

# Elements

An International Magazine of Mineralogy, Geochemistry, and Petrology

October 2015  
Volume 11, Number 5

ISSN 1811-5209

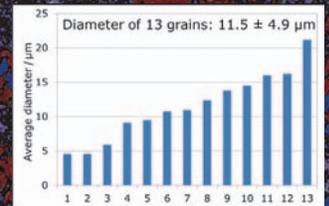
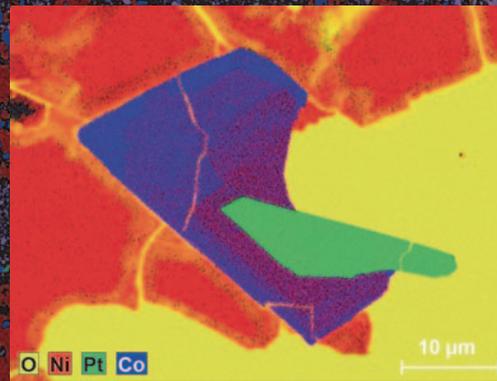
## Supergene Metal Deposits

MARTIN REICH and PAULO M. VASCONCELOS, Guest Editors

**Geological and Economic Significance**  
**Supergene Ores: From Nature to Humans**  
**Paleoclimatic Signatures**  
**Isotopes and Global Cu Cycles**  
**Electrochemistry and Corrosion**  
**Geomicrobiology**

# Micro-XRF Map of an Ore Thick Section

## Detailed EDS and Feature Analysis



Fe-KA Ni-KA Cu-KA Si-K

9 mm

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# Elements

An International Magazine of Mineralogy, Geochemistry, and Petrology



*Elements* is published jointly by the Mineralogical Society of America, the Mineralogical Society of Great Britain and Ireland, the Mineralogical Association of Canada, the Geochemical Society, the Clay Minerals Society, the European Association of Geochemistry, the International Association of Geochemistry, the Société Française de Minéralogie et de Cristallographie, the Association of Applied Geochemists, the Deutsche Mineralogische Gesellschaft, the Società Italiana di Mineralogia e Petrologia, the International Association of Geoanalysts, the Polskie Towarzystwo Mineralogiczne (Mineralogical Society of Poland), the Sociedad Española de Mineralogía, the Swiss Society of Mineralogy and Petrology, the Meteoritical Society, and the Japan Association of Mineralogical Sciences. It is provided as a benefit to members of these societies.

*Elements* is published six times a year. Individuals are encouraged to join any one of the participating societies to receive *Elements*. Institutional subscribers to any of the following journals—*American Mineralogist*, *Clay Minerals*, *Clays and Clay Minerals*, *Mineralogical Magazine*, and *The Canadian Mineralogist*—also receive one copy of *Elements* as part of their 2015 subscription. Institutional subscriptions are available for US\$165 (US\$180 non-US addresses) a year in 2015. Contact the executive editor (jross.elements@gmail.com) for information.

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Publications mail agreement no. 40037944

Printed in USA

ISSN 1811-5209 (print)

ISSN 1811-5217 (online)

[www.elementsmagazine.org](http://www.elementsmagazine.org)

[www.elements.geoscienceworld.org](http://www.elements.geoscienceworld.org)

 **GeoScienceWorld**  
Participating Publisher



Volume 11, Number 5 • October 2015

Supergene copper carbonates (green is malachite; blue is azurite) from the MacArthur mine, Yerington district, Nevada, USA. PHOTO CREDITS: FERNANDO BARRA, MARTIN REICH, AND CRISTIÁN PRADO

## Supergene Metal Deposits

Guest Editors: **Martin Reich** and **Paulo M. Vasconcelos**



### Geological and Economic Significance of Supergene Metal Deposits

Martin Reich and Paulo M. Vasconcelos



### Supergene Alteration of Ore Deposits: From Nature to Humans

Harald G. Dill



### The Paleoclimatic Signatures of Supergene Metal Deposits

Paulo M. Vasconcelos, Martin Reich, and David L. Shuster



### Copper Isotopic Perspectives on Supergene Processes: Implications for the Global Cu Cycle

Ryan Mathur and Matthew S. Fantle



### Predicting Geologic Corrosion with Electrodes

Devon Renock and Lindsay C. Shuller-Nickles



### The Geomicrobiology of Supergene Metal Deposits

Carla M. Zammit, Jeremiah P. Shuster, Emma J. Gagen, and Gordon Southam

## DEPARTMENTS

<b>Editorial – Resources and War</b> . . . . .	<b>299</b>
<b>From the Editors</b> . . . . .	<b>300</b>
<b>People in the News</b> . . . . .	<b>300</b>
<b>Meet the Authors</b> . . . . .	<b>302</b>
<b>Society News</b>	
Mineralogical Society of Great Britain and Ireland . . . . .	344
Società Italiana di Mineralogia e Petrologia . . . . .	346
Sociedad Española de Mineralogía . . . . .	346
Association of Applied Geochemists . . . . .	347
Mineralogical Society of America . . . . .	348
European Association of Geochemistry . . . . .	350
Geochemical Society . . . . .	351
Japan Association of Mineralogical Sciences . . . . .	352
Mineralogical Association of Canada . . . . .	353
Meteoritical Society . . . . .	354
Deutsche Mineralogische Gesellschaft . . . . .	356
International Association of Geochemistry . . . . .	358
<b>Meeting Report – 25<sup>th</sup> V. M. Goldschmidt</b> . . . . .	<b>361</b>
<b>CosmoElements – Meet Pluto and Charon... and Nix and Hydra!</b> . . . . .	<b>365</b>
<b>Elements Toolkit – The New Paradigm of Data Publication</b> . . . . .	<b>368</b>
<b>Book Reviews – Arsenic Environmental Geochemistry, Mineralogy, and Microbiology</b> . . . . .	<b>371</b>
Pyrite . . . . .	<b>372</b>
<b>Calendar</b> . . . . .	<b>373</b>
<b>Advertisers in this Issue</b> . . . . .	<b>373</b>
<b>Parting Shots – Wild and Wonderful</b> . . . . .	<b>375</b>
<b>Job Postings</b> . . . . .	<b>376</b>



**The Mineralogical Society of America** is for individuals interested in mineralogy, crystallography, petrology, and geochemistry. Founded in 1919, the Society promotes, through research, education, and publications, the understanding and application of mineralogy by industry, universities, government, and the public. Membership benefits include *Elements* magazine, access to the electronic version of the *American Mineralogist*, as well as discounts on journals, Reviews in Mineralogy & Geochemistry series, textbooks, monographs, reduced registration fees for meetings and short courses, and participation in a society that supports the many facets of mineralogy.

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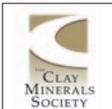
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**The Mineralogical Association of Canada** was incorporated in 1955 to promote and advance the knowledge of mineralogy and the related disciplines of crystallography, petrology, geochemistry, and economic geology. Any person engaged or interested in these fields may become a member of the Association. Membership benefits include a subscription to *Elements*, reduced cost for subscribing to *The Canadian Mineralogist*, a 20% discount on short course volumes and special publications, and a discount on the registration fee for annual meetings.

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**The Clay Minerals Society** (CMS) began as the Clay Minerals Committee of the US National Academy of Sciences - National Research Council in 1952. In 1962, the CMS was incorporated with the primary purpose of stimulating research and disseminating information relating to all aspects of clay science and technology. The CMS holds annual meetings, workshops, 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, discounts on the CMS Workshop Lectures, and *Elements*.

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**The Geochemical Society** (GS) is an international organization founded in 1955 for students and scientists involved in the practice, study, and teaching of geochemistry. Our programs include cohosting the annual Goldschmidt 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. GS annually recognizes excellence in geochemistry through its medals, lectures, and awards. Members receive a subscription to *Elements*, special member rates for GCA and *G-cubed*, and publication and conference discounts.

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Founded in 1985, the **European Association of Geochemistry** is a non-profit organization dedicated to promoting geochemistry internationally. The society is an active and dynamic organization of over 2800 members that leads the European Goldschmidt conference organization, publishes *Geochemical Perspectives* and *Geochemical Perspectives Letters*, recognizes scientific excellence through awards, organizes a Distinguished Lecture Program, sponsors workshops and conferences in Europe, supports students and Early Career Scientists, publishes job opportunities, newsletters, blogs, press releases and partners with other learned societies to strengthen geochemistry internationally.

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**The International Association of Geochemistry (IAGC)** has been a preeminent international geochemical organization for over 40 years. Its principal objectives are to foster cooperation in the advancement of applied geochemistry by sponsoring specialist scientific 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 Société Française de Minéralogie 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 *European Journal of Mineralogy, Elements*, and reduced registration fees for SFMC 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. It aims to advance the science of geochemistry as it relates to exploration and the environment, further the common

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**The Deutsche Mineralogische Gesellschaft** (German Mineralogical Society) was founded in 1908 to "promote mineralogy and all its subdisciplines 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. Ischermak, P. Eskola, C. W. Correns, P. Ramdohr, and H. Strunz. Today, the society especially tries to support young researchers, e.g. to attend conferences and short courses. Membership benefits include the *European Journal of Mineralogy, GMit*, 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, Plinius*, and *Elements*, and a reduced 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. Activities include the management of proficiency-testing programmes for bulk-rock and micro-analytical methods, the production and certification of reference materials and the publication of the association's journal, *Geostandards and Geoanalytical Research*.

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**The Polskie Towarzystwo Mineralogiczne** (Mineralogical Society of Poland), founded in 1969, draws 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. Membership benefits include subscriptions to *Mineralogia* and *Elements*.



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The International Mineralogical Association, the European Mineralogical Union, and the International Association for the Study of Clays are affiliated societies of *Elements*. The affiliated status is reserved for those organizations that serve as an "umbrella" for other groups in the fields of mineralogy, geochemistry, and petrology, but that do not themselves have a membership base.

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**The Sociedad Española de Mineralogía** (Spanish Mineralogical Society) was founded in 1975 to promote research in mineralogy, petrology, and geochemistry. The society organizes

annual conferences and furthers the training of young researchers via seminars and special publications. The *SEM Bulletin* published scientific papers from 1978 to 2003, the year the Society joined the *European Journal of Mineralogy* and launched *Macla*, a new journal containing scientific news, abstracts, and reviews. Membership benefits include receiving the *European Journal of Mineralogy, Macla*, and *Elements*.

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**The Swiss Society of Mineralogy and Petrology** was founded in 1924 by professionals from academia and industry and amateurs to promote knowledge in the fields of

mineralogy, petrology, and geochemistry and to disseminate it to 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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**The Meteoritical Society** is an international organization founded in 1933 for scientists, collectors, and educators to advance the study of meteorites and other extraterrestrial materials and their parent asteroids, comets, and planets. Members receive our journal, *Meteoritics & Planetary Science*, reduced rates for *Geochimica et Cosmochimica Acta*, which we cosponsor, the *Meteoritical Bulletin*, and *Elements*. We organize annual meetings, workshops, and field trips, and support young planetary scientists worldwide. Through our medals and awards, we recognize excellence in meteoritics and allied fields.

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**The Japan Association of Mineralogical Sciences (JAMS)** was established in 2007 by merging the Mineralogical Society of Japan, founded in 1955, and the Japanese Association of Mineralogists, Petrologists, and Economic Geologists, established in 1928. JAMS covers the wide field of mineral sciences, geochemistry, and petrology. Membership benefits include receiving the *Journal of Mineralogical and Petrological Sciences (JMPS)*, the *Ganseki-Koubutsu-Kagaku (GKK)*, and *Elements*.

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### RESOURCES AND WAR



Bernard Wood

In September 2015, we in Europe are being continually reminded of the plight of hundreds of thousands of Syrian refugees who are arriving at the southern and eastern borders of the European Union. Many are paying large amounts of money and risking their lives to be smuggled in small boats to Greece and Italy in the hope of finding safety from war. On reading some of the background to the Syrian conflict, I was struck by the likely influence of a shortage of resources in this Middle Eastern region. In a recent article, Kelley et al. (2015) argue that the war in Syria, which has multiple causes, has been greatly exacerbated by a multiyear drought between 2007 and 2011. The authors of the paper consider that long-term trends in precipitation, temperature, and sea-level pressure imply that anthropogenic forcing has increased the probability of severe and persistent droughts in the 'Fertile Crescent' and made the occurrence of a severe 3-year drought several times more likely than by natural variability alone. The events in Syria may, therefore, be regarded as an example of war and emigration explicitly linked to climate change, as Richard Seager commented in the London (UK) newspaper *The Independent* (8 September 2015). Syria was destabilised by the migration of 1.5 million people from the increasingly barren countryside to the peripheries of urban centres. At first sight, Syria's susceptibility to this drought arose partly because of the seemingly logical agricultural policy of increasing crop production by extracting groundwater and using that for irrigation. However, that policy was unsustainable. When the drought began in 2007, the agricultural system in the north-eastern region, which produced over two-thirds of the country's crops, collapsed (Kelley et al. 2015). The agricultural percentage of gross domestic product dropped from 25% to 17%, and a large fraction of livestock herds was lost with the corresponding drastic effect on the rural population. So, whatever the influences of 'Islamic State' and 'Opposition' fighters since 2011, Syria had already been significantly destabilised by the effects of drought and internal migration.

One doesn't have to look far back to find other conflicts in which access to resources may have played a significant role. David King, former Chief Scientific Advisor to the UK government, argued in a lecture to the British Humanist Association in 2009 that the Iraq war of 2003 was the first of this century's 'resource wars' in which powerful countries use force to secure valuable commodities. King considered that the war was more about access to energy supplies than the stated objective of destroying weapons of mass destruction. It doesn't take much imagination to concur

with King's prediction that the factors of population growth, ever increasing consumption of natural resources, and climate change will all put significant pressure on the planet and will lead to more 'resource wars'. Throughout history, in fact, access to resources, predominantly water, has played a major role in conflicts between nations. The Pacific Institute has a timeline and map of 343 historical conflicts involving water ([www2.worldwater.org/conflict/map/](http://www2.worldwater.org/conflict/map/)) stretching back to the Lagash-Umma (modern Iraq) border dispute of 2500 BCE. When one considers projected changes in rainfall as a response to climate change then Lebanon, Jordan, Israel, Iraq, and Iran are all likely to experience the stresses of declining water supplies. Elsewhere, the projected climate changes in sub-Saharan Africa (where the population is expanding) and in Central America (which is heavily reliant on agriculture) are likely to increase pressures on indigenous populations to emigrate en masse.

The current Syrian crisis has now led to about 4 million refugees temporarily accommodated in Turkey (~2 million), Lebanon (1.1 million) and Jordan (~1 million), with smaller numbers in neighbouring countries and in Europe. According to the United Nations High Commissioner for Refugees, displaced persons within Syria now number 7.6 million, which when taken with the number of refugees sums to ~60% of the country's pre-war population. Although some European governments have been unable to decide how best to respond to the arrival of the large numbers of Syrian refugees, many smaller local communities in the European Union have organised aid collections and extended a welcome. At a government level, the German government has expressed its willingness to accept all Syrian refugees who arrive in that country, perhaps as many as 800,000 this year. However, the lack of a coordinated response from the wealthier nations is worrying when one considers that the projected population growth and climate change in the Sahel region of Africa alone could lead within 40 years to >100 million people without sustainable food supplies (oasisinitiative.org). As senior UK politician Paddy Ashdown said in the UK newspaper *The Guardian* (8 September 2015), 'The numbers we see fleeing conflict will be dwarfed by the population movements we will see as global warming takes hold'.

