circulate. What struck us is how central geochemistry is to resolving these large-scale societal concerns.

Presentations and debate centered on how we can use fundamental science and improved global governance to better manage food, water, energy security, ecosystem services, disease, and climate change for the estimated 9 billion people likely to be living on Earth in 2050. A key is improved communication between the scientific community, which can provide solutions, the public, who need to better understand why and how changes are necessary, and the government, which has at times been slow to embrace scientifically based solutions. Nevertheless, some past successes have shown that these challenges can be addressed. Veerabhadran Ramanathan noted that current air pollution laws have been remarkably successful in reducing sulfate aerosols, an important greenhouse gas component. We anticipate that regular Earth’s Future events will both encourage our community to focus efforts on societal issues and attract the popular press to publicize major scientific advances. For those who might have missed the 2009 event, a webcast of these presentations can be seen at www.goldschmidt2009.org/ple naryRecordings.

Eric H. Oelkers
Toulouse, France
THE SOURCE CLAYS REPOSITORY

Even in relatively “pure” clay deposits, the assemblage of minerals and their compositions can change significantly within a few centimeters. In the early 1970s, the Clay Minerals Society recognized the need for a collection of clays from which researchers could obtain identical samples from a large stock of homogenized material. Largely through the leadership of William F. (Bill) Moll at Georgia Kaolin Company, but with the support of many individuals in the clay minerals industry and the Clay Minerals Society, the Source Clays Repository shipped its first materials in early 1973. The Repository was originally housed at the University of Missouri but moved to Purdue University (Indiana, USA) in August 2002, where it currently resides.

The Source Clays Repository contains two types of materials, the Source Clays and the Special Clays. The Source Clays consist of 8 different materials (KGa-1b, KGa-2, PFl-1, SHCa-1, STx-1b, SWy-2, Syn-1, and SAz-1) available in 125 or 250 gram units. For each Source Clay, sufficient raw sample was collected to provide one metric ton of processed material. Each sample was dried at low temperature, homogenized, and pulverized, and then stored in polyethylene bags. SAz-1 is currently depleted, but it is planned to obtain additional material this coming summer. The Special Clays consist of materials that have not been homogenized. Since the move to Purdue, the Repository has shipped 6159 units to countries throughout the world.

The Repository also houses the bentonite collection of the late Prof. Ralph E. Grim, which was donated by Prof. Necip Guven. The Grim Collection consists of about 360 samples ranging from a few grams to almost a kilogram of material. The Grim Collection is available to researchers who wish to utilize a significant number of the samples from the collection in their research.


Darrell Schultz

THE PRESIDENT’S CORNER

These days the quickest way for anyone wishing to obtain information about almost anything is to use the Internet, and so anyone wanting to find out what The Clay Minerals Society is and what it does will first find their way to the Society’s website, www.clays.org. Consequently it is vital that our website be easy to use and kept up to date. The CMS website was re-designed a couple of years ago, and renewed efforts have been made recently to update the information on its numerous pages. This is no easy task, and a number of members have contributed to pages relevant to their responsibilities. The co-ordinator of the information is the new Chair of the Committee on Electronic Communication, Covadonga Brime (University of Oviedo), and the technical changes are made by our webmaster Gordon Nord at the Society’s office. Please visit the website, where you will find a lot of useful information on all the activities of the Society. If you see anything that needs to be updated, please contact Covadonga at brime@geol.uniovi.es.

I hope you find the accompanying article about Haydn Murray as fascinating as I did. Haydn has had an extremely interesting life, much of it involved with an incredible variety of applications of clays, and his breadth of knowledge of clays is unsurpassed. He is a much respected father figure in CMS – he has made many valuable contributions to the Society and hopefully will continue to do so for many years yet.

Finally, congratulations and grateful thanks to Editor-in-Chief Joe Stucki and Managing Editor Kevin Murphy for the massive amount of work they accomplished in producing one of the largest volumes of *Clays and Clay Minerals* in many years. Volume 57 for 2009 contained 71 papers in 822 pages.

Derek Bain
President, The Clay Minerals Society
The Macaulay Institute, Aberdeen, UK
d.bain@macaulay.ac.uk

HAYDN HERBERT MURRAY – 2009 PIONEER LECTURER

Once upon a time on a farm near Kewanee, Illinois (USA), a bright high school senior, who was also a pretty good football player, had a particularly inspiring science teacher. This teacher took his class on a field trip to a nearby coal mine. Our bright high school senior was impressed enough with the operation that he decided he wanted to be a mining engineer. Among the schools interested in him as a football player, one emphasized the quality of their Department of Mining Engineering—the University of Minnesota. In 1942, the young man chose this as the place to pursue his interests.

Haydn Herbert Murray enrolled in college just before turning 18 years old, when he became eligible for the military draft as World War II was in full swing. He completed two semesters and half of the spring semester before entering the Army. Prophetically, he was shipped to Camp Wheeler, Georgia. At the time, he did not realize that the land on which Camp Wheeler was located was actually owned by Georgia Kaolin Company but had been assigned to the U.S. Army under “eminent domain” until 1947. Fifteen years later he joined Georgia Kaolin Company.

After his basic infantry training was completed, the Army sent him to the Army Specialized Training Program of the University of Alabama to study basic engineering subjects, one of which was geology, which he particularly liked. Later this interest was reinforced in the Philippines, where he worked with volcanic ashes and soils while building airstrips and roads. At the University of Alabama, he applied to the Officer Candidate School at Fort Belvoir, Virginia, and was accepted. He graduated from OCS on December 12, 1944. He had been told that he would probably be in the United States for at least six months. With this news, he married his high school sweetheart, Juanita Ara Appenheimer, on
December 16. Eleven days later he was ordered to report to Fort Lewis, Washington. When he checked in, the desk sergeant said, “Lt. Murray, you are alerted for immediate overseas duty.” He boarded a troop ship in Oakland, California, on February 5, 1945. When he arrived in New Guinea, he was assigned to the 856th Engineer Aviation Battalion on the island of Biak, which is 50 miles north of New Guinea and 50 miles south of the equator. After duty on Biak, the battalion was sent to the Philippines to repair and refurbish the airport at Nichols Field on Luzon near Manila.

After being discharged in August 1946, Haydn used the G.I. bill benefits to enroll at the University of Illinois, where he received three geology degrees in just five years. After completing his master’s degree in igneous petrology, he accepted a fellowship funded by Illinois Clay Products and offered to him by Dr. Ralph Grim. He says, “It was one of the best moves I ever made.” Grim had transferred to the Geology Department in 1948 after a 16-year career at the Illinois Geological Survey, so Haydn became Grim’s first PhD student and a clay mineralogist. His dissertation was titled “The Structure of Kaolinite and Its Relation to Acid Treatment.” In 1951, Grim recommended Haydn for a faculty position at Indiana University and for appointment as the clay mineralogist at the Indiana Geological Survey.

During his first year of teaching, Haydn attended the first Conference on Clays and Clay Minerals at the University of California, Berkeley. At this meeting, The Clay Minerals Committee was formed, with Ralph Grim as chairman. The National Academy and the National Research Council supported the Clay Minerals Committee for the next 12 years. At the 11th meeting of the group, in Ottawa, Canada, the NAS-NRC proposed that the Clay Minerals Society be formed, and the Clay Minerals Committee appointed Richards Rowland from Shell Oil, James Early from Gulf Oil, and Haydn Murray to charter The Clay Minerals Society, which was accomplished on July 18, 1962, as a 501(c)3-tax-exempt organization.

In 1957, Haydn resigned his positions at Indiana University and the Indiana Geological Survey to become the Director of Research and Development at Georgia Kaolin Company. What attracted Georgia Kaolin to Haydn was his work on factors that influenced the viscosity of kaolins at 70% solids. At Georgia Kaolin, he hired a first-rate group of clay mineralogists and chemists: Wayne Bundy, Robert Conley, Jack Harrison, William Moll, Colin Harvey, Andy Torok, Joe Weiss, and Tom Thompson. This group developed several new products for paper coating and filling, paint, ceramics, plastics, and other uses.

Haydn’s career at the Georgia Kaolin Company advanced with managerial appointments: Manager of Operations (1961), Vice President of Operations (1963), and Executive Vice President and Chief Operating Officer (1964). In the mid-1960s, Georgia Kaolin expanded through acquisitions: Benton Clay Company, located in Casper, Wyoming; Southern Clay Products, in Gonzales, Texas; New Zealand China Clays, in Maungaparerua, New Zealand; and a joint venture with Amberger Kaolin in Hirschau, Germany. These acquisitions gave Haydn an opportunity to learn about the applications of sodium and calcium bentonites, halloysite, and European kaolins. At Georgia Kaolin Company he had the opportunity to visit and evaluate many large kaolin deposits in Australia, on the island of Belitung in Indonesia, in South Africa, and in Mexico.

In 1973, Haydn returned to Indiana University as head of the Geology Department, a position he held until he left the teaching faculty in 1984 to focus on research. At Indiana he had an outstanding group of PhD students: Wayne Bundy, Jack Harrison, Colin Harvey, Robert Pruett, Tom Dombrowski, Jessica Elzea-Kobel, Jun Yuan, Roland Merkl, Tim Salter, Karen Keith, and Huitang Zhou. His doctoral students did theses on kaolins in Saskatchewan and China, halloysite in New Zealand, bentonite in Wyoming, and palygorskites in South Georgia, North Florida, and China. In all, Haydn has 96 theses on his shelf.