Let us hope that we are able to encourage and enable clearer thinking by our political leaders on these issues of resources and migration.

**Bernard Wood**  
Principal Editor

Kelley CP, Mohtadib S, Canec MA, Seager R, Kishnirc Y (2015) Climate change in the Fertile Crescent and implications of the recent Syrian drought. *Proceedings of the National Academy of Sciences of the United States of America* 112: 3241-3246

## THIS ISSUE

Next time you see or hear a news report about the price of copper or plug your cellphone into an electrical outlet, perhaps you will think about supergene metal deposits. These deposits are the primary sources for the metals (e.g. Al, Fe, Cu) that we use to build and maintain society. Our thoughts about ore deposits are often focused on exploration, mining operations, metal prices, and metal availability. However, as the articles in this issue will reveal, supergene metal deposits are more than sources for critical metals. These deposits can also be “mined” for information about climate evolution, archeology, corrosion science, geomicrobiology, and so much more. Supergene metal deposits are valuable resources in more ways than one!

## FROM THE ELEMENTS' EXECUTIVE COMMITTEE

Once per year, representatives from the 17 participating societies of the *Elements* family meet in person for the annual Executive Committee (EC) meeting. This year, nine society representatives or their substitutes (see photo) attended the meeting on Sunday, 16 August, preceding the 2015 Goldschmidt Geochemistry Conference in Prague, Czech Republic. The EC's primary responsibility is for the financial oversight of *Elements* magazine, which includes an array of associated issues. The EC is pleased to report that *Elements* is on sound financial footing, a welcome change from the early days when many required tasks were donated by society employees. Thanks to the diligent efforts of our founding Executive Editor, Pierrette Tremblay, and our current Executive Editor, Jodi Rosso, to minimize costs and to budget conservatively, *Elements* is financially secure. The transition of Executive Editors was seamless and less costly than anticipated. As such, the contribution for being in the *Elements* family has not increased in the past four years and, for the immediate future, no increase is anticipated. Our largest sources of revenue derive from the contributions of participating societies, advertising, and downloads via GeoScienceWorld. Looking to the future, we anticipate a revamping of the *Elements* website, making it easier to link to our advertisers and to our online content.



The Executive Committee members who attended the 2015 Annual EC meeting, Prague, Czech Republic. Shown standing (left to right) are Kevin Murphy (for Mark Hodson, MSGBI), Tom Bullen (IAGC), Jacinta Enzweiler (for Michael Wiedenbeck, IAG), and Klaus Mezger (DMG). Shown seated (left to right) are Heather Jamieson (MAC), Barb Dutrow (EC Chair, MSA), and Juan Jimenez Millan (SEM). Not pictured are Piotr Kowalski (for Marek Michalik, MSP) and Sasha Krot (for Cari Corrigan, MetSoc).

In addition to our annual meeting, the EC conducts its business via conference calls twice per year—in the Fall and Spring—across 14 time zones! Votes are taken via email so that all representatives have an opportunity to share their opinion. The dedicated EC members are the critical linkage between *Elements* and the societies. They keep the societies' interests at the forefront while maintaining an open line of communication between *Elements* and the societies. Several new EC members have joined and several long-serving EC members have moved off. I am grateful for all of their insights, ideas, humor, and service to *Elements*. Should you have any comments, concerns or suggestions, please contact a society representative listed on the masthead page.

**Barb Dutrow**, Chair  
*Elements* Executive Committee



Congratulations to Joaquin Bastias, a PhD student from the University of Geneva (Switzerland). At the 2015 Goldschmidt in Prague, he was the raffle winner for a collection of issues from *Elements* inaugural year (2005).

## PEOPLE IN THE NEWS

## 2015 IMA MEDAL TO RODNEY C. EWING



The International Mineralogical Association is honored to present its 2015 Medal of Excellence in Mineralogical Sciences to **Rodney C. Ewing**.

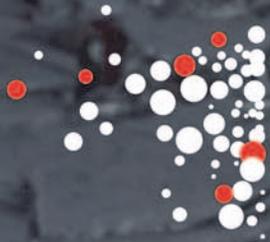
Rodney C. Ewing is a professor in the Department of Geological and Environmental Sciences in the School of Earth Sciences at Stanford University, and he is the Frank Stanton Professor in Nuclear Security in the Center for International Security and Cooperation at the Freeman Spogli Institute for International Studies.

Rodney C. Ewing is an intellectual pioneer. No scientist has made a greater contribution to our understanding of mineralogical solutions to the safe disposal of high-level nuclear waste and none have been more influential in developing the theoretical and experimental methods for studying the interactions between ionizing radiation and prospective storage materials. His eminence in the field of nuclear materials led to his appointment by US President Barack Obama to head the US Nuclear Waste Technical Review Board, the first mineralogist to lead this board.

Ewing has authored and coauthored over 650 research publications and edited or coedited 18 monographs, journal special issues, and proceedings volumes. He has published in some 100 different ISI journals on such subjects as long-term stability of nuclear waste forms; actinide mineralogy, crystal chemistry and geochemistry; mobility of radionuclides in the geological environment; nanocomposite materials; risk analysis in evaluating the safety of geologic repositories; and the development of policies for the protection of human health and the environment. He holds a patent for the development of a highly durable material for the immobilization of excess weapons plutonium. He is a founding editor of our very own *Elements*, which is now supported by 17 Earth science societies and associations.

Rod Ewing has received many honors, including the 2002 Dana Medal of the Mineralogical Society of America, the 2006 Lomonosov Gold Medal from the Russian Academy of Sciences, the 1997 and 2002 Hawley Medals from the Mineralogical Association of Canada. He will also receive the 2015 Roebling Medal of the Mineralogical Society of America and the American Geological Institute Medal in Memory of Ian Campbell. He also holds fellowships in the Mineralogical Society of America and seven other professional associations.

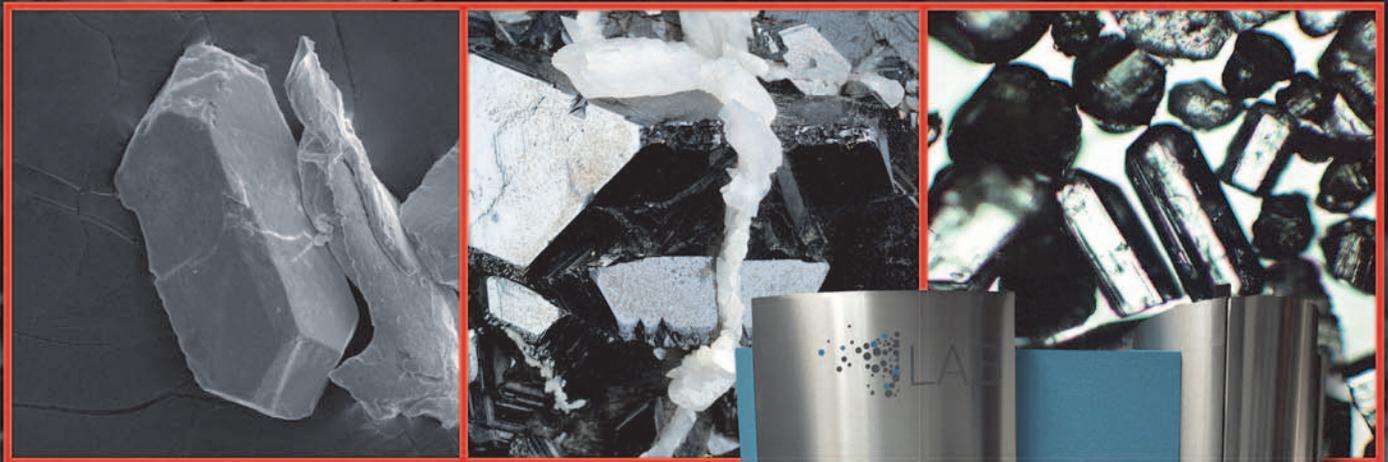
Please visit [cisac.fsi.stanford.edu/people/rodney\\_c\\_ewing](http://cisac.fsi.stanford.edu/people/rodney_c_ewing) for more information on Rodney Ewing, his research, and his other activities. A plenary lecture and presentation ceremony will be held at the 2<sup>nd</sup> European Mineralogical Conference in Rimini (Italy); on 11–15 September 2016 (see [emc2016.socminpet.it](http://emc2016.socminpet.it)).



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# Meet the Authors



**Harald G. Dill** studied (economic) geology, mineralogy and geography at the Julius-Maximilians-Universität Würzburg, the Friedrich-Alexander-Universität Erlangen-Nürnberg and the Rheinisch-Westfälische Technische Hochschule Aachen (all three in Germany). He holds a PhD in mineralogy, is a habilitated doctor (Dr. habil.) in economic geology, and is also a Dr. honoris causa. Over a 35-year career, he has worked in soil sciences (University of Bayreuth, Germany), economic geology, applied sedimentology, and technical mineralogy (at the Federal Institute for Geosciences and Natural Resources in Germany) in Hannover and has held a management position with the German Continental Deep Drilling Program. He has worked and taught on six continents. His “paperwork” includes 219 peer-reviewed papers, 101 abstracts and 1 patent. He was awarded the Quintino-Sella Prize at the Geological Congress, Florence (Italy).



**Matthew S. Fantle** is an isotope geochemist by training and is currently Associate Professor of Geosciences at Pennsylvania State University (USA), where he directs the Metal Isotope Laboratory, a clean laboratory facility that houses a Neptune Plus multiple collector inductively coupled mass spectrometer. He received a BA in Environmental Earth Sciences from Dartmouth College (New Hampshire, USA) and a PhD in geology from the University of California at Berkeley. His research interests revolve around applying stable metal and radiogenic isotope systems to global-scale geochemical cycling, seawater chemical evolution, and the fidelity of geochemical proxies over long time scales. Recent work includes exploring isotopic effects related to mineral precipitation, carbonate diagenesis, and hyperthermal events, oftentimes with the aid of simple numerical approaches.



**Emma J. Gagen** is a postdoctoral research fellow in geomicrobiology, in the School of Earth Sciences at the University of Queensland (UQ) (Australia). Emma is fascinated by the role that microorganisms play in geochemical processes and is currently investigating the role that microorganisms play in iron cycling systems. Prior to this, she was at the University of Regensburg (Germany) investigating microorganisms in the deep biosphere (below the seafloor). Her PhD was at UQ and was in the area of rumen microbial ecology.



**Ryan Mathur** is a professor at Juniata College (Pennsylvania, USA). He earned a BA in History and Geology from Juniata College in 1997 and PhD in economic geology and isotope geochemistry from the University of Arizona (USA) in 2000. He has worked on a large variety of ore deposits in many different areas, specializing in the geochronology of sulfide minerals and transition-metal isotope geochemistry, with the ultimate aim of developing new mineral exploration techniques and defining ore-deposit genesis.



**Martin Reich** is Professor of Geology at the University of Santiago (US) (Chile). He also holds appointments as Director of the Millennium Nucleus for Metal Tracing and is a Principal Researcher in the Andean Geothermal Center of Excellence at US. In 2001, he obtained a BSc and a professional geology degree from the University of Concepción (Chile), and in 2006 he was awarded his PhD in geology from the University of Michigan at Ann Arbor (USA). He currently studies the geochemistry and mineralogy of ore

deposits, specializing in their links to magmatism, tectonics, and climate. He was the recipient of the Society of Economic Geologists' Waldemar Lindgren Award in 2012.



**Devon J. Renock** received an MS in chemistry from Bowling Green State University (Ohio, USA) and a PhD in geology from the University of Michigan (UM) at Ann Arbor (USA) in 2010. His dissertation clarified the redox mechanisms that operate on iron- and arsenic sulfide mineral surfaces. After a postdoctorate at UM, he joined the faculty of the Department of Earth Sciences at Dartmouth College (New Hampshire, USA) in 2011. His research now focuses on understanding environmentally relevant processes at the mineral-water interface using a combination of surface-sensitive techniques (microscopic and spectroscopic), electrochemical methods, and molecular simulations.



**Lindsay C. Shuller-Nickles** is an assistant professor of mineralogy and radiogeochemistry in the Environmental Engineering and Earth Sciences Department at Clemson University in South Carolina (USA). She received her PhD in materials science and engineering from the University of Michigan at Ann Arbor (USA), where she was a Department of Energy Office of Civilian and Radioactive Waste Management Fellow. Her research combines experiments and computer simulations to understand the thermodynamic stability and kinetics that control the behavior of radionuclide-containing materials. Dr. Shuller-Nickles is a recipient of the Nuclear Forensics Junior Faculty Award and is part of a team that has been awarded a United States Department of Energy Experimental Program to Stimulate Competitive Research Implementation grant to study radioactive waste disposal.



**David L. Shuster** is an associate professor at the University of California at Berkeley (USA), where he is investigating the processes that occur at or near terrestrial, Martian, and lunar surfaces using laboratory-based geochemical observations. He is also developing analytical techniques and modeling tools to address these questions. Much of this work utilizes the relatively simple physical behavior of He, Ne, Ar, and Xe to constrain timescales, rates, and temperatures associated with orogenic and planetary processes and with chemical weathering. He is currently quantifying properties such as the diffusion kinetics, production rates, and open system behavior of cosmogenic nuclides. He pioneered  $^4\text{He}/^3\text{He}$  thermochronometry during his PhD research at Caltech and was awarded the American Geophysical Union's James B. Macelwane Medal.



**Jeremiah P. Shuster** is a postdoctoral research fellow at the School of Earth Sciences, University of Queensland (Australia). He received his PhD in 2013 from Western University (Canada). Jeremiah mainly researches how bacteria contribute to the biogeochemical cycling of gold, but also investigates what the (micro-)fossil record tells us of modern and ancient environments on Earth. His long-term goal is to fully understand the biogeochemistry of microbe-mineral interactions and how the lithosphere is able to support life.



**Gordon Southam** is a professor and the Vale-University of Queensland Chair in Geomicrobiology at the School of Earth Sciences, University of Queensland (Australia). His research on bacteria-mineral interactions encompasses microbiology, geochemistry and mineralogy, and has four themes: the role that bacteria play in the bioleaching of metal sulphides; the biogeochemical cycling of iron in near-surface environments (the canga of Brazil); the development of secondary gold (critical to the formation of dispersion halos and novel exploration methods development); and the control of greenhouse gas emissions via bacterial carbonation reactions. To Gordon, this research on life in extreme environments highlights the remarkable role that microbiology plays in many Earth-system processes.



**Carla M. Zammit** is a postdoctoral research fellow in the School of Earth Sciences at the University of Queensland (Australia). She researches the use that microorganisms have, or could have, for the mining industry. Such uses include how microorganisms break down sulfidic ores during mine processing (bioleaching); the development of microbial-based sensors for the detection of gold; and the in situ recovery of metals. This research bridges the fields of biotechnology and geology and will help improve mining processes and remediation. As we move towards the future, cost-effective, greener technologies are being sought out by the mining industry and are being met by the ever-expanding field of geomicrobiology.



**Paulo M. Vasconcelos** is a professor of geology at the School of Earth Sciences, University of Queensland (UQ, Australia). He received his BSc from the University of Kansas, his MA from University of Texas at Austin, and his PhD from the University of California at Berkeley (all three USA). At UQ, he built and runs the UQ-AGES facility, a noble gas laboratory that specializes in dating weathering processes, especially processes that operate, or have operated, in Australia, Brazil, and China. Paulo combines field characterization and sampling of supergene ore deposits, mineralogical and crystallographic investigation of ore minerals, and the development and application of geochronological tools to determine the timing of supergene mineral precipitation.

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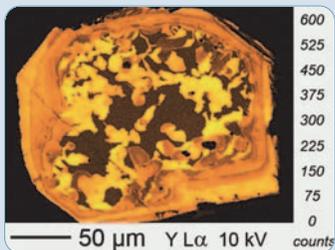
## Elemental & Isotopic Microanalysis in Geosciences



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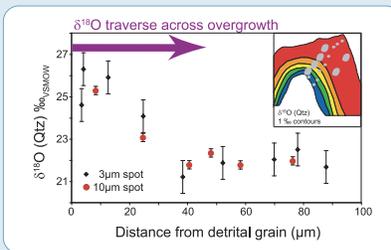
Distribution of Y in a grain from granite of Courmouls, France. Dated at  $343 \pm 20$  m.y by measuring Th, U, Pb and Y. Sample courtesy of Dr G. Wille, BRGM, France.



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In-situ oxygen isotopes analyses in Quartz overgrowth (50µm width) in the tenth-permil precision range at 10µm and 3µm lateral resolution. Courtesy of A.D. Pollington et al., *Geology* (2011).

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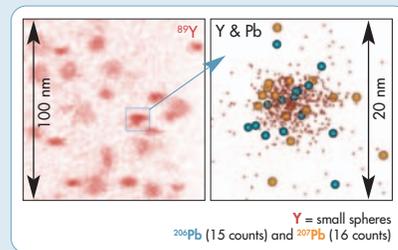
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Courtesy of Valley, J. et al. Hadean age for a post-magma-ocean zircon confirmed by atom probe tomography. *Nature Geoscience* (2014).



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# Geological and Economic Significance of Supergene Metal Deposits

Martin Reich<sup>1,2</sup> and Paulo M. Vasconcelos<sup>3</sup>

1811-5209/15/0011-0305\$2.50 DOI: 10.2113/gselements.11.5.305

**Supergene metal deposits form when common rock types or deeply buried primary ore bodies are exposed at or near the Earth's surface and undergo oxidation, dissolution and reconcentration of the metals. Supergene metal deposits are economically interesting because of their accessibility for extraction and increased grades. Scientifically they are attractive because of their mineralogical diversity and what they reveal about surficial history. Apart from supplying mankind's need for metals, supergene metal deposits provide clues about our past climate and offer an unparalleled opportunity to explore the long-term corrosion behavior of natural and man-made materials and their environmental impact.**

**KEYWORDS:** weathering, supergene processes, critical metals, strategic minerals, corrosion

## INTRODUCTION

Weathering and erosion are the Earth's primary natural mechanisms for redistributing mass on its surface, and these processes are driven by natural agents such as gravity, climate, animals, plants, and surface and ground waters. It is in this *Critical Zone*, i.e. Earth's complex outer layer of air, water, biota, organic matter and minerals, where combinations of geological, chemical, physical, and biological processes operate together on preexisting metal-bearing rocks to form supergene metal deposits. When rocks and ore deposits that were formed at high temperatures and high pressures are exposed at the Earth's surface (average  $T_{\text{atm}} \sim 15^\circ\text{C}$ ;  $P_{\text{atm}} \sim 1$  bar; and  $p\text{O}_2 \sim 0.2$  bar), their equilibrium is disturbed. This causes their mineral constituents to react and undergo transformations so as to adjust to the new lower temperatures, pressures, and higher oxygen concentrations and moisture conditions. Near-surface oxidation and leaching of originally deeply formed rocks and ore deposits are major ore-enriching (or ore-forming) processes. These processes may result in a two- to ten-fold increase in metal grades for such commodities as Cu, Al, Fe, Ni, Mn, U, Au and Zn. The resultant highly enriched supergene zone or "blanket" that forms above ore deposits (FIG. 1, LEFT PANEL) is usually accessible during the early stages of surface mining and contributes significantly to the overall viability of the mine. This has been the case since the dawn of civilization, when humans exploited the easily

accessible and colorful supergene metal ores (modern examples in Figs. 2A-C) for the production of goods, jewelry and weaponry (Dill 2015 this issue).

Apart from being hosts for economically important metals, supergene ores are of great environmental interest due to the significant isotopic fractionation of the metals from their primary sources to their later secondary, distal, sinks (Mathur and Fantle 2015 this issue). The metal fractionation processes provide natural analogues for the dissolution, transport, and subsequent deposition

of metals in man-made environments. For example, mining and mineral processing generates large volumes of waste material, including waste rock, mill tailings, and mineral refinery slags. Through the process known as acid rock drainage (or mine drainage), the oxidative dissolution of sulfides from ores and from mine wastes can release significant amounts of toxic heavy metals (e.g. Pb and Hg) and metalloids (e.g. As and Se) into the environment. Both aerobic and anaerobic microorganisms can actively contribute to supergene oxidation and leaching of ore deposits and mine wastes. They have a profound effect on the geochemistry of mineral dissolution and precipitation, which ultimately promotes changes in metal speciation, mobility and even toxicity (Zammit et al 2015 this issue).

The weathering processes that lead to ore formation are complex, and they occur over a variety of timescales (tens of years to millions of years) to produce enrichment patterns from mineral grain (micron to centimeter) right up to deposit (meter) and even district (kilometer) scales. The formation of supergene enrichment profiles involves dissolution of rock material, transport of soluble elements, and precipitation of new ore minerals. These processes are highly sensitive to tectonic, climatic, and biological forcing. This sensitivity is a boon to geochronologic studies. For example, one could investigate multiple weathering events using ore deposits and thereby determine long-term rates of geochemical, geomorphological and paleoclimatic processes (Vasconcelos et al. 2015 this issue). Constraining such rates is relevant not only to quantify the magnitude of geological processes or climatic events but also helps in assessing the long-term behavior of man-made materials. For example, supergene deposits are natural analogues for corrosive processes and so can provide information that can enable us to build better repositories for nuclear fuel waste and to predict how such repositories will behave over long timescales and under different climatic and geologic scenarios (Renock and Shuller-Nickles 2015 this issue).

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## SUPERGENE ENRICHMENT

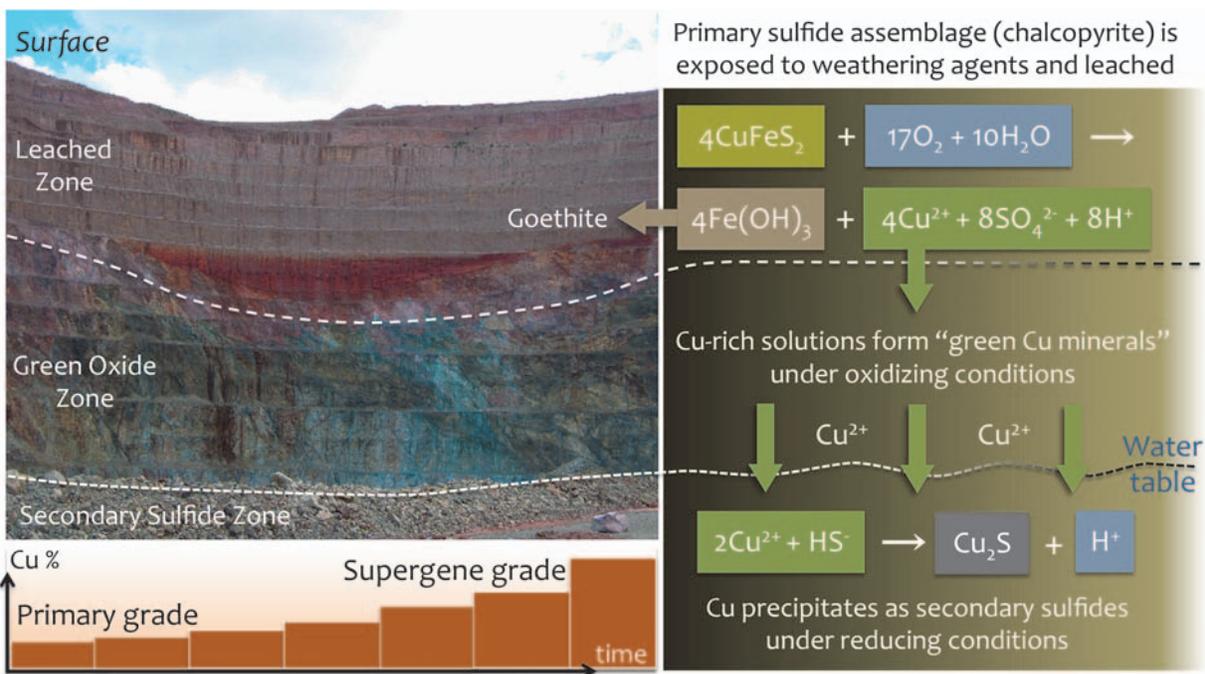
The phenomenon known as *supergene enrichment* refers to the secondary, in situ, accumulation of metals (e.g. Cu, Zn, Ag, Au, Ni, or U) as a result of three essential processes: (1) the electrochemical *oxidation* of primary sulfides, oxides or native metals (e.g. native copper Cu(0) to Cu(II)) (2) the *transport* of the released metals as soluble metal species (e.g.  $\text{CuSO}_4^0$ ,  $\text{AuCl}_4^-$ ); and (3) the *reprecipitation* of the metals by reduction (e.g. Cu(II) to native copper Cu(0)), by supersaturation (e.g.  $\text{Mg}^{2+}$  in magnesite deposits), or by cation-exchange (e.g.  $\text{Ni}^{2+}$  exchange for  $\text{Mg}^{2+}$  in smectite- or serpentine-group minerals). In particular, oxidation processes leading to mineral leaching are commonly catalyzed by specialized Fe- and S-oxidizing bacteria; oxidation processes are also active in the surficial vadose zone and the capillary fringe above the water table. Leaching processes also respond to changes in physicochemical properties, such as the partial pressure of oxygen ( $p\text{O}_2$ )—and its effect on the redox potential (Eh)—and the activity of  $\text{H}^+$  of descending aqueous solutions (Sillitoe 2005; Reich et al. 2009; Taylor 2011).

In FIGURE 1, the process of supergene enrichment of metals is exemplified by the Santa Rita (Chino) porphyry Cu deposit in New Mexico (USA). In most porphyry ore bodies, the stepwise hydrolysis and oxidation of primary pyrite-bearing assemblages leads to a decrease in the pH of descending groundwaters and the liberation of oxidized sulfur as  $\text{SO}_4^{2-}$  anions. There is a simultaneous breakdown of chalcopyrite ( $\text{CuFeS}_2$ ), which produces soluble  $\text{Cu}^{2+}$  ions that are transported downwards, encountering progressively greater reducing conditions deep into the profile. This process is accompanied by “capping,” the precipitation of iron oxyhydroxides in the leached zone from which Cu is removed. The thickness of the leached cap is highly variable but can reach several hundred meters in porphyry Cu deposits, particularly when the water table was deep enough during the supergene oxidation and enrichment phase (Taylor 2011).

Copper is concentrated within the subjacent oxide zone, which forms laterally extensive deposits composed of assemblages called “green oxides” or “copper oxides” (FIG. 1, LEFT PICTURE). This mineralogically and compositionally complex layer is composed of copper minerals including oxides, sulfates, hydroxy-chlorides, carbonates, silicates, and native copper. Among the copper minerals that may be encountered are cuprite ( $\text{Cu}_2\text{O}$ ), tenorite ( $\text{CuO}$ ), brochantite [ $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ], chalcantinite [ $\text{CuSO}_4 \cdot 5\text{H}_2\text{O}$ ], antlerite [ $\text{Cu}_3\text{SO}_4(\text{OH})_4$ ], malachite [ $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ] (FIG. 2A), azurite [ $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ] (FIG. 2A), atacamite [ $\text{Cu}_2\text{Cl}(\text{OH})_3$ ] (FIG. 2C), turquoise [ $\text{CuAl}_6(\text{PO}_4)_4(\text{OH})_8 \cdot 4\text{H}_2\text{O}$ ], native copper ( $\text{Cu}^0$ ) and chrysocolla ( $\text{Cu}^{2-x}\text{Al}^x\text{H}^{2-x}\text{Si}^2\text{O}^5(\text{OH})^4 \cdot n\text{H}_2\text{O}$ , among many others.

The precipitation of “green oxide” mineral assemblages in the vadose zone is largely controlled by the enclosing rock type and pH (FIG. 3), forming thick (<200–300 m) layers containing ore with >1 wt% Cu grade. Furthermore, Cu and other metals dissolved in groundwater can migrate laterally when hydraulic conditions are favorable and form large “exotic-type” Cu-oxide deposits in gravel sequences that are far (distal) from the source.

Under more reducing conditions, the remaining Cu in the descending metal- and sulfate-rich solutions will form secondary sulfides in the saturated zone below the water table where free oxygen is almost absent ( $p\text{O}_2 \sim$  below  $10^{-40}$  atm) (FIGS. 1 AND 3). Formation of secondary sulfides occurs by replacement of Fe by Cu in the hypogene sulfides (pyrite ( $\text{FeS}_2$ ), chalcopyrite ( $\text{CuFeS}_2$ ), and bornite ( $\text{Cu}_5\text{FeS}_4$ ). The secondary chalcocite ( $\text{Cu}_2\text{S}$ ) occurs on top, where  $\text{Cu}^{2+}/\text{HS}^-$  is high, while covellite ( $\text{CuS}$ ) precipitates below, where  $\text{Cu}^{2+}/\text{HS}^-$  is lower (FIG. 3). Enriched Cu sulfide zones in porphyry Cu deposits are usually tens to hundreds of meters thick and can contain more than 1.5 gigatons of ore with 0.4–1.7 wt% Cu, invariably reaching higher Cu grades than those found in the primary (hypogene) ore body (John et al. 2010).



**FIGURE 1** Schematic representation of supergene oxidation and enrichment processes for Cu. (LEFT) Photo showing a supergene profile in the south pit of the Chino (Santa Rita) copper mine, New Mexico. There is a ferricrete channel in the center (deep red zone) with “green oxide” development below. PHOTO BY RYAN

MATHUR. (RIGHT) Diagram showing representative Cu oxidation and enrichment reactions as relevant to the zones in the adjacent photo. (BOTTOM LEFT) Schematic plot showing the increase in ore grade that results from multiple cycles of supergene metal enrichment.