Haydn’s international work expanded at the same time he returned to Indiana University. In 1973, Haydn chaired the UNESCO Kaolins Genesis Committee, which was formed by Milos Kuzvart of Czechoslovakia. This group sponsored annual field excursions and conferences to study and report on kaolin deposits throughout the world. In 1984, he was asked by the Agency for International Development (AID) of the State Department to evaluate the clay deposits in Egypt. In 1985, he was asked by the Geological Survey of Chile to visit and evaluate Chilean industrial mineral operations. After he retired in 1994, Haydn formed a consulting company, H. H. Murray and Associates, whose activities took him to kaolinites in Argentina, Australia, Brazil, Canada, and China; to bentonites in Argentina, Germany, Italy, Great Britain, and the United States; and to palygorskites in the United States, China, and Senegal.

Over the years, various professional organizations honored Haydn. He served as president of The Clay Minerals Society in 1965; the Society for Mining, Metallurgy, and Exploration in 1988; the American Institute of Professional Geologists in 1991; and the International Clay Minerals Group in 1993. He was awarded the SME’s Hardinge Award in 1976. At the 2000 International Clay Conference, he was awarded an Honorary Doctor of Science degree from the University of Buenos Aires. In 2003, Haydn was elected to the National Academy of Engineering and he received the Department of Geology Alumni Achievement Award from the University of Illinois. In 2004, he received an honorary Doctor of Science degree from Indiana University, which especially pleased him because it was from his peers. In 2006, he served as vice-chair of the Peer Evaluation Committee in Section 11, Earth Resources Engineering of the National Academy of Engineers, and two years later he chaired this committee.

Haydn has published over 200 papers, chapters in books, and two books; he holds four patents. His latest book, Applied Clay Mineralogy (2007), sums up his experience as a productive clay mineralogist for 60 years. Looking back, Haydn says there is very little he would change. As Professor Emeritus of Economic Geology, Clays, and Industrial Minerals, he plans to continue his activities as long as he is able. He believes the best and highest-quality kaolin deposits are located in the Capim Basin in Brazil, the best sodium bentonites are in Wyoming, and the best calcium bentonites are in Greece, Italy, and Germany. He is currently involved in the study and development of a large palygorskite deposit in China. In addition, he is continually working on the kaolins of Georgia and adjusting his ideas on their environment of deposition and the effect of postdepositional alteration. Also, he is involved in exploration for bauxite with specific alumina, silica, and iron contents in Brazil and Suriname.

Combining Walter Keller’s donation of 650 specimens of clays and bauxites with Haydn’s 600 specimens probably makes the Indiana University collection the largest collection of clay minerals anywhere. Haydn has a very well-equipped laboratory for the study of clay minerals, which is now run by David Bish, who holds the Murray Chair of Applied Clay Minerals, established by Haydn and Juanita Murray in 2001. These facilities give Indiana University an active and ongoing clay minerals program.

Dewey Moore and Shelley Roberts**

* For an impression of what life was like for Haydn in the Pacific during WWII, see www.ibiblio.org/hyperwar/AAF/VII/AAF-VII-10.html.
** The authors found Wayne Bundy and Jessica Elzea-Kobel’s interview of Haydn in the CMS News (Spring 1998) to be helpful.
Open Access Journals – For Whom?

In December 2009, the White House Office of Science and Technology Policy organized an online public forum to discuss public access to data and publications that are based on federally funded research. According to the announcement in the Federal Register, “The administration is dedicated to maximizing the return on Federal investments in R&D.” Such US government backing, in addition to that of several European governments and funding organizations, will give new momentum to the movement for “open access” journals, that is, journals that are freely available to all readers. Various advocates, from individuals to universities, have supported open access to published papers since the establishment of the Internet, and many commented favorably about the idea on the White House blog. With the steady rise of subscription prices, both for libraries and for individuals, open access to journals sounds very appealing. But the likely consequences of a comprehensive open access policy may not be what the advocates imagine or have emphasized.

There are many good arguments for open access journals. Papers that are published in an open access journal can be read without charge by anyone with Internet access. Scholars, students, and others whose libraries might not be able to afford important journals can, nevertheless, read open access articles. Perhaps open access papers would, therefore, be more widely read and cited. If research is funded with public grant money, it seems unreasonable that a private journal publisher should profit from that research. Universities, too, provide support for faculty and student research. Shouldn’t the university be able to guarantee that its students, alumni, and other constituents have unlimited access to the papers published by its faculty? And if papers can be published online with no cost for printing, paper, and postage, shouldn’t online journals be free?

Although I would like every interested person to be able to read American Mineralogist and Elements papers online, the reality of open access publishing has a number of serious drawbacks. Most respected scientific journals are expensive to produce, whether published by a nonprofit society like MSA or by a for-profit publisher. For American Mineralogist, the current cost is about $250 per page. Why should it cost so much when the author prepares the text and figures, and when peer-review is done by volunteers? Part of the reason is that there is considerable management and editing needed to get a paper from submission to final professional form, beyond the excellent work done by our editors, associate editors, and reviewers. American Mineralogist has a staff of two and employs freelance help, which means an office, salaries, benefits, etc. There are expenses for manuscript tracking, copyediting, page layout, printing, mailing, computers, supplies, Internet service, online posting, subscription management, archiving, storage, accounting, audits, and more. Some of these costs, perhaps 20%, could disappear if there were no paper copies of the journal printed and there were no subscriptions. But most would not. Currently, subscriptions to American Mineralogist by libraries and individuals, along with a growing income from online access through GeoscienceWorld (GSW), cover the bulk of these expenses. Authors who can pay also contribute through their voluntary payment of the $75 page-charge fee, offset orders, and charges for printing in color. These author contributions offset expenses that otherwise would need to be supported by subscriptions. As a nonprofit publisher, with a primary goal of advancing research in mineralogy, crystallography, geochemistry, and petrology, MSA has always valued keeping subscriber costs down.

If American Mineralogist and other journals were open access, there would be no subscription income, and other sources of income would be needed to pay each journal’s expenses. The most commonly mentioned alternative is for authors to pay the entire cost of publication. Those authors who have sufficient funds to pay the estimated $250 per page fee would be able to publish in American Mineralogist. However, those authors who today can publish for free in American Mineralogist would have to find another publisher if they were not able to pay. Open access would be “open” only for the readers, not for the authors. Those with money would be able to publish. Those without money would not be able to publish. Alternatively, MSA could increase dues to about $350 per member to make American Mineralogist free to authors and to readers, or hope for that never-identified alternative source of support often alluded to by open access supporters.

It is already possible to publish articles in American Mineralogist that are freely available to all readers online, and several authors have chosen that route. To do so, the authors must pay the current full cost of publication ($250 per page). That makes American Mineralogist what some have termed a “hybrid journal.” Other hybrid journals can be found with open access fees ranging from $800 to $3000 per article. I urge those who have grant or university funds to pay for open access to do so. Open access fees, as with the voluntary author page charges and the income from GSW, would be used to keep subscription rates affordable. But if you value top scientific journals, like American Mineralogist, and if you value peer review, careful editing, consistency, and professional production, don't insist that all papers be open access without offering a realistic source of support. Our current, nonprofit business model works well—paying the bills with reasonable subscription charges and author payments. Open access would end American Mineralogist as we know it. Let’s keep our journal and keep it great.

John Brady (jbrady@smith.edu)
2010 MSA President
NOTES FROM CHANTILLY

• MSA will use electronic balloting for the 2010 election of MSA officers and councilors. The candidates are – President: David L. Bish; Vice President: George E. Harlow and Michael F. Hochella Jr.; Treasurer: Darrell Henry (runs unopposed for a second term); Councilors (two to be selected): Jay J. Ague, Pamela C. Burnley, Guy L. Hovis, and Kevin M. Rosso. Mickey Gunter continues in office as Secretary. Continuing as councilors are Penelope L. King, Marc M. Hirschmann, Wendy A. Bohrson, and Sumit Chakraborty.

MSA members will be sent a message to their current e-mail address with voting instructions in April. Make sure MSA has your most recent e-mail address! Those who do not wish to vote online can request a paper ballot from the MSA business office. As always, the voting deadline is August 1. Individuals elected to office decide on the direction of the Society. Voting is an important responsibility for all MSA members.

• MSA benefits from the labors of many volunteers. At the annual meeting, MSA recognized the contributions of Connie J. Manson, Olympia, WA, former geology librarian at the Washington Division of Natural Resources and president of the Geoscience Information Society. Connie exhaustively examined the archive of the American Mineralogist on the MSA website with two goals in mind: (1) She identified the references in GeoRef for the entire run of the American Mineralogist from 1916 to the present and provided information on possible additions, corrections, and links. (2) She checked the links in the tables of contents on the MSA website and compared the contents to the actual pdfs. Her work has resulted in thousands of live full-text links to the American Mineralogist archive being added to GeoRef. In addition, significant improvements in the quality of both the existing GeoRef references and the tables of contents links were made possible. This Herculean task was begun in March 2008 and ended in February 2009. Her efforts help to make the American Mineralogist more accessible to users—both web-surfers and GeoRef searchers alike—and MSA very much appreciates her efforts.

• If you or your institution has an aggressive spam blocker and you have not been getting the few announcements from MSA about new issues of the American Mineralogist online, voting, your renewal, or confirmation of your online orders, you may wish to see about allowing such messages to reach you. Otherwise, you will need to keep watch on the MSA website for them.

J. Alex Speer, (jaspeer@minsocam.org) MSA Executive Director

50- AND 25-YEAR MSA MEMBERS

The following individuals will reach 50 or 25 years of continuous membership in the Mineralogical Society of America during 2010. The MSA shows its appreciation for their long support of the Society by publishing their names in this list and by presenting them with 25- or 50-year pins, which are mailed in early January. If you should be on this list and are not, or have not received your pin, please contact the MSA business office.