**FIGURE 2** Examples of supergene mineral assemblages. (A) Supergene copper minerals from the Milpillas porphyry deposit in Mexico (northern Sonora). The green and blue minerals are the copper carbonates malachite [ $\text{Cu}_2\text{CO}_3(\text{OH})_2$ ] and azurite [ $\text{Cu}_3(\text{CO}_3)_2(\text{OH})_2$ ], respectively; the grey bands in the middle are cuprite ( $\text{Cu}_2\text{O}$ ). (B) Supergene alteration products of black uraninite ( $\text{UO}_2$ ) sample from Congo: lemon yellow schoepite [ $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12}\cdot 12\text{H}_2\text{O}$ ]; amber-colored becquerelite [ $\text{Ca}(\text{UO}_2)_6\text{O}_4(\text{OH})_6\cdot 8\text{H}_2\text{O}$ ]; orange curite [ $\text{Pb}_{3+x}[(\text{UO}_2)_4\text{O}_{4+x}(\text{OH})_{3-x}]_2\cdot 2\text{H}_2\text{O}$ ]. IMAGE FROM HAZEN ET AL. (2009). (C) Dark-green atacamite [ $\text{Cu}_2\text{Cl}(\text{OH})_3$ ] and orange copper iodide marshite ( $\text{CuI}$ ) from Mina Sur (Chuquicamata, Chile).

The presence of enriched supergene blankets often enhances the economic viability of metal mining operations, especially considering the fact that metal grades of the enriched sulfide zones can be up to 3–4 times higher than the primary sulfide grades (Sillitoe 2005, 2013). However, the often-complex mineralogy of supergene ores poses serious challenges to extractive metallurgy (or mineral processing), and many supergene enrichment blankets will remain unmined or unprocessed until such time as viable metallurgical processes can be developed. However, harvesting microorganisms from the supergene zone and using them in bioleaching (Zammit et al. 2015) is a promising avenue for a more efficient use of supergene deposits and their enriched blankets.

## SUPERGENE METALS AS COMMODITIES

### *Demands for Metals in a Sustainable World*

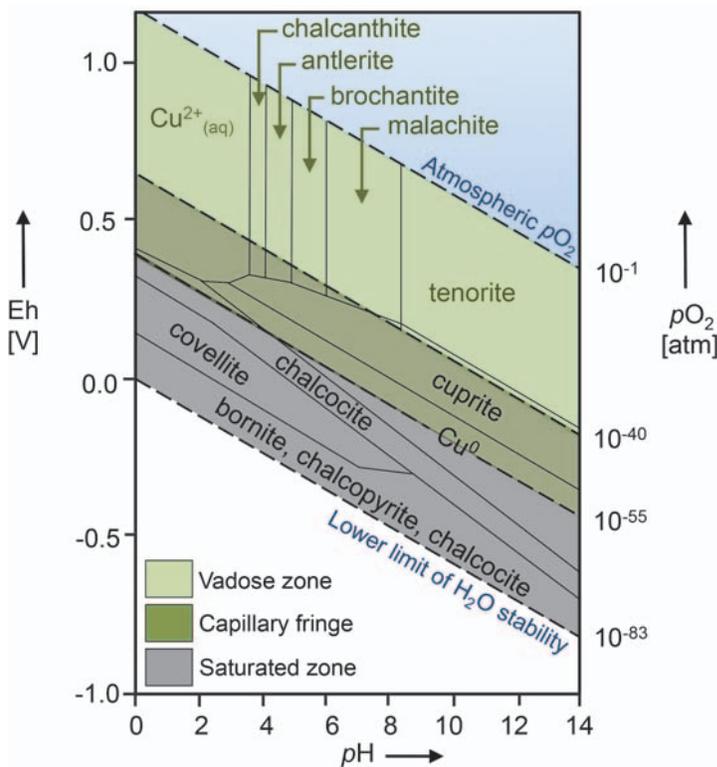
Mineral resources have been extracted and used by mankind since the Stone Age and are vital to modern civilization. Therefore, a thorough understanding of their distribution, consequences of their use, and the potential effects of mineral supply disruption is important for sound public policy (e.g. GSA 2013). Apart from the increasing demand for staples such as copper, gold, nickel and iron, demand has increased significantly for ores containing elements such as the rare earth elements (REEs), the platinum group elements (PGEs), as well as cobalt, beryllium, lithium, iodine, tellurium, gallium and rhenium, among others. This increased demand is due to these elements' use in a variety of manufacturing, high-tech, and energy applications, such as renewable energy devices, high-power magnets, and liquid crystal displays (LCDs). The minerals in which these strategic elements occur have been defined as "critical minerals" by the National Research Council (NRC 2008) because they are essential to modern society and yet subject to the risk of supply restriction.

## Supergene Ores as Sources of Strategic Metals

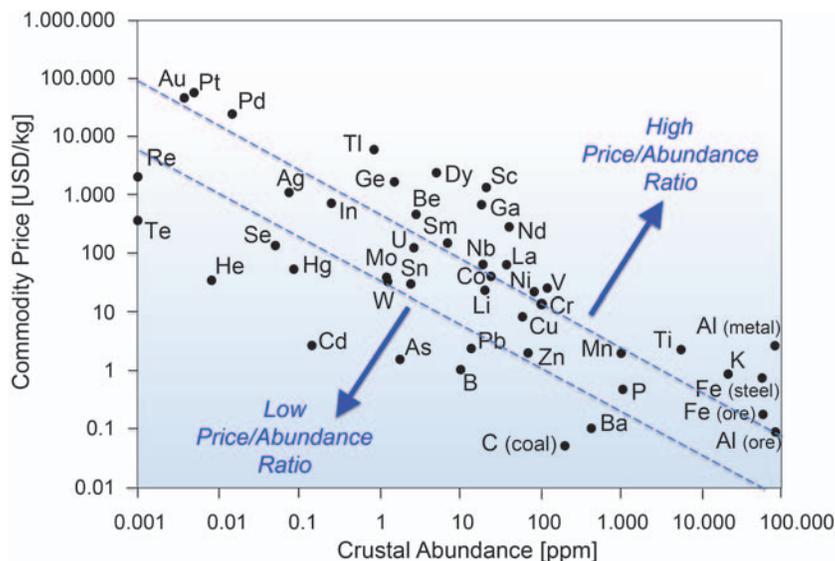
Supergene metal deposits are advantageous for exploitation due to their proximity to the surface and their increased metal grades. But they also provide valuable clues to the possible location, and the primary assemblages of, hidden ore bodies at depth. Supergene deposits, apart from their major metal components, can contain economic or near-economic concentrations of trace elements, making these deposits attractive targets for the exploration and exploitation of "critical metals"—those metals that are both essential for modern societies and subject to the risk of supply restriction (GSA 2013). In FIGURE 4, the price in US dollars per kilogram of metal commodities are plotted against the crustal abundance in parts per million (ppm). FIGURE 4 shows, in a broad sense, that the less abundant or less available elements are generally more expensive (Price 2013). This is the case for the "critical" REEs of dysprosium (Dy) and neodymium (Nd) and the noble metals of palladium (Pd) and platinum (Pt), among others.

## Base and Structural Metals

Supergene metal deposits contribute significantly to the world's supply of selected base metals (Cu, Zn, Ni, Co) and structural metals (Al, Fe, Ni, V). Giant porphyry Cu deposits contribute about 70% of the total global Cu inventory and have median grades at ~0.4 wt% Cu (with hypogene and supergene Cu grades often being reported together; Sillitoe 2013). Supergene grades in most deposits are higher than hypogene grades, and in the world-class northern Chile



**FIGURE 3** Graph of redox (Eh) and partial oxygen pressure ( $p\text{O}_2$ ) versus pH showing the stability of dissolved copper species and copper minerals in the supergene environment. The diagram maps out possible occurrence of stable phases under particular redox and pH conditions along a supergene profile. Conditions shift vertically from the more reducing, saturated zone in grey at the bottom (below the water table), to the more oxidizing conditions towards the top of the profile (vadose zone, where the soil and rock pores contains air as well as water). MODIFIED AFTER SILLITOE (2005).



**FIGURE 4** Price (in US dollars per kilogram) versus the crustal abundance (in parts per million) for selected elements. Supergene deposits are increasingly being explored and exploited for “critical metals,” which have high price/abundance ratios. MODIFIED FROM PRICE (2013).

copper district, protracted weathering has been a principal factor in this region becoming the greatest producer of Cu in the world (Sillitoe 2005; Reich et al. 2008, 2009).

Over the past decade, economic interest in supergene Zn deposits has increased significantly because Zn concentrations are of higher grade (up to >30 wt% Zn) than in hypogene sulfide ores and can be extracted easily by open-pit methods (Hitzman 2003). These “non sulfide” Zn ores are mixtures of Zn-bearing silicates (e.g. willemite,  $Zn_2SiO_4$  and hemimorphite,  $Zn_4(Si_2O_7)(OH)_2 \cdot H_2O$  and carbonates (e.g. smithsonite,  $ZnCO_3$ ). Non sulfide Zn ores have been known from Roman times up to the 18<sup>th</sup> century as “calamine” or “zinc oxides” and were used for the production of brass, a Zn–Cu ± Sn alloy widely used throughout Europe and the Mediterranean (Boni et al. 2003). Supergene nonsulfide Zn deposits are predominantly carbonate-hosted, and their formation is primarily controlled by the combined effect of climate, bedrock, topography, time and biota.

Some of the world’s most economically important supergene ore deposits occur in Australia. In the Hamersley province of Western Australia, there are channel iron deposits (CIDs), which are aggraded paleoriver channels containing such large concentrations of ferruginized sediments that they constitute a high-grade iron-ore deposit. CIDs are Fe-rich detrital accumulations comprising coarse sand to fine gravel-size granules—iron oxyhydroxide pelletoids (ooids and pisoids) and ferruginized wood—and a porous goethitic matrix that envelops the granules. These deposits are strongly tied to the tectonic and climatic evolution of Western Australia during the Miocene, where Fe-rich sediments sourced from upstream outcrops of banded iron formations (BIFs) were deposited into river channels. During a later stage, the supergene Fe ores formed by precipitation from ferriferous alluvial groundwater, either directly or by replacement of clastic particles (Heim et al. 2006). This style of supergene mineralization supplies 40–50% of the iron currently mined in Australia, and making Australia one of the leading Fe-producing countries in the world, along with China and Brazil.

Laterites, also called “lateritic profiles” (Anand and Paine 2002), are another type of supergene metal deposit, and these can contain exploitable reserves of metals such as Fe, Al, Mn, Au, Ni and Co. Lateritic profiles are chemically stratified weathering zones, ranging from 30 m to 500 m in thickness, that develop through intensive rock weathering under humid tropical to subtropical conditions, under present and/or past climatic regimes (Vasconcelos 1999). Bauxites, the well-known highly aluminous variety of laterite, form on granites, basalts, volcanic ash, or shales and yield most of the global Al production; world production is presently dominated by Australia, Brazil, China and India. These highly aluminous varieties of laterites are made of mixtures of Al hydroxides—gibbsite ( $Al(OH)_3$ ), boehmite ( $\gamma-AlO(OH)$ ) and diasporite ( $\alpha-AlO(OH)$ )—and certain by-products of bauxite formation, e.g. vanadium and gallium. Similarly, nickel-rich laterites dominate the global supply of Ni (over 60%, as produced by Australia, New Caledonia,

Brazil, Cuba, Indonesia, the Philippines). The Ni-laterites develop from the intense weathering of serpentinites or unserpentinized ultramafic rocks. They tend to contain one or more horizons of exploitable reserves of Ni and other elements, such as Co (Butt and Cluzel 2013), and their supergene grades (1–7 wt% Ni) exceed those of magmatic Ni deposits (0.5–5 wt% Ni) (Arndt and Ganino 2012).

### Precious Metals and Metalloids

Many precious metal (Au, Ag, PGEs) deposits occur in lateritic profiles or supergene enrichment zones within deeply weathered terrains. For example, gold-bearing laterites of economic interest are found in Western Australia, Africa, Brazil, the Guyanas, and India, and they usually overlie, or occur immediately adjacent to, primary (hypogene) lodes. These secondary supergene deposits contain free particles of high-purity Au (>99 wt% Au), making them amenable to low-cost open-pit mining. The occurrence of Au grains in supergene environments, such as soils, sediments, and placers, is controlled by the chemical and physical processes that redistribute the primary Au. However, recent evidence shows that high-purity and finely crystalline secondary Au may also result from biogeochemical transformations (Reith et al. 2012; Zammit et al. 2015).

Some precious metals and metalloids are produced entirely as by-products of the refining of major metals. For example, Te is produced from Cu refining, Re from Mo, In and Ge from Zn, Ga from Al, and Co from Ni. Although most critical metals and metalloids rarely form primary ores, geological processes such as supergene enrichment can concentrate them efficiently to economic grades, which in some cases can outweigh the main commodity in revenue. Significant attention is now being paid to alternative sources of critical metals and metalloids for the new types of energy technologies, including Te, Ga, In, and Ge for solar cell applications and the REEs (Nd, Dy, Pr, Sm, Tb, Eu, and La) for high-performance magnets used in wind turbines and electric cars. Geological sources include bauxite and laterite deposits, where Ga and the REEs can reach economic grades and so make the cost of mining low (Cocker 2014). In fact, an important part of the world supply of Ga metal for GaAs and GaN semiconductors comes from the mining of bauxite. And REEs in previously subeconomic lateritic horizons are becoming increasingly viable to mine.

## SUPERGENE DEPOSITS AS NATURAL ANALOGUES FOR CORROSION

One of the more unusual reasons, certainly as far as most people are concerned, to study supergene deposits is because they can act as models for corrosion. The oxidation and leaching processes that affect the primary rocks, and that lead to the formation of supergene metal deposits, are actually analogous to corrosive process that occur in man-made materials. For example, the green-colored atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ; FIG. 2C) was massively formed as a “natural” corrosion product of hypogene Cu deposits in the Atacama Desert of northern Chile (Reich et al. 2008). Atacamite is rare in similar deposits elsewhere, with the exception of saltwater alteration assemblages of seafloor Cu sulfides and as the green corrosion patina that covers bronze monuments in coastal cities, such as the Statue of Liberty (New York, USA) (FIG. 5A). Therefore, considering that atacamite only forms from seawater-like fluids and dissolves rapidly or undergoes phase changes when exposed to fresh, meteoric water, its study can provide insights about, for example, the long-term corrosion behavior of Cu-bearing pipes or archeological artifacts (FIG. 5B) in dry, saline environments and coastal localities.

The study of natural analogues is often used to support long-term predictions on how corrosion will affect man-made products in geologic environments (Renock and Shuller-Nickles 2015 this issue). Because many ore deposits have been subjected to multiple cycles of weathering and enrichment, supergene metal blankets can help to bridge the extrapolation gap for the way that materials and systems behave (experimentally) over the short-term, typically about one year, to what might happen over comparatively long periods. For example, studies of the famous ~2 billion-year-old Oklo uranium deposit (Gabon), considered a natural fission reactor, have provided evidence of uranium migration over geologic timescales and, thus, help to answer specific questions related to underground repositories for nuclear waste and “cruds,” or radioactive corrosion products (Evins et al. 2005) (FIG. 5C). In another example, the study of supergene deposits shows that noble metals (Au, Pd, Pt), presumed inert under most surface conditions, undergo effective dissolution–reprecipitation as the result of metal–microbe interactions. This finding may one day be used to efficiently extract metals from industrial waste.