50-Year Members
- Daniel S. Barker
- Petr Černý
- Gail E. Dunning
- Robert L. Freed
- Seymour Geller
- Richard P. Hight
- Wallace D. Kleck
- William F. Moll Jr.
- Duane M. Moore
- Bruce W. Nelson
- Donald C. Noble
- Norman J. Page
- Peter Robinson
- Della M. Roy
- William R. Smith
- Leendert Van Der Plas
- Hans Wondratschek

25-Year Members
- Paul M. Ashley
- Charles R. Bacon
- W. Robert Baragar
- Craig R. Bina
- Georges Calas
- Sumit Chakraborty
- Jeremy S. Delaney
- Denton S. Ebel
- Della A. Fleming
- Robert C. Liebermann
- Robert C. Liebermann
- William R. Smith
- Della A. Fleming
- Robert C. Liebermann
- William R. Smith

PACROFI X 2010

Las Vegas, Nevada, USA

June 7–10

on the University of Nevada, Las Vegas campus

Information and registration at http://geoscience.unlv.edu/PACROFI2010.html

INVITATION TO REQUEST A 2010–2011 MSA DISTINGUISHED LECTURER

The Mineralogical Society of America is again offering a lecture program for the 2010–2011 academic year, with the arrangement that the MSA will pay travel expenses of the lecturers, and the host institutions will be responsible for local expenses, including accommodation and meals. The program will include three lecturers, one of whom resides in Europe. Depending on the response, one or more lecture tours will be arranged outside North America.

Names of the 2010–2011 Distinguished Lecturers and their lecture titles are not yet available, but will be posted soon on the MSA website. If your institution is interested in requesting the visit of an MSA Distinguished Lecturer, check the website for lecturers and titles, and e-mail your request to the Lecture Program Administrator: Prof. Steven R. Dunn, Dept. of Geology & Geography, Mount Holyoke College, 50 College St, South Hadley, MA 01073-6419, USA; e-mail: sdunn@mtholyoke.edu; tel.: +1 (413) 538-2531; fax: +1 (413) 538-2239. The Lecturer program is designed to run from September 2010, through April 2011. Lecturer requests received by May 12, 2010, will be given priority. Late applications will be considered on a space-available basis. In making your request please include (1) airport proximity and travel time to your institution, (2) the name of a contact person at your institution for the months of May and June (when schedules will be assembled), (3) contact e-mail addresses and phone numbers, (4) flexibility on Lecturer preference, and (5) for schools outside the U.S. the starting and ending dates of your academic term. Because of travel and schedule constraints, it is normally not possible to satisfy requests for tightly constrained dates such as seminar days.

VOTE

2010 MSA ELECTIONS

April 2010
FROM THE PRESIDENT

In late 2009, the Association of Applied Geochemists elected five new councillors to serve for a two-year period, joining 18 other Council members to steer the association on behalf of its 600 members. These Council members are domiciled in Canada, USA, Chile, Brazil, UK, Netherlands, Italy, France, South Africa, China, and Australia, and represent industry, government, and academia. Their diversity in terms of both geographic spread and employment sector reflects that of the whole association, and shows that the AAG is a true international organization that caters to all scientists associated with applied geochemistry. However, hidden in the diversity of its members is another aspect: the experience they bring to AAG. For example, of the five newly elected councillors, one is a French-trained geochemist who has explored for mineral deposits in the Middle East, Africa, and the Mediterranean, and another is an Australian-trained geochemist who has taught courses on applied geochemistry in India.

The benefits of a Council spread throughout the world are in part offset by a few opportunities they have to meet in person. As a consequence, the affairs of the association are dealt with by twice-yearly telephone hook-ups, with more pressing matters resolved by e-mail. The rarity of the opportunities to meet underlines the importance of AAG’s biennial meeting, the International Applied Geochemistry Symposium (IAGS). April 2010 marks the 44th anniversary of these meetings, the first having been held on 20–22 April 1966 in Toronto. Following the second meeting in Golden (Colorado) in 1968, a group of geochemists, including Alan Coope, John Hansuld, and Bob Garrett, started up the Association of Exploration Geochemists (now the AAG). Of note is that the first symposium volume was compiled by Elion Cameron (and published by the Geological Survey of Canada) who, although now retired, continues to be active in the association and judiciously looks after AAG’s financial affairs. Since then, symposia have been held in locations throughout the world, including Tel Aviv, Beijng, Vancouver, Perth, Santiago, Dublin, and Oviedo. At these symposia, AAG members can attend a plethora of oral and poster presentations related to exploration and environmental geochemistry, join in field excursions, and experience the culture of the host country via a range of symposium-related events. The impetus for these symposia and the eventual creation of the Association of Exploration Geochemistry (AEG) was the huge amount of interest in exploration geochemistry in Canada; so it is fitting that the next IAGS, in Rovaniemi (Finland) in August 2011, will be in large part hosted by the Finnish Geological Survey (GTK). This organization has had a long history of exploration geochemistry programs, including the development and implementation of techniques for detecting mineral deposits in glaciated terrains. I suggest that you have a look at its excellent website (www.iags2011.fi) and invite you to join AAG members at this symposium.

Paul Morris, AAG President

IOStipend

Acme Analytical Laboratories Ltd. and ioGlobal have taken the bold initiative of aiding students in the geosciences via the ioStipend. The ioStipend is a grant available to students conducting exploration-related geochemical studies at a recognized educational institution. The grant is in the form of analytical services using any package pro-

ElEmEnts

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ElEmEnts

FROM THE PRESIDENT

In late 2009, the Association of Applied Geochemists elected five new councillors to serve for a two-year period, joining 18 other Council members to steer the association on behalf of its 600 members. These Council members are domiciled in Canada, USA, Chile, Brazil, UK, Netherlands, Italy, France, South Africa, China, and Australia, and represent industry, government, and academia. Their diversity in terms of both geographic spread and employment sector reflects that of the whole association, and shows that the AAG is a true international organization that caters to all scientists associated with applied geochemistry. However, hidden in the diversity of its members is another aspect: the experience they bring to AAG. For example, of the five newly elected councillors, one is a French-trained geochemist who has explored for mineral deposits in the Middle East, Africa, and the Mediterranean, and another is an Australian-trained geochemist who has taught courses on applied geochemistry in India.

The benefits of a Council spread throughout the world are in part offset by a few opportunities they have to meet in person. As a consequence, the affairs of the association are dealt with by twice-yearly telephone hook-ups, with more pressing matters resolved by e-mail. The rarity of the opportunities to meet underlines the importance of AAG’s biennial meeting, the International Applied Geochemistry Symposium (IAGS). April 2010 marks the 44th anniversary of these meetings, the first having been held on 20–22 April 1966 in Toronto. Following the second meeting in Golden (Colorado) in 1968, a group of geochemists, including Alan Coope, John Hansuld, and Bob Garrett, started up the Association of Exploration Geochemists (now the AAG). Of note is that the first symposium volume was compiled by Elion Cameron (and published by the Geological Survey of Canada) who, although now retired, continues to be active in the association and judiciously looks after AAG’s financial affairs. Since then, symposia have been held in locations throughout the world, including Tel Aviv, Beijng, Vancouver, Perth, Santiago, Dublin, and Oviedo. At these symposia, AAG members can attend a plethora of oral and poster presentations related to exploration and environmental geochemistry, join in field excursions, and experience the culture of the host country via a range of symposium-related events. The impetus for these symposia and the eventual creation of the Association of Exploration Geochemistry (AEG) was the huge amount of interest in exploration geochemistry in Canada; so it is fitting that the next IAGS, in Rovaniemi (Finland) in August 2011, will be in large part hosted by the Finnish Geological Survey (GTK). This organization has had a long history of exploration geochemistry programs, including the development and implementation of techniques for detecting mineral deposits in glaciated terrains. I suggest that you have a look at its excellent website (www.iags2011.fi) and invite you to join AAG members at this symposium.

Paul Morris, AAG President

IOStipend

Acme Analytical Laboratories Ltd. and ioGlobal have taken the bold initiative of aiding students in the geosciences via the ioStipend. The ioStipend is a grant available to students conducting exploration-related geochemical studies at a recognized educational institution. The grant is in the form of analytical services using any package pro-
SOCIETY NEWS

FROM THE PRESIDENT

With the support of the new council, and thanks to the hard work of our past presidents Catherine Mével and Patrick Cordier, I would like to pursue our goal of making the SFMC a vibrant, stimulating, convivial association; a society aware of the role of science in societal issues and of its impact on industrial research, industrial imperatives and public demands. In this period of deep reforms in French universities and at the CNRS, vice presidents Christian Chopin and Guy Libourel and I hope that the Society will become a recognized actor in fostering relationships between academic structures and researchers, particularly the promising young generation of scientists. Certainly the objectives are ambitious...and thrilling!

Anne Marie Karpoff, President, SFMC

SFMC ELECTION RESULTS FOR 2010–2012

President Anne Marie Karpoff (EOAT, Strasbourg)
Vice-Presidents Christian Chopin (ENS, Paris), Guy Libourel (ENSG-INPL, Nancy)
Secretary Étienne Balan (IMPMC, Paris)
Assistant secretary Maryse Ohnenstetter (CRPG, Nancy)
Treasurers Stéphanie Rossano (U. de Marne-La-Vallée), Anne-Line Auzende (UPMC, Paris)
Auditors Anne-Marie Boullier (LGIT, Grenoble), Jannick Ingrin (LMTG, Toulouse), Michel Madon (U. de Marne-La-Vallée)
Bulletin Editor Jean Dubessy (G2R, Nancy)

The Society thanks outgoing secretary Daniel Neuville and treasurer Audry Charpentier (CRPG, Nancy) for their valuable contributions, and councilors Martine Buatier, Bertrand Devouard, Michel Dubois, Dominique de Ligny, Dimitry Prêt and Jérôme Rose for four years of dedicated service.

WELCOMING NEW COUNCIL MEMBERS FOR 2010–2012

Muriel Andreani has been an assistant professor at the University of Lyon since 2008. She obtained her PhD in 2003 from the University of Grenoble, where she studied the deformation mechanisms of serpentine from the field to the TEM scale, and their implications for the behavior of active faults on continents. During a postdoc in Paris and Montpellier, she worked on fluid–rock interactions and deformation in the oceanic lithosphere. She combines the study of natural seafloor samples with experimental petrology and mineralogy, and is also interested in CO2 storage and new energy production.

Anne-Line Auzende obtained her PhD in Earth sciences from Clermont-Ferrand University in 2003. She worked on serpentine minerals involved in subduction processes, focusing on their microstructures and physical properties. She turned to high-pressure experimental petrology during a postdoc at IMPMC (Paris), where she studied Earth’s deep interior and element partitioning between lower-mantle phases and melts. She currently works as an assistant professor at Paris-Diderot University. Anne-Line is the new vice-treasurer of the Society.

Marc Blanchard is a research scientist at the Institut de Minéralogie et de Physique des Milieux Condensés (CNRS and UPMC, Paris). He applies atomistic simulation techniques to the study of processes occurring at the mineral–solution interface, such as the fate of toxic metals and isotope fractionations. His research also focuses on hydrogen speciation and atomic diffusion in nominally anhydrous minerals.

Valérie Chavagnac received a PhD in geochemistry in 1998 from the University of Bern and the University of Rennes, where she studied the behavior of the Sm–Nd isotope system during metamorphism. During her stay at MIT (USA), she studied Archean komatiites of the Barberton Greenstone Belt. She moved to the National Oceanographic Centre, Southampton (UK) in 2000 and studied oceanic hydrothermal activity. Since 2007, she has been a CNRS research scientist at the Laboratoire des Mécanismes et Transferts en Géologie in Toulouse. Her main research interest is the geochemistry of hydrothermal fluids, especially those rich in hydrocarbons and hydrogen.

Delphine Charpentier received her PhD in 2001 from the University of Nancy. Since 2005, after postdoc appointments at the University of Liverpool, G2R in Nancy and LMTG in Toulouse, she has been an assistant professor at the Franche-Comté University in Besançon. Her research interests are in geochemical and mineralogical transformations due to fluid–sedimentary rock interactions. She is particularly interested in processes involving clay minerals, in mass transfers and mineralogical changes in fault zones, and in redox modifications in iron-rich systems. She combines high-resolution mineralogical characterization with geochemical modeling.

Stéphanie Duchène has been an assistant professor at the Centre de Recherche Géologie et Pétrologie of the CNRS and University of Nancy since 1999. Her research is focused on Sm–Nd and Lu–Hf geochronology, chemical diffusion of major and trace elements in minerals, crystal growth and textures of magmatic rocks, exhumation kinetics of high-pressure rocks in mountain belts and crystallization kinetics in lava lakes.

Denis Testemale, after academic studies in physics, was attracted to hydrothermal geochemistry research. He has studied hydrogen bonding and ion pairing in supercritical aqueous fluids using synchrotron X-ray absorption and diffusion techniques. He focuses his research on metal transport in hydrothermal fluids, using in situ autoclave experimentation and synchrotron tools. He is currently a researcher at Institut Néel, CNRS (Grenoble) and is involved in the French absorption beamline for Earth Sciences, FAME, at ESRF.

23e RÉUNION DES SCIENCES DE LA TERRE (RST)

The Earth Sciences biennial meeting, jointly organized by the Fédération Française de Géologie (FFG), the SFG, the SFMC and the Université de Bordeaux, will be held in Bordeaux, France, from October 25 to 29, 2010. For more information, visit www.rst2010.epoc.u-bordeaux1.fr
**Geochemical Society**

**GEOCHEMICAL CAREER CENTER**

The Geochemical Society’s Geochemical Career Center is a web-based service open to the entire geochemical community offering an easy-to-use and highly targeted resource for online employment connections.

Employers can use the Geochemical Career Center to reach qualified candidates. For a nominal fee, employers can post job openings, search for qualified candidates based on specific job criteria, and create an online resume agent to e-mail qualified candidates. Through May 31, 2010, employers can take 25% off their job postings by using promotion code GCC25.

For job seekers, the Geochemical Career Center is a free service that provides access to employers and geochemistry jobs. In addition to posting resumes, job seekers can browse and view available jobs based on their criteria and save those jobs for later review if they choose. Job seekers can also create a search agent to provide e-mail notifications of jobs that match their criteria.

If you are looking for a job or have a job you want to post, go to the Geochemical Career Center at www.geochemsoc.org.

**CALL FOR NOMINATIONS FOR GS OFFICERS**

The Nominations Committee of the Geochemical Society is seeking names of potential nominees for the positions of treasurer and secretary for 3-year terms beginning on January 1, 2011. The incumbent treasurer is Louise Criscenti (Sandia National Laboratory), who has the option of running for another 3-year term. The incumbent secretary is Neil Sturchio (Argonne National Laboratory), who also has the option of running for another 3-year term. Potential nominees should have reputations of leadership in geochemistry and be willing to devote considerable time and effort to the work of the Society. Suggestions should be communicated by July 31, 2010, to any member of the 2011 Nominations Committee or to the GS business office. More information regarding the duties and responsibilities of Board positions can be found on the Geochemical Society website.

**GEOCHEMICAL SOCIETY BUSINESS OFFICE**

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**Kathryn Hall,** Administrative Assistant

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**ANNOUNCING THE 2010 GEOCHEMICAL SOCIETY AwarDEES**

The following awards will be presented at Goldschmidt2010 in Knoxville, Tennessee, USA.

**V.M. Goldschmidt Award**  
Minoru Ozima (Professor Emeritus, University of Tokyo)

**C.C. Patterson Award**  
Robert F. Anderson (Columbia University)

**F.W. Clarke Award**  
Thorsten Kleine (University of Muenster)

**Paul Gast Lecturer**  
Awarded jointly by the Geochemical Society and the European Association of Geochemistry.

Jérôme Chappellaz (Laboratoire de Glaciologie et Géophysique de l’Environnement)

**Geochemical Fellows**  
Geochemical Fellows are recognized jointly by the Geochemical Society and the European Association of Geochemistry.

Janne Blichert-Toft (Ecole Normale Supérieure de Lyon)  
Joel D. Blum (University of Michigan)  
Daniele J. Cherniak (Rensselaer Polytechnic Institute)  
Patricia Dove (Virginia Polytechnic Institute)  
William F. McDonough (University of Maryland)  
Scott M. McLennan (Stony Brook University)  
Robert Raiswell (University of Leeds)  
F. J. Ryerson (Lawrence Livermore National Laboratory)  
William E. Seyfried Jr. (University of Minnesota)  
Steven B. Shirey (Carnegie Institution of Washington)
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 visit our website at www.geochemsoc.org or contact the business office.

GS AT GSA DENVER

The 2010 Geochemical Society Program Committee and the new GSA Mineralogy, Geochemistry, Petrology, and Volcanology Division have worked hard to propose 38 sessions for the GSA meeting in Denver. Abstract submission for these sessions opens in April and will conclude on August 10. For more information on the next GSA meeting, visit http://geosociety.org/meetings/2010/. Below is a list of Geochemical Society–sponsored sessions and their primary organizers.

GEOCHRONOLOGY OF THE AMERICAN WEST
In Honor of the Careers of Bill Cobban and John Obradovich and the Roots of EARTHTIME (Samuel Bowling)

FronTiers in Geochemistry
Kinetics and Thermodynamics of Chemical Reactions in Earth Environments through Integrated Field, Experimental and Theoretical Studies: In Honor of J. Donald Rimstidt (Patricia Dove)

EARTHTIME
In Honor of the Contributions of James Mattinson to High-Precision U–Pb Geochronology (Samuel Bowling)

INNOVATIVE TECHNIQUES AND APPLICATIONS FOR DETRITAL THERMO- AND GEOCHEONOMIC DATA (Todd LaMaskin)

GEOCHEMISTRY AND MINERALOGY OF FOSSILS (Matthew Kohn)

MINERAL BEHAVIOR AND MOLECULAR-SCALE PROCESSES IN THE ENVIRONMENT (Aaron Celestian)

REDUCING THE ENVIRONMENTAL IMPACT OF URANIUM IN SITU RECOVERY (Ardyth Simmons)

MARINE REDOX EVOLUTION: CONTROLS AND CONSEQUENCES (Bradley Sageman)

SYMBIOSIS AS A DRIVER OF GLOBAL CHANGE IN ANCIENT AND MODERN EARTH SYSTEMS (Laurie Anderson)

Abstract submission deadline is August 10.

Mineralogical Society of America and Geochemical Society
Short Course Announcement

DIFFUSION IN MINERALS AND METALS
December 10–12, 2010
Napa Valley Marriott Hotel & Spa
Napa, CA, USA

(Convenor)

Convenors

Youxue Zhang
University of Michigan

Daniele Cherniak
Rensselaer Polytechnic Institute

More information and registration: www.minsocam.org
THE PETROGENESIS OF A-TYPE GRANITES AND RELATED ROCKS

Granites come in different flavors. Granitic suites of orogenic (O) character differ in fundamental ways from suites of anorogenic (A) granites, just like Oranges differ from Apples. Those of A type are less well understood and appreciated than those of O type, not only because they do not get much “air time” in university curricula, but also because they are inherently more challenging to understand from several points of view. There are standard metaluminous A-type granites, some displaying a rather reduced mineralogy, whereas others crystallized from an oxidized magma. To complicate matters, mildly peraluminous variants may be found also. In other intrusive complexes, the metaluminous members of the suite may be associated with peralkaline granites and related volcanic products of comenditic or pantelleritic tendencies. It is not unheard of to find nepheline-normative intrusive units closely associated with the peralkaline granites. And these suites may well be mineralized, for example, in tin, molybdenum, niobium, and the rare earths.