### WHY ARE SUPERGENE METALS IMPORTANT?

The fact that the formation of supergene ores is strongly tied to local and global changes in the atmosphere and hydrosphere is one of the reasons why supergene metal deposits have attracted significant attention (e.g. Alpers and Brimhall 1987). Furthermore, the fact that metals can undergo large fractionation in supergene settings offers an unparalleled opportunity to explore the rates of oxidation of Earth materials over long geologic timescales. Supergene metal deposits provide critical evidence for reconstructing Earth’s past climatic history, and they can constrain when there were favorable geological periods for the development of weathering profiles and metal enrichment on a global scale (Vasconcelos et al. 2015). Given present concerns over metal supplies, supergene metal deposits should provide far-reaching opportunities to expand the mineral resource potential of new and historic mining districts through innovative exploration. However, global exploitation of supergene metal deposits faces significant challenges, largely because ore bodies are found near the surface and must be mined by open-pit operations. Whilst supergene ore deposits are the only viable sources for some metals (e.g.



**FIGURE 5** Corrosion products of man-made objects. (A) Copper sulfate and chloride patinas give the Statue of Liberty (New York City, USA) its characteristic green color. (B) 100-year-old, atacamite-coated, miners’ boots recovered from a deep gallery in a copper mine around Sierra Gorda in the Atacama Desert (Chile) (PHOTO FROM REICH ET AL. 2008). (C) Yellow-colored “crud” that has formed on the cladding (or outer coating) of nuclear fuel rods. IMAGE TAKEN FROM [WWW.ENGIN.UMICH.EDU/COLLEGE/ABOUT/NEWS/STORIES/2012/NOVEMBER/NUCLEAR-CRUD](http://WWW.ENGIN.UMICH.EDU/COLLEGE/ABOUT/NEWS/STORIES/2012/NOVEMBER/NUCLEAR-CRUD)

Al), their extraction may disturb large tracks of pristine environment (e.g. bauxite mining in the Amazon), and processing such deposits comes with significant environmental risks in its potential for spreading toxic components and polluting water resources. Thus, the study of supergene processes is highly relevant to understand the dispersion of heavy metals (Cu, Fe, Mn, Zn, Pb, Cd) and metalloids (As, Se, Sb) from their primary ore bodies into local and regional surroundings. Thus, supergene metal deposits hold huge interest both geologically and for the well-being of a modern society, but there are associated dangers to be

navigated between the need to secure resources for societal development and the impact that mining can have on Earth's environment, climate, and local communities.

## ACKNOWLEDGMENTS

The authors thank John Valley and Bernard Wood for their editorial handling and revision of this manuscript,

which benefited from helpful reviews by Larry Meinert and Steve Kesler. Martin Reich thanks support from ICM grant #130065 "Millennium Nucleus for Metal Tracing along Subduction", and CONICYT funding through Fondecyt and Fondap grants. Our special thanks go to Fernando Barra for providing mineral samples, and Cristián Prado for assistance with photo shots of mineral specimens. ■

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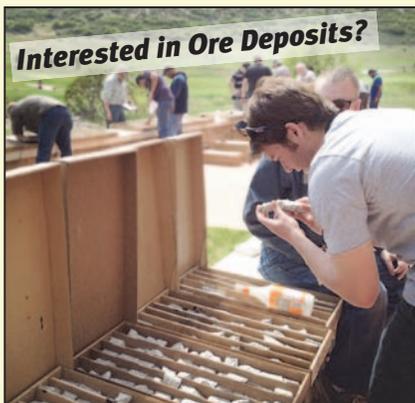
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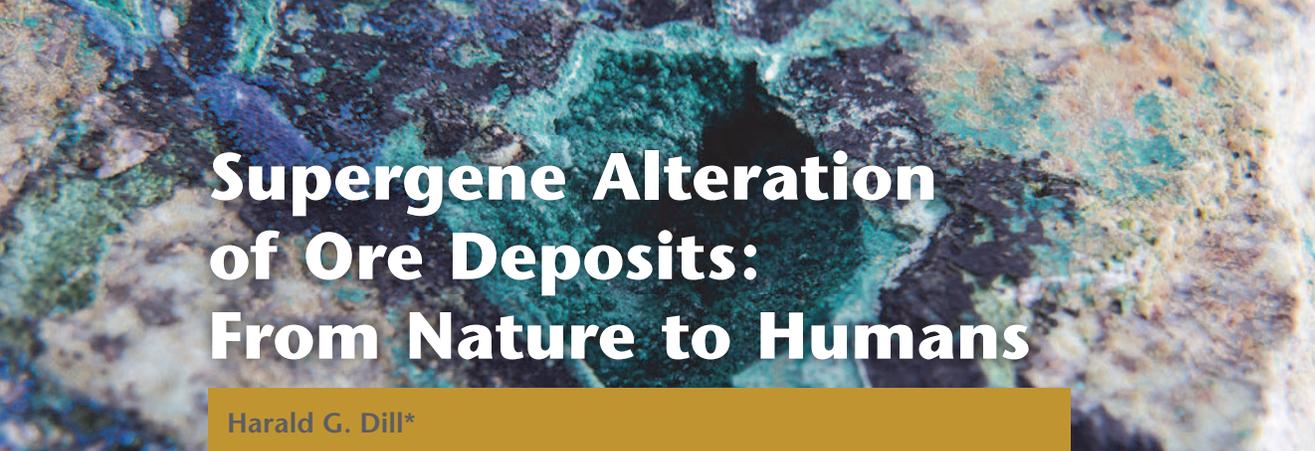


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# Supergene Alteration of Ore Deposits: From Nature to Humans

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1811-5209/15/0011-0311\$2.50 DOI: 10.2113/gselements.11.5.311

**S**upergene minerals form under near-ambient conditions on the Earth's surface. Supergene mineralization is controlled by the parent rock composition, climatic conditions, geomorphological environment, and chemical compounds added during mineral processing. They appear in alteration zones called "orecretes." Bronze Age miners exploited these easily accessible high-grade soft ores for Fe, Cu, Pb, and Ag. Some supergene minerals can also grow in poorly ventilated mining galleries and shafts, coat metal mining artifacts and smelting residues, and form from disastrous blasts and fires in ancient mining settlements. Supergene deposits bridge the gap between humans and metal resources at the interface between rock, soil, air, water, and living organisms. These deposits provide essential clues to geological, environmental, and archeological studies.

**KEYWORDS:** supergene alteration, critical zone, gossan, orecrete, Bronze Age, post-mining minerals, tailings, slags

## INTRODUCTION

Supergene processes, irrespective of their natural or anthropogenic origin, lead to the formation of oxygen-bearing minerals from the polar to the tropical climatic zones. This type of mineralization can occur as gossans or as anthropogenic chemical compounds that can coat smelter slags, grow in tailing ponds, or cover the walls of adits and galleries as a result of post-mining oxidation (Brimhall and Crerar 1987; Ettler et al. 2001; Manasse and Mellini 2002; Dill et al. 2002, 2013a,b; Belogub et al. 2008; Dill 2010). Supergene minerals have even been derived from human-induced disasters like fire. All such minerals form in the *Critical Zone*—the contact zone where the atmosphere, biosphere, pedosphere, and hydrosphere interact (Brantley et al. 2007) (Fig. 1). In the deepest portions of the hydraulic zone of a gossan (equivalent to the classical "cementation zone"), reducing conditions immediately atop the primary sulfide ores provoke secondary sulfides, such as covellite (CuS) or chalcocite (Cu<sub>2</sub>S), to precipitate and increase overall grades (Fig. 2). Some recent reviews address this deeper hydraulic zone (e.g. Titley 2009). Other authors have focused on the common duricrusts (hard crusts that form on or in soil in semiarid climates owing to cementation of soil particles) regardless of whether these deposits are of geomorphological significance or achieve economic relevance, such as laterites or bauxites (Taylor and Eggleton 2001; Boyle 2003; Arancibia et al. 2006; Dixon and McLaren 2009). And a very specific type of supergene enrichment takes place under tropical climatic conditions on Co- and

Ni-enriched parent rocks that leads to blankets of Fe-bearing Ni-Co laterites (Bergman 2003; Marsh et al. 2013; Reich and Vasconcelos 2015 this issue).

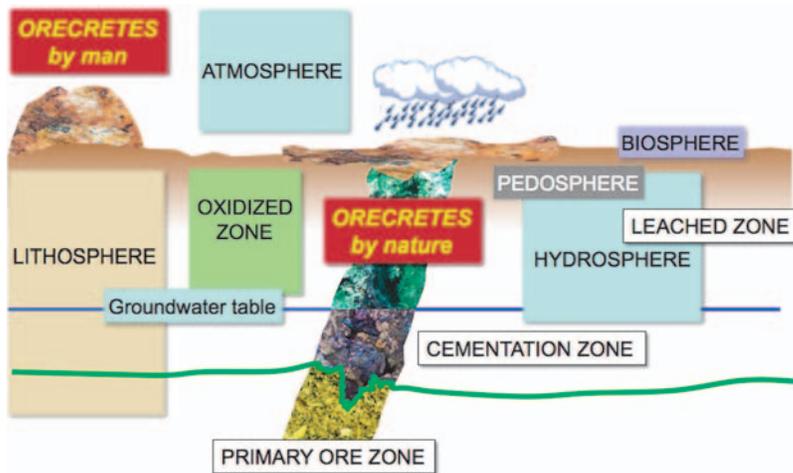
Supergene mineral deposits and orecretes have played key historical roles in the economic development of ancient and modern societies, but also have resulted in natural and anthropogenic contamination and modification of local environments and adjacent surroundings. In the present review, examples are given to bridge the gap between natural and anthropogenic supergene alteration, including copper and uranium enrichment in gossans and anthropogenic supergene mineral formation in ancient mines and settlements due to metallurgical activities and fires and blasts.

## KEY FACTORS CONTROLLING SUPERGENE ALTERATION

The deposits resulting from supergene alteration in the oxidized zone are called "orecretes" (Dill et al. 2013a). Orecretes can be subdivided into oxicrotes (oxide plus hydrate), carbocreates (carbonate), silicocreates (silica), halocreates (halogenides: Cl, I, F, and Br), sulcretes (sulfate plus aluminium phosphate sulfate minerals), phosocreates (phosphates), arsenocreates (arsenates), and vanadocreates (vanadates). For more precision, metal names are added as a suffix to the orecrete term, e.g. Pb-Zn carbocreates. Supergene copper and uranium mineralizations are representative model systems of the pathway from the primary ore through the topmost orecretes and will be used herein as cases in point.

Supergene alteration processes, accountable for the development of orecretes, are controlled by three basic factors. The first, and most important, factor is that of the parent material. This can be the country/wall rocks (e.g. limestone) and primary ore minerals (e.g. galena), all of which significantly influence the development of orecretes. Limestones favor the precipitation of carbocreates, whereas Se-Mo orecretes and arsenocreates only develop on parent material strongly enriched in the marker elements As, Se and Mo that were contained in the primary ore minerals (Fig. 3). The second factor is the local landform, which is shaped by hydrological and pedological processes coupled with the geodynamic evolution of the crustal section under consideration. In low-relief areas (e.g. lowlands, plateaus, and deeply eroded mountain belts), the full range of orecretes may be expected. The third factor is the (paleo)climate

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**FIGURE 1** Cartoon showing controls on supergene mineralization in the “Critical Zone” where the biosphere, atmosphere, lithosphere, pedosphere (soil), and hydrosphere intersect. Orecretes are the mineralized deposits left behind from the supergene alteration of primary ore bodies or deposits left behind by human mining activities. Orecretes are found in the oxidized leached zone.

and it has the most decisive and balancing effect on the physico-chemical regime under which the orecretes form. Vanadocretes, halcretes, sulcretes, and, to a lesser extent, siliccretes are genetically related to latitudinal climatic zonation around the Earth. The same is true also for regions with a rugged or mountainous relief, where the same sort of orecretes observed during latitudinal changes show up again but as function of altitude.

### MINERALOGICAL VARIETY AT THE WATER–ROCK INTERFACE

The geologic, climatic and economic significance of some of the world’s largest supergene metal deposits are reviewed by Reich and Vasconcelos (2015 this issue) and Vasconcelos et al. (2015 this issue). In this article, however, the focus is on selected localities around the world where oxidation and enrichment processes of ores have resulted in a large mineralogical variety, and where studies focusing on the archeological aspects of supergene mineralization are available.

In the historic Nabburg–Wölsendorf mining district of northeastern Bavaria (Germany), different minerals are associated with various types of fluorite and contribute to the formation of supergene mineralization: silicates, sulfates, sulfides, carbonates minerals, phosphates, oxides, and oxyhydrates. The ore veins cluster along a prominent NW–SE-striking shear zone and are predominantly hosted by granites and, to a lesser extent, by paragneisses (Dill et al. 2013a). The primary hydrothermal vein mineralization took place during the early Permian (295 Ma) through the Late Jurassic (145 Ma) at temperatures below 200 °C (Fig. 2N). From the Neogene (9.6 Ma) through the Pleistocene (0.1 Ma), the Nabburg–Wölsendorf veins were subjected to a pervasive chemical weathering that differed significantly from that of the temperate–humid morphoclimate zone of today. The ages of formation have been obtained from U–Pb dating of uranium minerals (Fig. 2K–N).

In the fluorite–barite veins, primary chalcopyrite gave rise to a wide variety of supergene copper minerals in the oxidized zone (e.g. azurite, chrysocolla, brochantite, langite, libethenite, linarite, malachite) and in the chemically reduced

zone (e.g. cuprite, chalcocite, digenite, covellite, berzelianite, umangite). The most diagnostic Cu minerals are shown in FIGURE 2(B–J). Chalcopyrite is locally preserved as an “armored relic” in fluorite and barite and is preserved in the orecretes even under oxidizing conditions (FIG. 2B–J). There is no sharp contact between the various hydraulic zones illustrated in the idealized scheme of FIGURE 2A due to the strongly fluctuating groundwater table, itself a consequence of changes in the local drainage system. Selenides are closely linked to uranium minerals but are formed under more oxidizing, higher-Eh conditions than the associated U oxides.

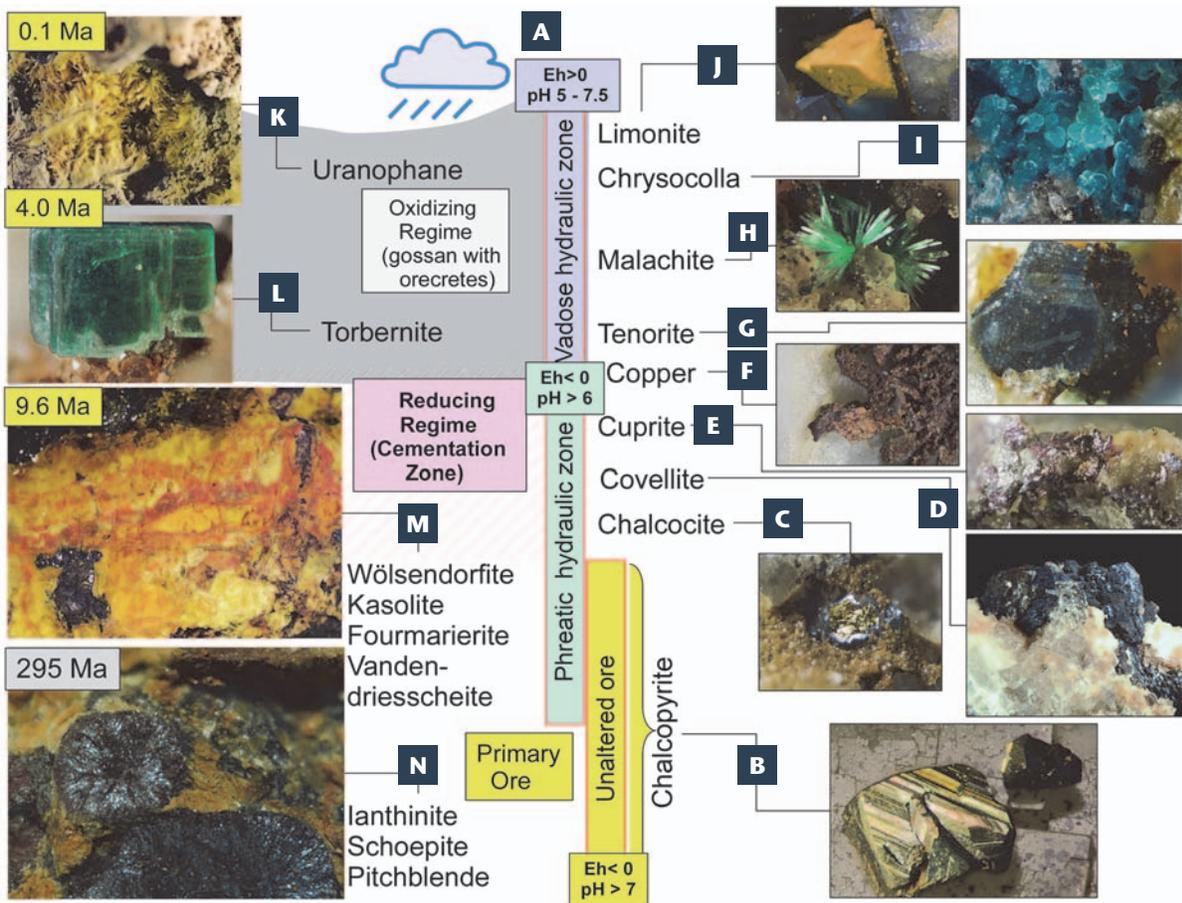
The decomposition of iron disulfides (mainly pyrite) produces acidic meteoric fluids. Pyrite is more susceptible to weathering than chalcopyrite and thereby helps speed up the process of supergene alteration of vein-type minerals and the dissolution of apatite in the adjacent granitic wall rocks (Rimstidt et al. 1994). The dissolution of the apatite

provides the source for the phosphate anions in minerals like torbernite. Carbon is present in the atmosphere and biosphere and so carbonate minerals like malachite need no particular source. Azurite, on the other hand, is only stable under elevated partial pressures of carbon dioxide ( $p\text{CO}_2$ ), a condition fulfilled only in mineral assemblages containing calcareous gangue. For the formation of chrysocolla, alkaline solutions are needed prior to its formation. And covellite precipitated in the cementation zone around galena grains, which happens by an electrochemical reaction between Pb and Cu.

A drastic lowering of the groundwater level and resultant transfer of secondary minerals from the phreatic into the vadose hydraulic zone can lead to perimorphoses (pseudomorphism by coating) in the Nabburg–Wölsendorf mining district (FIG. 2). The “chalcocite blanket,” composed of chalcocite and native copper, marks the transition from the cementation zone into the oxidized zone. A protracted decomposition of native copper on deepening of the water level accounts for the presence of native copper even in the oxidizing zone and gossan. At the passage from the vadose to the phreatic zone, tenorite was found associated with torbernite (FIG. 2G). Nontronite, secondary copper minerals, and uranium micas are paragenetic and were formed during the Pliocene. This is confirmed by K–Ar dating of cryptomelane, yielding Pliocene ages of formation (~4 Ma) that are similar to the “yellow U ore” mineralization determined by laser ablation inductively coupled plasma mass spectrometry (LA–ICP–MS) U–Pb dating (Dill et al. 2013a).

### SUPERGENE URANIUM MINERALIZATION: A CLOCK FOR THE CENOZOIC

Dating supergene uranium minerals is easier than for most other rock-forming minerals because of the inherent radioactive decay of U and these minerals’ rapid response to chemical and physical changes in the hydraulic regime. The close interdigitating of geological processes and ample data on age of formation enabled us to fine-tune the evolution of the landscape and geomorphology of the supergene mining district in Nabburg–Wölsendorf (Dill et al. 2013a) (FIGS. 2, 3). One of the most appropriate group of minerals to tackle the wide range of issues of supergene alteration in U-bearing systems is the commonly called “yellow uranium ore,” illustrated in FIGURE 2. These minerals can be used for age dating and constraining the physico-chemical regime. Uranyl ( $\text{U}^{6+}$ ) phosphates (e.g. torbernite, autunite), hydrated uranyl silicates (uranophane), and “gummities” (e.g. schoepite, fourmarierite) are observed at various



**FIGURE 2** A comparison of secondary Cu and U minerals (U yellow ore) in fluorite vein-type deposits in Nabburg–Wölsendorf, Germany. (A) Cartoon illustrating the weathering and hydraulic zones in Variscan granitic terrains at the western edge of the Bohemian Massif. The physico-chemical regimes of the fault-bound mineralization are based on thermodynamical calculations: primary ore (yellow), reducing regime (pink/stippled), and the oxidizing regime (grey). The primary ore originates from *per ascensum* (hypogene) mineralization. The gossan with the orecretes (oxidizing regime) and the cementation zone (reducing regime) are derived from *per descensum* mineralization (supergene). (B–J) Photographs of minerals found in the different mineralization regimes. (B) Chalcopyrite ( $\text{CuFeS}_2$ ) growing on white fluorite – Erika Mine. (C) Chalcocite ( $\text{Cu}_2\text{S}$ ) coating chalcopyrite in yellow brown fluorite (“honey spar”) – Wölsendorf Mine. (D) Covellite ( $\text{CuS}$ ) covering chalcopyrite in quartz – Wölsendorf Mine. (E) Cuprite ( $\text{Cu}_2\text{O}$ ) red with specks of native copper (metallic luster) and black tenorite – Roland Mine. (F) Native copper (Cu) on

quartz – Marienschacht Mine. (G) Tenorite ( $\text{CuO}$ ) pseudomorphing chalcopyrite. The green tabular crystals are torbernite ( $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 12\text{H}_2\text{O}$ ) – Roland Mine. (H) Malachite ( $\text{Cu}_2(\text{OH})_2\text{CO}_3$ ) on quartz – Marienschacht Mine. (I) Chrysocolla ( $\text{Cu}_4\text{H}_4(\text{OH})_8\text{Si}_4\text{O}_{10} \cdot n\text{H}_2\text{O}$ ) – Roland Mine. (J) Limonite (goethite) ( $\alpha\text{-FeOOH}$ ) pseudomorphing chalcopyrite crystal between black fetid fluorite (left) and colorless fluorite (right) – Marienschacht Mine. (K–N) Photographs of mineralization representing the different stages of supergene alteration that occurred between 295 Ma and 0.1 Ma. (K)  $\beta$ -uranophane ( $\text{Ca}_2(\text{UO}_2)_2(\text{SiO}_3)_2\text{OH} \cdot \text{H}_2\text{O}$ ) – Johannes Shaft; (L) Torbernite ( $\text{Cu}(\text{UO}_2)_2(\text{PO}_4)_2 \cdot 11\text{H}_2\text{O}$ ) – Roland Mine; (M) “Gummite” formed of wölsendorfite ( $(\text{Pb,Ba,Ca})\text{U}_2\text{O}_7 \cdot 2\text{H}_2\text{O}$ ), kasolite ( $\text{PbUO}_2\text{SiO}_4 \cdot \text{H}_2\text{O}$ ), fourmarierite ( $\text{Pb}(\text{UO}_2)_4\text{O}_3(\text{OH})_4 \cdot 4\text{H}_2\text{O}$ ) and vandendriesscheite ( $\text{Pb}(\text{UO}_2)_{10}\text{O}_6(\text{OH})_{11} \cdot 11\text{H}_2\text{O}$ ) – Girnitz Mine; (N) Pitchblende ( $\text{U}_3\text{O}_8$ ) globules with schoepite ( $(\text{UO}_2)_8\text{O}_2(\text{OH})_{12} \cdot 12\text{H}_2\text{O}$ ) and lanthinite ( $\text{UO}_2(\text{OH})_2$ ) – edge Johannes Shaft. Images B–J scale is ~10 mm, images K–N scale is 10–50 mm.

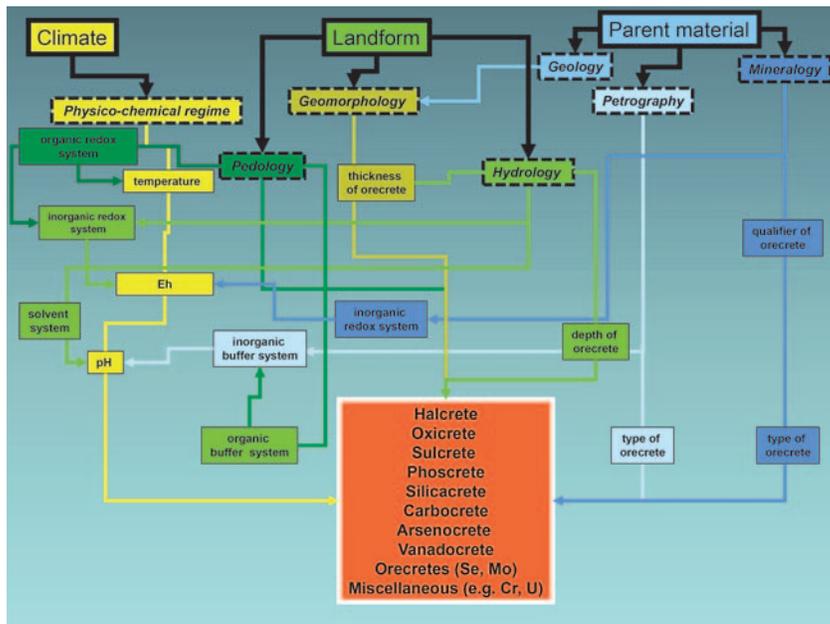
erosion levels in the late Paleozoic granites and country rocks in southeastern Germany. LA–ICP–MS dating allows for a fine-tuning of the stratigraphy of supergene alteration and sheds light on the chronology of geomorphological, pedological, and hydrogeological processes (Fig. 2K–N).

Supergene alteration of the Nabburg–Wölsendorf uraniumiferous granites can be divided into four stages, the development of which depended on changes in Cenozoic climate, geomorphology, and pedology Stage I (U mineralization in the infiltration zone) mirrors the relic granitic landscape with high-altitude divides and high-altitude alluvial and fluvial terraces on an ancient peneplain. Stage II (U mineralization in the infiltration zone, regolith and saprock) includes planation and exhumation, resulting in the exposure of inselbergs/bonhardts and quartz reefs. Stages III and IV (U mineralization in the percolation zone and saprock) are controlled by the incision of the trunk river Donau (Danube) in the foreland. Rapid incision caused tors to form, whereas periods of decreased fluvial incision

caused their destruction and pitting. A subtropical climatic regime and the availability of water are the most crucial factors for a full-blown cycle of supergene alteration to develop, which in this case lasted from 9.6 Ma through 0.1 Ma (Dill et al. 2013a). Therefore, alteration of primary U minerals during supergene oxidation and enrichment can significantly contribute to the evolution of the landscape and can be used to constrain the physico-chemical regime of weathering and hydrology (Fig. 2K–N).

### BRIDGING NATURAL AND ANTHROPOGENIC SUPERGENE ALTERATION: CHRONOLOGY AND TEMPERATURE OF FORMATION

Geochronology dating methods— $^{14}\text{C}$ , U–Pb, K–Ar, Ar–Ar, (U–Th)/He, U-series disequilibrium, and optically stimulated luminescence dating—have been used to constrain the timing of weathering and supergene mineralization in a wide variety of supergene settings (Geyh and Schleicher



**FIGURE 3** Flow chart of how orecretes (orange) form. First-order factors (framed by bold-faced lines): climate (yellow), landforms (green), and parent material (blue). Second-order factors (framed by stippled lines): related to climate (yellow), related to landforms, pedology (dark green), geomorphology (olive green), hydrology (bright green) and related to parent material geology (light blue), petrography (gray blue), mineralogy (dark blue). Third-order factors (framed by normal lines) and their interaction: related to the physical-chemical regime (temperature, Eh, pH), related to pedology (organic redox system, organic buffer system), related to geomorphology (thickness of orecrete), related to hydrology (inorganic redox system, solvent system, organic buffer system, depth of orecrete), related to petrography (type of orecretes, inorganic redox system), related to mineralogy (inorganic redox system, qualifier of orecretes, type of orecretes).

1990; Wagner 1995; Vasconcelos 1999; Shuster et al. 2005; Reich et al. 2009; Vasconcelos et al. 2015). Furthermore, significant knowledge has been obtained from the study of conventional and non conventional stable isotope fractionation in supergene systems (Mathur and Fantle 2015 this issue); thus, combined stable and radiogenic isotope analysis of supergene minerals can have a broad application in understanding climatic and geomorphic evolution of selected areas, with increasing temporal resolution and precision.

For example, supergene Cu-, Zn-, and Pb carbonates (azurite, malachite, cerussite, and smithsonite) have two advantages in terms of isotopic dating and fingerprinting recent supergene processes. First, they can be used for radiocarbon age dating of geological processes up to ~30 ka, extending supergene dating into the archeological realm (e.g. Dill et al. 2013b). Secondly, their oxygen and hydrogen compositions offer a tool to determine the paleotemperature of Zn-, Cu-, and Pb carbocretes (Melchiorre and Enders 2003).