The December 2009 issue of The Canadian Mineralogist, a thematic one entitled The Petrogenesis of A-Type Granites and Related Rocks, was an outgrowth of the “Symposium on Magmatism, Crustal Evolution, and Metallogenesis of the Amazonian Craton” held in Belém, Brazil, in 2007. Many articles focus on Brazilian suites of Proterozoic age, but there are also fine contributions on Finnish, Norwegian, and Czech examples. Drs. Robert Dall’Agnol and Tapani Rämö acted as guest editors. The volume gave me detailed insight into recent interpretations into what is going on petrogenetically. I will single out two areas that excited me to the point of wanting to “get involved.” The first concerns the real challenge of explaining the mineralization at the Pitinga mine in northern Brazil. Two groups of authors, Costi et al. and Bastos-Neto et al., have investigated the mineralized Madeira granite, of peralkaline flavor, and come to rather different interpretations about the relative merits of fractional crystallization, liquid immiscibility, and hydrothermal processes to explain what they found. I was thrilled to edit these juxtaposed articles, and to realize that there are still interesting studies begging to be done to resolve the issues. As the Pitinga Sn–Nb mine is in production and will soon start to process the lens of massive cryolite, the questions raised go beyond the realm of academic discussions and do have a socioeconomic dimension.

I was also fascinated to read in detail about the long-term efforts of T. Andersen and his coinvestigators to systematically sample zircon in A-type granites in southwestern Fennoscandia. By carefully monitoring the Lu–Hf systematics of zircon in A-type granites emplaced in the interval 920–1170 Ma, three different crustal sources could be identified. The initial Hf isotope composition of the igneous zircon is compatible with mixing of Paleoproterozoic and Mesoproterozoic Fennoscandian crustal material with juvenile material derived from the sublithospheric depleted mantle. So there is hope! The petrogenetic antecedents of A-type granites can be decoded!

The final IGCP-510 symposium will take place in August 2010 in Helsinki. It promises to be an exciting exchange of views!

Robert F. Martin, Editor
The Canadian Mineralogist

2009 MAC TRAVEL AND RESEARCH GRANTS

MAC awarded 15 student travel and research grants in 2009 for a total amount of $12,125. Four grants were awarded to undergraduate students: Melissa Anderson (Brandon University), Yee Ping Chau (University of Calgary), Darren LeFort (St. Mary’s University), and Tingting Wang (University of Waterloo); five to MSc students: Suzanne Byron (University of Alberta), Taryn Gray (St. Mary’s), Varina Smith (McGill University), Albert Stoffers (Carleton University), and Eva Wadoski (University of Maine); five to PhD students: Christopher Charles (University of Toronto), Colin Cooke (University of Alberta), Matthew Izawa (University of Western Ontario), Dawn Kellett (Dalhousie University), and Adrian Van Rythoven (University of Toronto). We congratulate these deserving students and present highlights of their reports:

Suzanne J. Byron (University of Alberta) participated in the 10th Biennial Meeting of the Society for Geology Applied to Mineral Deposits (SGA), held in Townsville, Australia. She presented the results of her MSc in a talk entitled “Giant Quartz Vein Zones in the Great Bear Magmatic Zone, Northwest Territories, Canada.” Her studies were conducted under the supervision of Dr. S. A. Gleeson, and were focused on petrography, cathodoluminescence, fluid inclusion microthermometry, and stable isotopes of mineralized (Cu ± U) and non-mineralized giant quartz-vein systems. She also attended a field trip entitled “Breccias, Fluids and Copper Mineralization in the Mt. Isa and Cloncurry Region, NW Queensland,” where she found many similarities between the hydrothermal and IOCG deposits in Australia and the deposits in the Great Bear magmatic zone.

Colin Cooke is a PhD candidate at the University of Alberta. With financial assistance from a MAC student travel grant, Colin presented a talk and a poster at the 6th International Symposium on Ecosystem Behavior (BIOGEOMON) in Helsinki, Finland. Colin’s talk summarized recent efforts aimed at using lake-sediment geochemistry to reconstruct the over 1500-year history of mining and metallurgy at Cerro de Pasco, Peru, which was once the world’s largest silver mine. In his poster, Colin presented biogeochemical results from a unique ~200,000-year-old lake core from the Canadian Arctic. His results help to place 20th-century environmental change in a long-term perspective and highlight the role human activities have played.
Darren LeFort, with financial aid provided by a MAC travel grant, travelled to Granada, Spain, where he presented the findings of his bachelor's thesis at the 20th European Current Research on Fluid Inclusions Conference. Fluid inclusion studies are fast becoming an important method for interpreting geological systems and processes. His thesis at St. Mary's University in Halifax, Nova Scotia, documented the genetic link between a low- to intermediate-sulfidation epithermal-style process and an alkalic Cu–Au porphyry system at the Mt. Milligan Cu–Au deposit in British Columbia.

Taryn Gray, a second-year master's student at Saint Mary's University, Halifax, attended the Joint Assembly meeting in Toronto. She was especially interested in the sessions “Complex Processes of Metal Enrichment in Ore-Forming Systems,” chaired by Jean-François Moyan and Jacob Hanley, and “Recent Advances in Trace-Element and Isotopic Microanalysis of Accessory Minerals,” presided by Taryn Gray. She also used a portion of the grant to support her research. As she is comparing the geochemical and petrographic variation exhibited in two different volcanic complexes in New Brunswick, it is imperative that she demonstrate any variability in the composition of the source rock(s).

Matthew Izawa, a PhD student at the University of Western Ontario, demonstrated that bioalteration textures in basaltic glasses from in situ oceanic crust of the Ontong Java Plateau are associated with fine-grained titanite (Izawa et al., submitted to The Canadian Mineralogist). This study, however, was performed using a ~50 μm micro-XRD beam, and therefore each analysis contains many hundreds of individual bioalteration textures. A logical next step is to determine the mineralogy within a single tubular bioalteration structure. To this end, he has prepared electron-transparent ultrathin sections across a tubular structure using a focused ion beam and is in the process of characterizing these sections using a variety of electron, X-ray, and ion microbeam techniques. This research was greatly assisted by funding from the Mineralogical Association of Canada for preparation of the ultrathin sections.

Dawn Kellett, a PhD candidate at Dalhousie University, received a MAC research grant to date in situ monazite from the Himalayan orogen by the U(–Th)–Pb method at the NERC Isotope Geosciences Laboratory, UK. The dated samples are tectonites associated with the South Tibetan detachment system (STDS), a low-angle, normal-sense detachment system that formed parallel to and coeval with continental collision. The resulting monazite ages were combined with thermobarometric estimates to construct pressure–temperature–time paths for footwall and hanging wall tectonites, and these results are compatible with numerical model predictions that suggest the STDS was the upper boundary of a lateral, low-viscosity channel.

Dirk Schumann, a PhD student at McGill University in Montreal, participated in the 14th International Clay Conference, held in Castellana Marina, Italy (13–20 June 2009). He was an invited speaker at a session on the Cretaceous–Paleogene and Paleocene–Eocene boundary events. He presented his work on newly discovered “giant” magnetofossils in a talk entitled “Gigantic Biogenic Magnetite in Boundary Clays at the Paleocene–Eocene Thermal Maximum” (see Schumann et al. 2008, Proc. Nat. Acad. Sci. 105: 17648–17653). These new and hitherto unknown forms of magnetofossils were extracted from clay-rich sediments deposited during the Paleocene–Eocene thermal maximum in an area that is now the coastal plain of New Jersey, USA. He also presented a part of his PhD-related research on high-resolution transmission electron microscopy investigations of synthetically produced and naturally occurring 2:1 layer silicates.

Varina C. Smith (McGill University) received funding from MAC to help her collect data from vesuvianite crystals using a single-crystal X-ray diffractometer at McMaster University. Unit cell parameters were obtained on pairs of nonequivalent prismatic forms. The data collected through the diffraction study contributed another line of evidence for lowered symmetry in vesuvianite from Jeffrey Mine, Asbestos, Québec. This complemented the rest of her MSc thesis project, in which she investigated the role of growth steps in inducing disequilibrium using optical microscopy, atomic force microscopy, and electron microprobe analysis.

Albert Stoffers, an MSc student at Carleton University, used his MAC research grant to carry out oxygen isotope work on 20 volcanic-rock samples from the northern Sierra Nevada. Very little work has been done on volcanic rocks located between Mt. Lassen and Lake Tahoe, leaving a substantial gap in our understanding of the tectonic and volcanic evolution of the ancestral and modern Cascade arcs. The transition between the two may be abrupt, signifying a sharp lithospheric or slab boundary, or it may be gentle, suggesting a temporal change in geochemical characteristics as opposed to a geographical change. Albert will use whole rock, trace element, isotopic, and petrographical data to evaluate the nature of the transition between the modern and ancestral arcs.

Eva Wadoski (University of Maine) attended the 2009 Joint Assembly in Toronto, where she presented a poster entitled “Compositional Evolution of Tourmaline-Group and Associated Minerals from Pegmatites in the Larsemann Hills, East Antarctica” in the session “Tourmaline: An Ideal Indicator of Its Host Environment.” Her participation provided her an opportunity to receive valuable feedback, which she incorporated into her thesis manuscript. Her poster presented part of her master’s research, which combined microstructural observations with chemical composition data from six borosilicates (tourmaline-group minerals, prismatite, dumortierite, grandidierite, boralisite, and wendingite). By examining the reaction textures and chemical variations within tourmaline-group minerals and their associated borosilicates, she will evaluate the changes that occur in B-rich anatectic pegmatites.