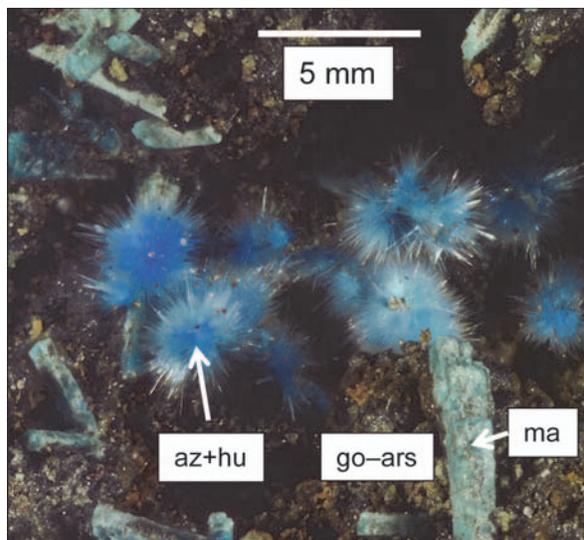
In supergene studies, two different temperatures have to be distinguished from each other: (1) the zonal temperatures that change with the latitude and the altitude in, for example, high-relief areas, and (2) the temperature of formation. Other factors that play a role include sulfate-bearing fluids, which are the most important part during decomposition of sulfides (Rimstidt et al. 1994). Geologists also need to consider the actions of bacteria such as *Thiobacillus ferrooxidans*, which can increase the sulfate concentration (Kasama and Murakami 2001). The production of organic matter, the availability of water, and the depth of the weathering profile can all stimulate bacterial

activity during the formation of orecretes. There is a slight increase in the temperature of formation of carbocretes relative to the paleotemperature in the humid mid-latitudinal zones around the globe, and a conspicuously strong increase when passing into the tropical humid zone. Elevated, tropical zone-style oxidation temperatures have been reported in the carbocretes from pyritiferous Cu–Pb–Zn deposits in Myanmar and the Democratic Republic of Congo (~51°C and 53°C), where the latitudinal temperature values stood between 21°C and 23°C (Dill et al. 2013a).

It is important to highlight that the natural alteration phenomena discussed in the previous sections lead to the formation of secondary mineral assemblages that record chronological, physico-chemical, and environmental information. These data are necessary for reconstructing supergene alteration histories, but also provide important evidence in archeological studies. In the following section, some examples are provided on how ancient mining activities have disturbed the natural oxidation and enrichment of ore deposits and associated mining artifacts to form anthropogenic supergene alteration assemblages.

## SUPERGENE ALTERATION OF MINING ARTIFACTS AND TAILINGS

Anthropogenic mining residues—or post mining mineral assemblages—result from descending meteoric waters in galleries and opencasts. Efflorescence (or loss of water by a hydrated salt) is triggered in cave and underground mine environments by ventilation and the exposure of minerals to subaerial processes. In the ancient adits of the Mega Livadi Mine, a skarn deposit at Serifos (Greece), Cu–Pb arsenates, Cu humate–oxalates, and Cu humate–carbonates were found and dated (Dill et al. 2010) (Fig. 4). Radiocarbon dating of humate–oxalates yielded a <sup>14</sup>C calibrated age of 3325 to 2890 BC, which suggests the Bronze Age. This type of mineralization is of importance in three ways. First, it



**FIGURE 4** Copper-carbonate mineralization found in the adits of the Mega Livadi Mine (Serifos, Greece), which operates the gossan of a Cu–Fe skarn deposit. Visible are sprays of lavender-blue acicular azurite (az) coating a Cu humate-oxalate (hu); lath-shaped prisms of a vivid green malachite (ma) are older than the az+hu blue aggregates. These Cu carbonate and humate-oxalate assemblages developed on rust brown deposits of goethite and arsenates (go-as).

offers an insight into the most recent weathering processes of base-metal mineralization in the Aegean Sea region. Secondly, it gives an overview of mining activities across Europe from Cyprus, the “Cradle of Cu mining,” to Great Britain during the Bronze Age. And finally, the physicochemical features of this multistage alteration may be employed to explain the compositional variation under (sub)tropical through temperate climatic conditions in tailings derived from beneficiation of As–Cu ores elsewhere. In the case of the Matchless chalcopyrite–pyrite deposit in Namibia, mineralogical, geochemical, and microbiological processes operating in the tailings ponds under semiarid climates have produced orecretes that originated from the alteration of primary sulfides and carbonates left over after metallurgical recovery (flotation) and from chemical agents (e.g. lime, phosphate) added during ore processing. The tailings discharge and the early diagenetic alteration led to a pronounced bedding and the development of distinct layers. In the tailings impoundment this produced gypsum–carbonate (e.g. huntite), gypsum–sulfate (e.g. melanterite), gypsum–phosphate (e.g. brushite), gypsum–chloride (e.g. halite), while at the surface there was a sulfate–gypsum efflorescence (e.g. copiapite). The tailings and surface supergene mineralogy provides an overview of the history of mineral processing (Dill et al. 2002) (Fig. 5). Excluding the influence of manmade chemicals used during processes such as flotation, anthropogenic supergene alteration systems such as Matchless provide detailed information that is valuable for reconstructing near-surface alteration histories in supergene metal deposits (e.g. Martycak et al. 1994, Boyle 2003, Belogub et al. 2008, and Taylor 2011).

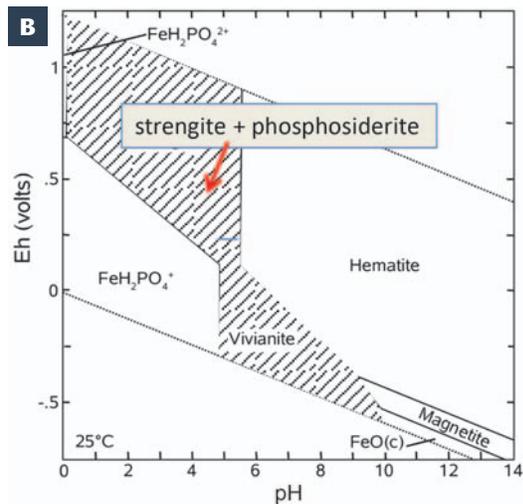
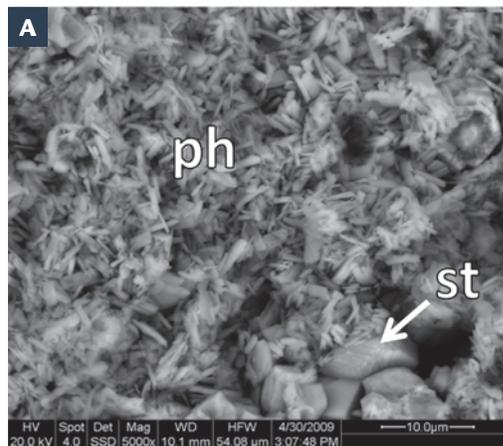
### SUPERGENE ALTERATION OF SMELTING RESIDUES AND DISASTER-INDUCED ALTERATION

After the Bronze Age around 1200 BC, the onset of the Iron Age was characterized by weapons and ornaments made of Fe instead of Cu alloyed with Sn. During the La Tene period (late Iron Age), Celtic miners and smelters headed north into the foreland of the North Eastern Bavarian Basement (Germany), exploiting soft iron ore. The minerals most typical of such archeometallurgical artifacts are fayalite, leucite, wuestite, quartz, cristobalite, magnetite, native iron, and glass. Mining residues dumped near the blast furnaces used to be covered with goethite and “limonite”. Around 1600 AD, miners and smelters from southeastern Germany went further north in search of Cu and successfully exploited the gossans of stratabound volcanogenic massive sulfide (VMS) deposits. The slag heaps from the Kupferberg site (Germany), for example, are covered with brochantite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6$ ), a supergene copper sulfate.

Early mining and smelting operations during the Bronze Age in Greece, Cyprus, and the Middle East left behind large dumps that produced sulfate mineralization of much greater diversity than the equivalent mineralization in Germany. These dumps have had a longer time to form secondary supergene-type minerals, and the quality of the slags, plus the semiarid climate, were pivotal for the ubiquitous development of brochantite, wroewolfeite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot 2\text{H}_2\text{O}$ ), posnjakite ( $\text{Cu}_4\text{SO}_4(\text{OH})_6 \cdot \text{H}_2\text{O}$ ), and devilline ( $\text{CaCu}_4(\text{SO}_4)_2(\text{OH})_6 \cdot 3\text{H}_2\text{O}$ ) in the vugs and cracks of metallurgical relics. In places, the mining residues were not only exposed to atmospheric processes, which mainly caused sulfates to precipitate, but also to human-related physico-chemical processes, such as blazes or fires in the

PROCESS	STAGES OF ORECRETE FORMATION						ORECRETE
	Stage I oxidation of S	Stage II oxidation of Fe	Hydrolysis	Carbonatization	Dehydration	Re-sulfatization	
Fe sulfide oxidation and sulfate mineralization (mediating effect of bacteria)	Fe (I) sulfate (melanterite)	Fe (II) sulfate (copiapite)			Fe oxyhydroxide (e.g. $\alpha$ - $\text{FeOOH}$ )		Oxcrete-(Fe)
			Fe (III) hydroxide		Fe oxyhydroxide		
Ca-bearing minerals, Fe sulfide		gypsum				K-Fe hydro-sulfate	Sulcrete-(K-Fe)
Phosphatization			brushite				Sulcrete-(Ca)
Carbonatization	mediating effect of bacteria			huntite			Carbocrete-(Mg)
Chloridization					halite		Halcrete-(Na)

**FIGURE 5** Supergene mineralization of mining residues at Matchless copper pyrite deposit, Namibia, in the tailing ponds under acidic semiarid environments. The inset shows brushite and gypsum viewed with a scanning electron microscope.



**FIGURE 6** Supergene “disaster” minerals. (A) Aggregates of intimately intergrown crystals of thin tabular crystals of phosphosiderite (ph) with prismatic crystals of strengite (st) from Naila–Marmormühle (Germany) viewed with a scanning electron microscope; (B) Eh–pH diagram to show the physical–chemical conditions under which  $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$  formed.

miners' settlements. These artificial processes gave rise to a totally different mineral association, either of mixed sulfate–phosphate type or pure phosphate mineral assemblages. Coquimbite ( $\text{Fe}_2(\text{SO}_4)_3 \cdot 9\text{H}_2\text{O}$ ), for example, originated from recombining Fe and S in slags as a result of fires set ablaze by either the dwellers of the settlement or by lightning strikes. Phosphosiderite and its polymorphous compound strengite ( $\text{FePO}_4 \cdot 2\text{H}_2\text{O}$ ) is thought to result from anthropogenic sources of phosphate (Fig. 6). Hilgenstockite ( $\text{Ca}_4\text{P}_2\text{O}_9$ ), a chemical compound exclusively formed in Fe slags rich in apatite, has been derived from the ore gangue and been preserved as a relic in the lower temperature parts of a blast furnace (Dill et al. 2013b).

## CONCLUSIONS

Because supergene alteration develops at the critical zone, its products (or “orecretes”) become a link between the solid, liquid, and gaseous constituents of the Earth under near ambient conditions. A wide range of disciplines must

be utilized to fully explain the emplacement and often complex physico-chemical regime of supergene mineral formation. Despite their common occurrence in the geological record, it is in the most recent part of the Earth's history that orecretes have played, and are playing, a prominent role. Supergene mineralization is a link between minerals, society, and history.

## ACKNOWLEDGMENTS

I have to express my gratitude to many colleagues as I was conducting my studies along the chain from gossans to archeological artifacts. One of them I would like to thank in particular, my colleague and friend Berthold Weber who passed away on 4 October 2013. I would like to thank two reviewers of *Elements*, M. Leybourne and F. Barra, for their comments to the manuscript, and I extend my gratitude also to M. Reich for his encouragement to write this review and his editorial handling of the resultant article. ■

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# The Paleoclimatic Signatures of Supergene Metal Deposits

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1811-5209/15/0011-0317\$2.50 DOI: 10.2113/gselements.11.5.317

**Supergene metal deposits host a comprehensive record of climate-driven geochemical reactions that may span the entire Cenozoic. Products of these reactions can be dated by a variety of radiogenic isotopic methods, such as  $^{40}\text{Ar}/^{39}\text{Ar}$ , (U–Th)/He, U–Pb, and U-series. The frequency of mineral precipitation, determined by dating a representative number of samples of a particular mineral collected from distinct parts of the supergene ore body, reflects times in the geological past when weathering conditions were conducive to water–rock interaction. The frequency of mineral precipitation through time permits identifying periods in the geological past when climatic conditions were most conducive to chemical weathering and supergene ore genesis.**

KEYWORDS: weathering geochronology, supergene minerals,  $^{40}\text{Ar}/^{39}\text{Ar}$ , (U–Th)/He, climate

## INTRODUCTION

Supergene ore deposits form when chemical weathering promotes the dissolution, remobilization, and reprecipitation of elements of economic interest at or near the Earth's surface. Recurrent dissolution, transport, and redeposition of metals through time can create a chemically stratified weathering profile (e.g. Reich and Vasconcelos 2015 this issue) that contains a comprehensive record of chemical reactions occurring at the Earth's surface. The rates of these reactions are invariably climate-dependent, reflecting ambient temperature, availability of liquid water (i.e. rainfall intensity and seasonality), evapotranspiration rates, and biological and microbiological activity (Vasconcelos 1999a). Because supergene deposits form during protracted periods, in some cases spanning more than 70 Ma (Vasconcelos 1999b), they preserve valuable information about the climatic history of the planet at specific continental locations.

Retrieving this mineral precipitation history and extracting useful paleoclimatic records from supergene ore bodies require three tasks: (i) identifying the chemical reactions that lead to the precipitation of specific mineral phases in each chemical-stratigraphic horizon (mineral paragen-

esis usually determined by optical and scanning electron microscopy) (FIG. 1A, B); (ii) unraveling the geochemical conditions (e.g. solution concentrations, pH,  $f_{\text{O}_2}$ ,  $T$ ) that prevailed during mineral precipitation (geochemical thermodynamics) (FIG. 1C); (iii) determining when the reactions in (i) occurred (the weathering geochronology). We will focus here on the combination of (i) and (iii), which may lead to inferences about (ii).

Supergene ore bodies provide an important advantage in the study of paleoclimates: direct access to

complete sections through the weathered crust. Weathering profiles hosting supergene ore deposits may extend down to 800 m below the surface, but they are mostly inaccessible to scientific investigation (FIG. 2A, B). When these systems are drilled for their mineral potential (FIG. 2C) and eventually exposed by open-pit mining operations—some open pits may be 5–6 km wide and more than 1 km deep—they provide access to paleoclimatic records that are otherwise unavailable (FIG. 2A, B). Close cooperation among scientists and exploration and mining geologists offers a unique opportunity for retrieving, studying, and preserving this past climatic record.

We will illustrate how the combination of ore microscopy/microanalysis and weathering geochronology, aided by geochemical considerations, helps retrieve paleoclimatic records from supergene ore deposits. We will also show examples of paleoclimatic records derived from mineral precipitation histories in selected supergene systems. We will focus our discussion on copper, iron, and manganese deposits because they are the most thoroughly studied systems, providing a regional or global climatic record not available from other types of supergene ore deposits. But before illustrating the climatic records retrieved from these deposits, it is useful to briefly review the geochronological approaches that allow us to extract vital timing information from supergene minerals.