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Elements 125 April 2010

11th INTERNATIONAL SYMPOSIUM ON METAL ENRICHMENT IN ORE-FORMING SYSTEMS

ONTARIO CANADA JUNE 21-24 2010
Dear Members of the DMG,

Balloting for the new council and committee members of the DMG closed at the end of November 2009. I would like to thank all the 342 DMG members who sent me their postal ballots. The ballots were counted on December 9, 2009, by J. Göske (council member of DMG) and three other DMG members. The results of the elections are as follows, with the number of votes in parentheses:

**VICE-PRESIDENT for 2010 and PRESIDENT-ELECT for 2011–2012** – Rainer Altherr (286)

**SECRETARY (2010–2011)** – Michael Meyer (304)

**TREASURER (2010–2011)** – Joachim Hoefs (301)

**ADVISORY COMMITTEE**
- (2011–2012) – Thomas Malcherek (258)

**EJM CHIEF EDITOR (2010–2011)** – Roland Oberhänsli (293)

**EDITOR DMG-FORUM (2010–2011)** – Michael Burchard (292)

**DGK LIAISON OFFICER (2010–2011)** – Ulrich Bismayer (296)


**ADVISORY COMMITTEE**
- (2011–2012) – Thomas Malcherek (258)

**EJM CHIEF EDITOR (2010–2011)** – Roland Oberhänsli (293)

**EDITOR DMG-FORUM (2010–2011)** – Michael Burchard (292)

**DGK LIAISON OFFICER (2010–2011)** – Ulrich Bismayer (296)


**VICE-CHAIRPERSONS 2010 and CHAIRPERSONS-ELECT 2011–2012** for the following sections:

**CHEMISTRY, PHYSICS AND CRYSTALLOGRAPHY OF MINERALS** – Susanne Schorr (57)

**GEOCHEMISTRY** – Thorsten Kleine (78)

**PETROLOGY AND PETROPHYSICS** – Alan Woodland (102)

**APPLIED AND ENVIRONMENTAL MINERALOGY** – Richard Wenda (66)

**COMMITTEES for 2011–2012:**

**ABRAHAM-GOTTLOB-WERNER MEDAL** – Hans Keppler, Walter Maresch, Gregor Markl, Klaus Mezger, Carsten Münker, Andrew Putnis, Wolfgang Schmahl (293)

**VIKTOR-MORITZ-GOLDSCHMIDT PRIZE** – Michael Bau, Susanne Faulhaber, Marcus Nowak, Uwe Reimold, Heinz-Günter Stosch (291)

**GEORG-AGRICOLA MEDAL** – Cornelia Boberski, Jürgen M. Göske, Thomas Holzapfel, Hans-Joachim Kleebe, Klaus Nickel (278)

**TEACHING AND UNIVERSITY AFFAIRS for 2010–2011** – Lutz Hecht, Patrick O’Brien, Burkhard Schmidt, Roland Stalder (275)

I congratulate the newly elected members of the DMG council and also thank all resigning council members for their efforts and commitment to the DMG. I wish you all the best for 2010 and hope to see you at the annual DMG meeting in Münster.

Yours sincerely,

**Falko Langenhorst**, President
NEW APATITE NOMENCLATURE

In 2008, with the goal of “tidying up” mineral nomenclature, a scheme for the application of suffixes, hyphens, and diacritical marks was published (Burke 2008). The historical context and full rationale of the nomenclature revision are provided in that paper.

Among the changes implemented in that revision were the renaming of fluorapatite, hydroxyapatite, and chlorapatite to apatite-(CaF), apatite-(CaOH), and apatite-(CaCl), respectively. Nomenclature changes made to these and other minerals with the apatite structure did not completely consider the structural complexities of these minerals. Furthermore, the new nomenclature changes could rationely be extended to other apatite-group minerals, for example, by changing pyromorphite to apatite-(PbCl). In addition, such naming replaces many traditional names given to honor worthy individuals.

For these and other reasons outlined by Pasero et al. (2010), an International Mineralogical Association (IMA) Commission on New Minerals, Nomenclature and Classification (CNMNC) subcommittee was convened to reevaluate the nomenclature of minerals belonging to the “apatite group” and to propose a new and consistent nomenclature for that group. This subcommittee included an international group of scientists, all of whom have worked on the structures and crystal chemistry of apatite-group minerals. Following the recently approved standardization of mineral group hierarchies (Mills et al. 2009), the apatite-group minerals, which have traditionally included phosphates (e.g. fluorapatite), arsenates (e.g. mimetite), and vanadates (e.g. vanadinite), have been expanded to form a “supergroup” that is composed of all minerals with the apatite structure, including silicates (e.g. britholite), silicate-sulfates (e.g. ellestadite), and sulfates (e.g. cesanite). The nomenclature recommendations put forth by this committee for the apatite supergroup have been accepted by the IMA-CNMC and published in scientific papers, treatises and museum catalogues over the last 150 years. The new mineral IMA 2008-009, approved without a name, is here named stronadelphithe. Apatite-(SiOH) is renamed fluostrophite. Delonite-(Ce) is renamed delonite. The new mineral IMA 2009-005 is approved with the name fluorbritholite-(Y).

2. Potentially new mineral species The following end-member compositions are eligible for status as distinct mineral species. The proposed name, if any, is given in parentheses: Ca$_2$Fe$_2$(AsO$_4$)$_3$(OH) (hydroxyphosphohedyphane); Ca$_2$Pb$_2$(PO$_4$)$_3$(OH) (hydroxyphosphohedyphane). Ca$_2$Sr$_2$(PO$_4$)$_3$F (new root name); Mn$_2$Ca$_3$(PO$_4$)$_3$Cl (new root name); Pb$_2$(SiO$_4$)$_3$(SiO$_2$)$_3$(OH) (hydroxyimattheddeite).

3. Minerals and mineral names which could be discredited The mineral ellestadite-(Cl) is not thought to exist and should be discredited; the name melanocerite-(Ce) should be discontinued [= tritomite-(Ce)].

4. Changes of status from distinct species to polymorphic variants Fermorite is the monoclinal polymorph of johnbaumite- [= johnbaumite-M]; clinohydroxyapatite is the monoclinal polymorph of hydroxyapatite (= hydroxyapatite-M); clinnomomitite is the monoclinal polymorph of mimetite (= mimetite-M).

5. Recognition of a new polymorphic variant A new monoclinal polymorph of apatite is recognized (chlorapatite-M).

6. Changes to end-member formulae The ideal chemical formula of morelandite is Ca$_2$Ba$_3$(AsO$_4$)$_3$Cl instead of Ba$_3$(AsO$_4$)$_3$Cl; the ideal chemical formula of deloneite is (Na$_2$O)$_3$(REE$_{0.25}$Ca$_{0.25}$)(Ca$_{0.75}$REE$_{0.25}$)$_{3.5}$ (CaNa$_{0.25}$REE$_{0.25}$) (PO$_4$)$_3$ F$_{0.5}$(OH)$_{1.5}$-.
Forty-three students from 13 countries attended the School. Lectures and practical exercises were delivered by Faiza Bergaya, George Christidis, Jan Elsen, Katja Emmerich, Giovanni Ferraris, Sabine Petit, Eric Pirard, Paul Sardini, Peter Scott, Michael Stamatakis and Tamas G. Weiszburg. A high academic level of teaching ensured the success of the School, and participants also enjoyed the beautiful Cretan landscape and the warm local hospitality. A volume in the series EMU Notes in Mineralogy, with chapters written on all the topics covered during the School, will be published in 2010. The book aims at becoming a reference textbook for lecturers and students in academic institutions dealing with the mineral sciences.

George Christidis, Technical University of Crete, Greece

INTERNATIONAL YEAR OF PLANET EARTH (IYPE), PLANET EARTH LISBON EVENT 2009

As a student in Earth sciences, I had the pleasure to be an ambassador for Canada at the closing event of the International Year of Planet Earth, held in Lisbon, Portugal, on November 19–22, 2009. The Planet Earth Lisbon Event 2009 (PEL2009) was organized by IYPE, the Portuguese National Committee for IYPE, and Bombazine, a professional event-organizing company. PEL2009 brought together scientists, politicians, and industrial leaders to celebrate the closing of the International Year of Planet Earth triennium (2007–2009). The aims of PEL2009 were to evaluate the results of the IYPE and launch new initiatives building on the IYPE legacy. The event was divided into three main sessions: Renewable Energy, Sustainable Land and Water Management, and Planet Ocean. These themes were discussed from the political, scientific, and industrial points of view. Furthermore, two students from each of the 80 IYPE nations were invited to the event to emphasize the important role for the next generations in reaching the sustainable development goals of the United Nations.

In the Renewable Energy session, I learned how Portugal became one of the leaders in the production of sustainable energy, and I discovered how palm oil can be used in tropical areas to produce energy sustainably. The Sustainable Land and Water Management session taught me to pay attention to how we use the land and how to get the most from each piece of land. Efficient water management is one of the key ways to reach this goal. The importance of understanding our oceans was emphasized in the Planet Ocean session. Being surrounded by scientists, politicians, and industrial leaders allowed me to diversify my knowledge in a broad spectrum of topics related to Earth science. The “Youth and Earth” conference was specifically dedicated to the invited students. Several organizations, such as Y.E.S., BIG Mama, and Earth Science Olympiads, provided tools to students who want to get involved and gave them ideas about how to reach a more sustainable planet Earth.

Speakers mentioned the importance of new initiatives to increase sustainability and the necessity of good communication and networking. Students were also invited to take part in a brainstorming session where they were asked to share their ideas on the question: What should our generation do to promote the geosciences to the younger generation?

Participating in this event allowed me to share my research with other students and to exchange ideas about Earth’s future with students, researchers, politicians, and industrial leaders with diverse backgrounds. I sincerely thank the IYPE organizers, the Portuguese National Committee for IYPE, and Bombazine, who provided the funding to allow me to attend this stimulating event.

Caroline Richer, University of New Brunswick, Canada
ASTROMATERIALS WORKING GROUP MEETING

The Mineralogical Association of Canada sponsored a one-day Planetary Science Research Symposium in the Earth Sciences Centre at the University of Toronto, held on October 7, 2009. The symposium consisted of 15 talks by researchers from across Canada, including five talks by students. The topics ranged widely, reflecting the diversity of planetary research currently being undertaken in Canada.

The common theme of the symposium was astromaterials, which are defined as solid samples of other planetary bodies in the solar system, including meteorites from asteroids, the Moon, and Mars; samples returned by robotic and human missions; and impact-affected and analogous materials on Earth. Attendees were treated to the latest-and-greatest results from the application of mineralogical, petrological, and geochemical methods to astromaterials. The morning consisted of a series of talks about meteorites. Topics included X-ray diffraction as a tool for assessing the degree of impact shock witnessed by enstatite chondrites (Izawa and coauthors, University of Western Ontario, UWO), organic matter in the Tagish Lake meteorite (Herd, University of Alberta), and constraints on the timing and duration of events in the early solar system from $^{26}$Al abundances in primitive grains in carbonaceous chondrites (Srinivasan, University of Toronto). In all cases the texture and mineralogy of the meteorites provided important context for interpretation of the data, showing that the fundamentals of petrography are alive and well in the Canadian astromaterials community.

The afternoon began with a visit to the Moon, led by UWO researchers who study “dark haloed craters” (Antonenko), the complex region in and around Schrödinger Crater (Shankar), and a feldspathic granulite lunar meteorite (Dammeier). The rest of the day consisted of talks about impact structures on Earth, including an overview of the ten largest (Thompson, University of New Brunswick), a new scheme for classification of impactites (Osiniski, UWO) and its application to the Rochechouart Crater (Sapers, UWO), and an overview of the Banc Ouellet Crater, possibly associated with the start of the YoungerDryas (Higgins, Université du Québec à Chicoutimi).

The diversity of talks and the participation of students bode well for the future of planetary science in Canada. The Astromaterials Working Group, originally commissioned by the Canadian Space Agency, consists of 16 members from across Canada with expertise in the curation and analysis of astromaterials (http://cms.eas.ualberta.ca/adwg/). The business meeting of the group, which took place the day following the symposium, provided an opportunity to share updates on meteorite collections and to continue to expand the network of astromaterials researchers and resources. The Astromaterials Working Group maintains that the application of advanced analytical tools available in this country to its world-class meteorite collections can raise the international profile of astromaterials research in Canada and establish Canada as a reliable and uniquely qualified world-class partner in space missions involving sample return.

Chris Herd, University of Alberta, Canada
The Mineralogical Association of Canada Short Course Series Volume 41, Secondary Ion Mass Spectrometry in the Earth Sciences – Gleaning the Big Picture from a Small Spot, is a collection of review papers edited by Mostafa Fayek. The papers were presented in a short course held prior to the Joint Assembly of AGU, GAC, MAC, CGU, and IAH, in Toronto, Ontario, May 22–23, 2009.

A variety of applications of secondary ion mass spectrometry (SIMS) to geological investigations are presented, in a mix of introductory and advanced discussions. While SIMS instruments have been employed since the 1950s in the semiconductor industry, the application to mapping chemical compositions of solid surfaces was pioneered by Raimond Castaing and George Slodzian (Paris, France) in the 1960s. Applications to Earth sciences have developed since the 1970s, and this volume presents a few of the methods most recently developed using modern instruments.

The introductory chapter by Richard Stern (University of Alberta) includes a glossary of terms for SIMS instrumentation and methods. This is a helpful tool for those interested in learning SIMS applications and understanding the literature. Stern emphasizes the point that useful analyses of geological materials depend on having standards with compositions similar to those of the unknowns being analyzed. The best analyses are obtained when a standard is mounted together with the unknown. High-quality analyses rely on chemically similar standards because the physical-chemical process of extracting ions from a solid surface is not theoretically constrained. For now, the key to reliable in situ analyses of minerals is to use appropriate standards measured under identical instrumental conditions.

Each of the next three chapters gives an introduction to the analytical setup options specific to different instruments and a presentation of geological applications. John Valley and Noriko Kita (University of Wisconsin) review oxygen isotope applications and provide a valuable discussion of the statistical analysis of SIMS results, ultimately based on useful ion yields (ions detected per atom sputtered). The volume of atoms available in the area of interest thus limits the analytical precision of SIMS data. Efficient detection of ions from a mineral surface depends on the chemical composition of the surface, ease of ionization of the element of interest, transmission of the mass spectrometer, sensitivity of the electrometers, and detection efficiency of the electron multipliers.

The third chapter, by Mostafa Fayek (University of Manitoba), focuses on H, C, N, and S analyses used for studying the interactions between minerals and organic compounds. The matrix effects of samples with mixed mineralogy or organic compositions remain the most difficult challenge to interpreting these analyses, which can routinely reach per mil–level precision. Because of the rapid development of SIMS in Earth science, many new studies show the versatile uses of different primary ion beams for sputtering and detection of secondary ions. It is now common to use an O+ primary ion beam to study electronegative secondary ions (e.g. C, F, S, and Cl). A Cs+ primary beam is best for measuring very low concentrations of H and C and for determining D/H ratios, but careful adjustment of the electron gun (for charge compensation) is required on the small-radius SIMS instruments due to the proximity of the secondary magnet to the charge-compensating electrons. Small shifts in the electron cloud during shifts of the magnet significantly affect the measured ion ratios. Discoveries of such instrumental effects and analytical solutions lead advances in this field.

Other light-element isotopic systems (i.e. B, Li, and Cl) are now increasingly used to investigate geologic problems. These isotopic systems vary by 10–100‰ in natural rocks and associated waters, potentially revealing more significant variations in source, temperature, and chemical conditions of formation than the major elements. The chapter by Graham Layne (Memorial University of Newfoundland) discusses many of the advantages and disadvantages of the analyses of B, Li, and Cl.

Contamination is a critical problem when studying trace elements; therefore presputtering the sample is essential for removing surface contaminants. Chemical pretreatments may also be used to remove contaminants from drilling, sawing, and polishing fluids that may contaminate samples. Sputtering of mineral surfaces to clean off contaminants is not always adequate, especially when analyzing nanominerals with high relative surface areas (e.g. clays). The discussion of mass resolving power and energy filtering as options to remove interfering species is well explained and demonstrates the versatility of SIMS for exploring many new isotopic systems. Layne discusses the effect of the instrument on production and detection of ions. Using standards, one can measure the instrumental mass fractionation. Emphasis is placed on the magnitude of the instrumental fraction for each isotope, which differs depending on the ionization potential and detection, but is inconsequential as long as the standards constrain the fractionation for each analytical session. A good analysis depends on limited instrumental drift during the analysis of unknowns.

Axel Schmitt (University of California, Los Angeles) gives a thorough review of uranium-series dating of minerals by SIMS and of applications of SIMS to Quaternary geology. The focus is on eliminating interferences from a variety of molecular ions. Such analyses require very high mass resolving powers, readily achieved by larger SIMS instruments. The advantage of such instruments in the future development of dating techniques lies in their high spatial resolution and low sample consumption.

Jerry Hunter (Virginia Tech), in the final chapter, addresses depth profiling, which is the primary technique for which SIMS is known in the semiconductor industry. Depth resolution is very good and ideal for evaluating chemical gradients due to diffusion of elements in minerals. This chapter provides an excellent discussion of the variables that affect ion yields and detection, the effects of surface roughening during analysis, methods to enhance ion yield (e.g. oxygen flooding), and the interpretation of data. A good summary is given of improvements to standard semiconductor depth profiling most applicable to geological samples.

Awareness of the SIMS analytical capabilities in the geological sciences is the goal of this volume, and it is a much-appreciated beginning. Mostafa Fayek notes in the preface that there are some omissions, particularly in the areas of geochronology, trace element analysis, cosmochemistry, ion imaging, and nanoSIMS. There are many applications of SIMS yet to be established as primary techniques for the geological sciences. The future requires collaboration between the scientists who study the physical chemistry of the ionization process and those who apply the analytical capability to geological problems. This volume is a good representation of the melding of these disciplines and bodes well for the future of SIMS as an important tool in the geological sciences.

Lynda Williams, Arizona State University

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Teaching Energy and Sustainability in the Field

Field-based courses have had a tremendous influence on my education and career by providing invaluable experience in making first-hand observations and grappling with complex scientific problems. As hard as we try as college instructors to make the classroom environment more interactive, there is no substitute for the impressions formed by students when they see the complexities of natural processes unfold in front of them. Field courses also require students to focus on a single topic for weeks at a time, free from the distractions of campus life and our “wired” society, resulting in more engaged learning. And finally, interaction with practitioners in the “real world” provides a perspective that cannot readily be obtained from academicians.

Last summer my colleague Rod Ewing and I taught a field course, and the experience was so rewarding that we thought it was worth sharing with the Elements readership. For many years we have taught courses in geology and ecosystem science at the University of Michigan Camp Davis Rocky Mountain Field Station (UM-RMFS) in Jackson Hole, Wyoming, USA. As we drove past energy-related sites, they piqued student interest, but we never had time to visit them or discuss the science of energy production in detail. In response to student interest, we developed the course Sustainable and Fossil Energy: Options and Consequences, which is devoted entirely to the study of energy systems. The premise is that students cannot fully understand and form opinions about the pros and cons of various energy options until they have seen the fuel cycles for themselves. We base the course curriculum around visits to energy facilities in Wyoming and Idaho, discussions with individuals working at these facilities, and experiments with energy usage and renewable energy systems at our field station.

Last summer we followed fuel cycles from the mining of raw materials all the way to the production of energy. We began with fossil fuels and a tour of one of the largest coal mines in North America, where we learned about coal extraction and postmining land remediation. We witnessed the vast railway system that brings coal from Wyoming to power plants across the country, and a railcar with 100 tons of coal became our standard unit of energy for comparison with other energy sources. This was followed by a visit to a coal-fired power plant, where students learned about the combustion process, turbine design and operation, the water needs of power generation, and the technologies used to control emissions of sulfur dioxide, mercury, and other pollutants. We also traveled through several oil and gas fields and visited an operating oil refinery as well as a former refinery site where we learned about groundwater and soil remediation. We also witnessed the vast railway system that brings coal from Wyoming to power plants across the country, and a railcar with 100 tons of coal became our standard unit of energy for comparison with other energy sources. This was followed by a visit to a coal-fired power plant, where students learned about the combustion process, turbine design and operation, the water needs of power generation, and the technologies used to control emissions of sulfur dioxide, mercury, and other pollutants. We also traveled through several oil and gas fields and visited an operating oil refinery as well as a former refinery site where we learned about groundwater and soil remediation.

Next we explored the nuclear fuel cycle, beginning with a visit to an in situ–leaching uranium mine. Of particular interest were the vast well-fields and the chemical processing of leachate into uranium oxide or “yellowcake.” A uranium mine ghost town provided the perfect setting to discuss the volatile economics of uranium. We visited the Idaho National Laboratory to learn about nuclear reactors and toured the first reactor ever to generate electricity (EBR-1) as well as an operating advanced test reactor. A highlight of this visit was peering into the water pool and observing the “blue glow” of the Cherenkov radiation caused by the spent fuel rods. The students were amazed to be standing less than 25 feet above spent nuclear fuel, and this experience had a profound effect on many of the students’ views of nuclear energy.

The second half of the course explored renewable energy resources. We surveyed and installed a micro–hydroelectric generator at the field station and studied the relationships between head, flow rate, and power generation. The light powered by this generator was a beacon reminding the class of the renewability of hydroelectric power. Next we visited a major power station on the Snake River, where we learned the intricacies of syncing turbines to the grid and discussed the challenges imposed by dramatic seasonal fluctuations in river discharge. This was followed by a visit to a small run-of-the-river hydroelectric plant that was recently certified as “low-impact” because it has only minimal impact on the stream ecology. The juxtaposition of these highly contrasting hydroelectric projects made the students stop and consider the differences between high- and low-impact installations.

The town of Jackson (Wyoming) provided an ideal setting for sparking a debate among the students over what it really means to be “carbon neutral.” Jackson has admirably initiated a plan to make the public works department carbon neutral by purchasing all its power from the low-impact hydroelectric plant that we visited, and the town pays a “green premium” for this energy. The town has also installed grid-connected photovoltaic systems on public buildings and at its wastewater treatment plant, and has constructed energy-efficient buildings. A visit to these facilities and discussions with town officials about the energy-sustainability project was a highlight for many students interested in sustainable systems.

The final alternate-energy visit was to the wind farms that are rapidly being built in eastern Wyoming thanks to recent tax incentives. We visited an operating wind farm and a facility being installed on the former site of an oil refinery. We had the opportunity to peer up into the vertical support of a wind turbine and were all impressed by its immense size. The students were able to form their own opinions about the noise associated with turbines and their impact on the aesthetics of western landscapes. We met with local experts and discussed the ecological and economic impacts of wind power, and the need to balance the variable output of wind generators on the grid.

As a culminating exercise, the students researched and reported on an alternate energy plan for UM-RMFS. Students monitored energy usage across the facility through a 24-hour cycle. They collected and analyzed data on energy production from an on-site solar photovoltaic array, a micro–hydroelectric turbine, and weather stations that provided wind-speed data. They also surveyed various parts of the property to assess the feasibility of hydroelectric power on two different rivers and to evaluate the potential of pumped storage. Finally, students were challenged to use all that they had seen and learned during the course to develop recommendations for an energy plan for the State of Wyoming. Judging from student reactions to this course, I am confident that it transformed many of their views on energy issues and technology. Classes such as this can be expensive, and we are grateful for support from the Graham Environmental Sustainability Institute and the Provost’s Office at the University of Michigan. When financially possible I urge educators to consider using field courses to maximize student–faculty interaction, allow students to interact with experts, and enhance student understanding. Needless to say, this is not the type of experience one can gain in the classroom, nor is it what most educators think of when they discuss the trend toward distance learning!

Joel D. Blum
Professor of Geological Sciences and Director of UM-RMFS
Ann Arbor, Michigan, and Jackson Hole, Wyoming, USA
| November | EURISPET: Experimental Petrology and Rock Deformation, Zürich, Switzerland. Details: Peter Ulmer, Swiss Federal Institute of Technology (ETH) Zurich, e-mail: peter.ulmer@erdw.ethz.ch; web page: www.eurispet.eu |
| November 13–14 | Bio- & Hydrometallurgy ’10, Cape Town, South Africa. Contact: Barry Wills, e-mail: bwill@smin-eng.com; web page: www.min-eng.com/biohydromet10 |
| November 14–18 | Third International Congress on Ceramics, Osaka, Japan. Web page: www.ceramic.or.jp/icc3 |
| November 19–20 | Eighth Swiss Geo-science Meeting, Fribourg, Switzerland. Web page: http://geoscience-meeting.scatweb.ch |
| December 8–11 | 11th European Meeting on Environmental Chemistry: Chemistry for the Environment, Portorož, Slovenia. E-mail: emec11@ung.si; web page: http://habotin.ung.si/~EMEC11 |
| December 10–12 | MSA and GS Short Course: Diffusion in Minerals and Melts, Napa, CA, USA. Web page: www.minsocam.org/MSA/SC |
| December 13–17 | American Geophysical Union (AGU) Fall Meeting, San Francisco, CA, USA. Web page: www.agu.org/meetings |
| January 23–28 | 35th International Conference and Exhibition on Advanced Ceramics and Composites, Daytona Beach, FL, USA. Web page: www.ceramics.org/meetings/index.aspx |
| February 27–March 3 | The Minerals & Metals Society (TMS) Annual Meeting, San Diego, CA, USA. E-mail: mtgserv@tms.org; web page: www.tms.org/meetings |
| March 21–25 | Chapman Conference on Climates, Past Landscapes and Civilizations, Santa Fe, NM, USA. E-mail: chapman-climatesociety@agu.org; web page: www.agu.org/meetings/chapman/2010/ |
| March 27–31 | 241th American Chemical Society (ACS) National Meeting & Exposition, Anaheim, CA, USA. Web page: www.acs.org |
| April 10–13 | AAPG Annual Convention & Exhibition, Houston, TX, USA |
| May 2–6 | Concurso Geologico Argentino, Neuquen, Republica of Argentina. E-mail: infog@congressoeligologo.org.ar; web page: www.concursogeologico.org.ar |
| May 15–19 | 12th European Workshop on Modern Developments and Applications in Microbeam Analysis, Angers, France. Web page: www.emas-web.net |
| May 22–27 | IUMAS-V: 5th Meeting of the International Union of Microbeam Analysis Societies, Inchon, South Korea. E-mail: sanson@samsung.com |
| June 20 | The Mineralogical Society’s Annual Meeting: Frontiers in Environmental Geoscience, University of Aberystwyth, Wales, UK. Details: N. Pearce, e-mail: np1@aber.ac.uk; web page: www.minsoc.org/pages/meetings/frontiers-2011/frontiers-2011.html |
| June 27–July 7 | XXVth International Union of Geodesy and Geophysics (IUGG) General Assembly, Melbourne, Australia. E-mail: ray.ca@sci.monash.edu.au; web page: www.iuugg2011.com |
| July 4–9 | Seventh Hutton Symposium on Granites and Related Rocks, Avila, Spain. E-mail: hutton@ugr.es; web page: www.seventh-hutton.org/meeting/Wel come.html |
| July 10–20 | EMU School – Bulk and Surface Structures of Layer Silicates and OXides: Theoretical Aspects and Applications, Rome, Italy. Web page: www.unive.ac.at/Mineralogie/EMU |
| July 20–27 | International Union for Quaternary Research (INQUA) XXVII Congress, Bern, Switzerland. Website: www.inqua.tcd.ie/congress.html |
| July 30–31 | MSA and GS Short Course: Applied Mineralogy of Cement and Concrete, Trondheim, Norway. Details: Maarten A.T.M. Broekmans, e-mail: maarten.broekmans@ntnu.no; website: www. icam2011.org |
When magmas of different composition, temperature, and viscosity come together, they commonly create spectacular igneous structures. The 1.37-billion-year-old Matamec Complex in the eastern Grenville Province (Québec, Canada) is known for its Cu-Ni occurrences and also for its fine examples of magma mingling and mixing involving gabbro-noritic and monzonitic magmas\(^1\), \(^2\). The Matamec Complex (80 km × 40 km) is composed of gabbro-norite sill-like bodies and lesser mangerite, monzonite, granite, and paragneiss, all metamorphosed to granulite facies. In PHOTO A, irregular to lenticular bodies of gabbro-norite (dark) are enclosed in a matrix of porphyritic monzonite. Note the lobate contacts, as well as the fine-grained, lighter-colored borders on the gabbro-norite bodies, indicating rapid cooling due to a temperature difference between the mafic and felsic magmas. In PHOTO B, elongation of the structures is due to flow of the mingling magmas. PHOTO C shows a hybrid zone between two contrasting magmas in which the more mafic magma is contaminated by rounded, plagioclase-rimmed, mesoperthitic orthoclase crystals (rapakivi texture) plucked from adjacent monzonitic magma. The yellow pencil-magnet and black marker provide scale.

Thomas Clark and André Gobeil
Ministère des Ressources naturelles et de la Faune, Québec

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