## WEATHERING GEOCHRONOLOGY

The application of radiogenic isotopes to measure the timing of mineral precipitation in soils and weathering profiles—known as weathering geochronology—is a relatively new development (Vasconcelos 1999a and references therein). Several geochronological tools are suitable, but high spatial resolution methods have distinct advantages when dating minerals from soils and weathering profiles that contain complex assemblages of intimately

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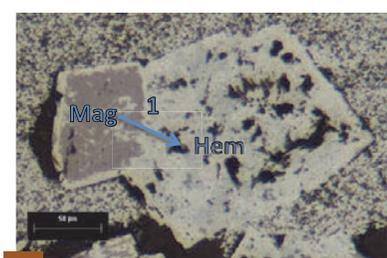
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intergrown minerals precipitated at distinctly different times. The most commonly used geochronological methods for weathering geochronology are  $^{40}\text{Ar}/^{39}\text{Ar}$  laser incremental heating analysis of K-bearing supergene minerals (particularly hollandite-group K–Mn-oxides and alunite-group sulfates) and (U–Th)/He analysis of supergene oxides and hydroxides (hematite and goethite). These methods have provided the bulk of our knowledge about the history of mineral precipitation in the weathering environment. Alternative approaches include U–Pb dating of supergene carbonates (Woodhead et al. 2006), U-series disequilibrium dating of supergene oxides (Short et al. 1989; Bernal et al. 2006) or  $^{36}\text{Cl}$  dating of supergene chlorides (Reich et al. 2008). These latter techniques have only seen limited application to supergene ore deposits, but they do provide useful complementary information on the effects of paleoclimates on supergene processes.

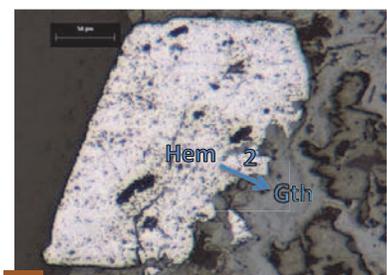
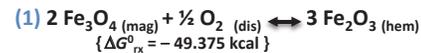
The  $^{40}\text{Ar}/^{39}\text{Ar}$  method is most widely applied because many minerals precipitated by weathering reactions contain K, and many of these minerals are relatively stable once formed. If these phases retain  $^{40}\text{K}$  and  $^{40}\text{Ar}$  quantitatively, then nuclide abundances can be used to determine when

the mineral formed (details in Vasconcelos 1999b). The analysis of a representative suite of K-bearing supergene minerals from a vertical section through a weathering profile may be used to estimate weathering rates and to infer paleoclimatic conditions (de Oliveira Carmo and Vasconcelos 2006). A probability density distribution of mineral precipitation ages identifies times in the past when climatic conditions favored mineral dissolution and reprecipitation. Chemical reactions recorded by mineral precipitation require water as a reactant; therefore, the frequency distribution of ages through time permits one to identify periods in the geological past that were relatively wet (Vasconcelos 1999a,b) (Fig. 2D).

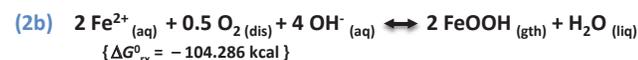
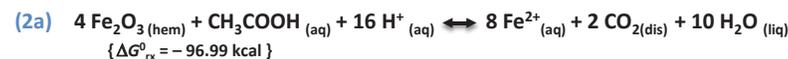
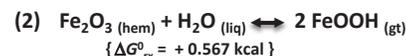
As with K-bearing minerals, the Fe-bearing goethites and hematites generated by water–rock interactions during the formation of supergene ore bodies can be dated. The decay of trace amounts of U and Th in goethite and hematite (Wernicke and Lippolt 1994; Lippolt et al. 1998) results in  $^4\text{He}$  by-products that can be used for dating mineral precipitation, as long as  $^4\text{He}$ , U, and Th are retained. But properly quantifying  $^4\text{He}$  retention in goethite and hematite was not possible until scientists combined the



**A** Oxidation of magnetite

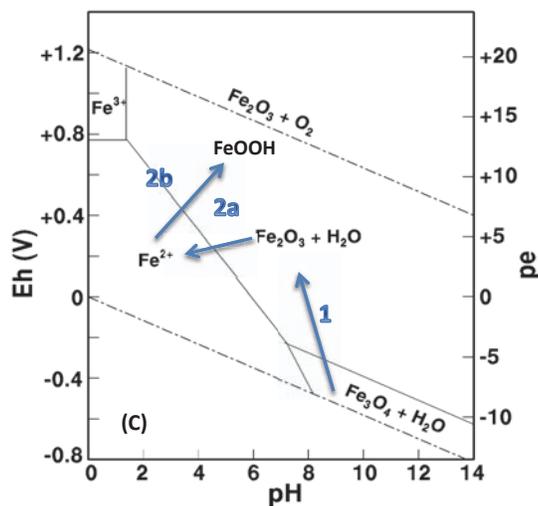


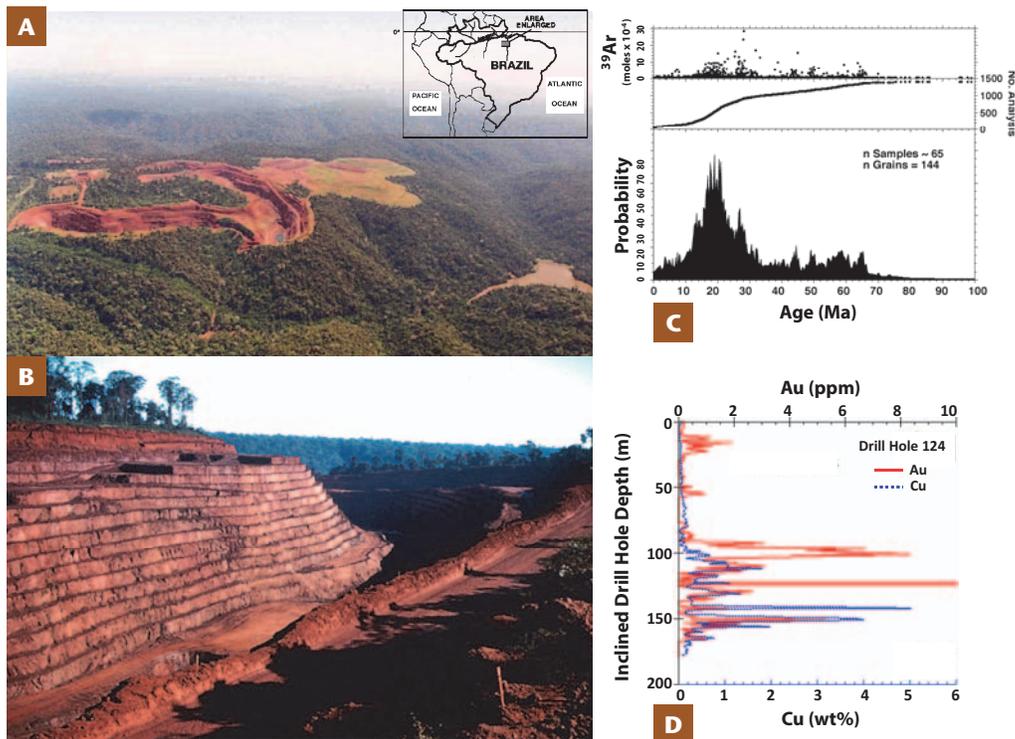
**B** Hydration of hematite



**FIGURE 1** Minerals found in supergene ore deposits record information about chemical reactions and geochemical (and paleoclimatic) conditions prevailing during the formation of the deposits. For example, the oxidation of magnetite (Mag) to hematite (Hem) and the hydration of magnetite or hematite to goethite (Gth) are the product of chemical reactions (identifiable through ore microscopy) within supergene blankets overlying lateritic iron deposits. **(A)** As reaction (1) indicates, direct oxidation of magnetite to hematite is thermodynamically favored ( $\Delta G^{\circ}_{\text{reaction}} = -49.375 \text{ kcal}$ ) when rocks, which formed under reducing conditions, enter the oxidation zone near the Earth's surface. This is illustrated in the Eh–pH diagram with blue arrow labeled 1. This process can be dated by the (U–Th)/He analysis of supergene hematite. **(B)** Direct hydration of supergene hematite (martite) to goethite, on the other hand, is not thermodynamically favored (reaction 2;  $\Delta G^{\circ}_{\text{reaction}} = +0.567 \text{ kcal}$ ). Yet, goethite formed

after hematite is abundant in duricrusts overlying supergene iron deposits. It appears that the hydration of the primary ore oxides involves a two-stage process involving reactions thermodynamically favorable in the supergene zone of ore deposits. First, hematite is reductively dissolved to soluble  $\text{Fe}^{2+}$  by carboxylic acids (e.g. acetic acid, a common organic acid in weathering profiles) (reaction 2a;  $\Delta G^{\circ}_{\text{reaction}} = -96.99 \text{ kcal}$ ). This is followed by the subsequent re-oxidation of  $\text{Fe}^{2+}$  by dissolved  $\text{O}_2$  in weathering solutions (reaction 2b;  $\Delta G^{\circ}_{\text{reaction}} = -104.286 \text{ kcal}$ ). Microscopic evidence also suggests close links between these reactions and microorganisms (Monteiro et al. 2014). Dating supergene goethite by (U–Th)/He helps to identify times in the past conducive to hematite dissolution and goethite precipitation. **(C)** Eh–pH diagram for the Fe– $\text{O}_2$ – $\text{H}_2\text{O}$  system. Blue arrows illustrate the thermodynamically favored pathways for the oxidation (1), dissolution (2a), and precipitation (2b) reactions in parts B and C.





**FIGURE 2** (A) Tropical rain forests blanketing the Carajás Mountains (Pará, Brazil) conceal weathering profiles that may exceed 500 m in depth. (B) Open pit mining operations expose these deep and chemically stratified weathering profiles (the profile exposed in B is ~110 m deep). (C) Geochronology of supergene cryptomelane samples collected during mining operation reveals that the lateritic profile at Igarapé Bahia was already forming at ~67 Ma. (D) Possibly intermittent but recurrent wet conditions during weathering throughout the entire Cenozoic promoted the effective leaching of Cu from the upper 100 meters of the weathering profile. This is seen in the concentration vs. depth plot. Copper is shown in blue. Weathering resulted in some copper redeposition at depth but also significant Cu loss from the system. Gold, on the other hand, was redistributed and enriched within preferential horizons within the profile (shown in red), forming a rich (> 110 tons) lateritic gold deposit.

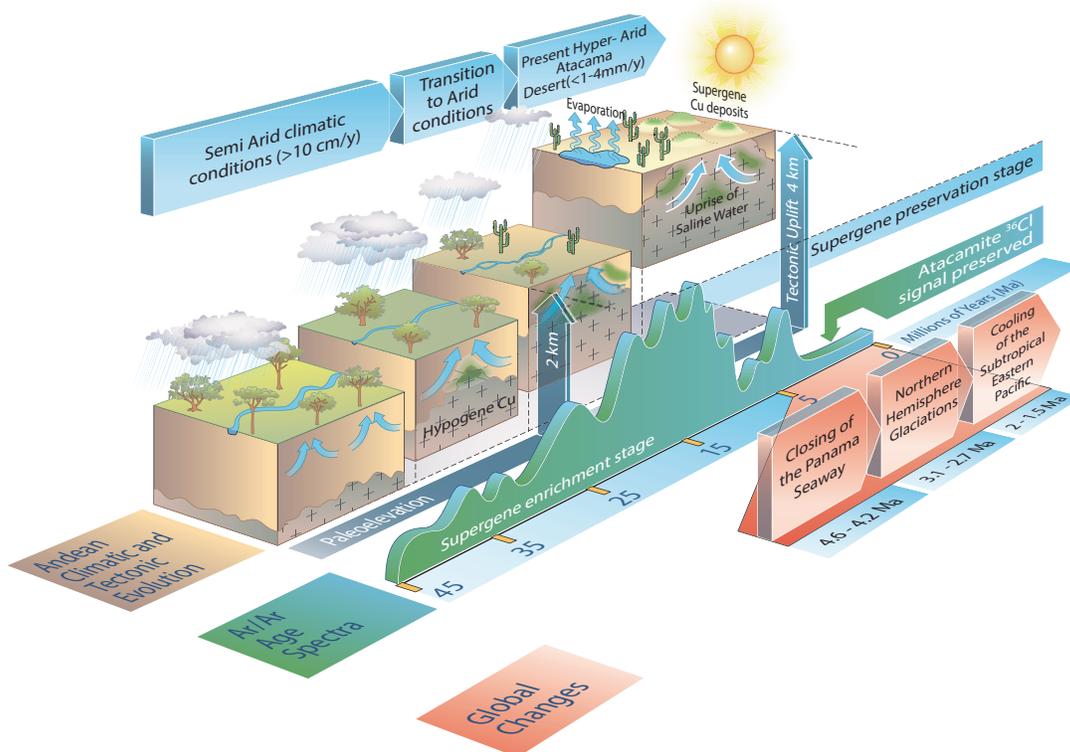
(U–Th)/He and  $^4\text{He}/^3\text{He}$  methods (Shuster et al. 2005; Heim et al. 2006; Monteiro et al. 2014). We will illustrate the application of  $^{40}\text{Ar}/^{39}\text{Ar}$ , (U–Th)/He and  $^4\text{He}/^3\text{He}$  to the study of selected supergene deposits below and discuss less frequently applied methods. But first: What is the evidence that links mineral precipitation in the weathering crust with climatic, not tectonic, drivers in the geologic past?

Feng and Vasconcelos (2007) illustrate the role that climate has played on supergene mineral precipitation. These authors'  $^{40}\text{Ar}/^{39}\text{Ar}$  results for Pleistocene supergene Mn deposits in southeastern Queensland (Australia) yield age clusters that correspond to warm periods previously noted in the oceanic stable isotope record (Imbrie et al. 1984). One of the  $^{40}\text{Ar}/^{39}\text{Ar}$  age clusters also corresponds to a cluster of U-series ages of Fe oxyhydroxides from the Ranger Uranium orebody in the Northern Territory of Australia (Bernal et al. 2006). The clustering of independent geochronological results that have been derived from different methods and applied to distinct minerals from weathering profiles >2,000 km apart from areas under contrasting tectonic regimes and showing very different tectonic histories suggest a weak tectonic control on chemical weathering. On the other hand, the correspondence of results between the continental and the oceanic records provide strong evidence that climate plays a major role in the dissolution–reprecipitation of minerals in weathering profiles and supergene ore bodies. It also suggests that histograms and probability density plots of supergene age distributions are robust approaches for extracting paleoclimatic signals from age distributions.

### Dating Climate Changes from South American Supergene Copper Deposits

Supergene enrichment is essential for the economic viability of many porphyry copper deposits (Reich and Vasconcelos 2015 this issue), and determining when and how supergene enrichment has occurred is important when exploring for enriched and exotic copper deposits (Mote et al. 2001). As host for the largest and richest porphyry copper deposits in the world, the Andean region of South America has

been at the center of research on the topic. The first use of dated supergene minerals for climate reconstruction was by Alpers and Brimhall (1988), who interpreted the cessation of supergene alunite precipitation at ~14.7 Ma at the La Escondida (Chile) porphyry copper deposit as evidence for the start of hyperaridity in the Atacama Desert. Supergene enrichment and formation of high-grade copper deposits occurred during wetter, but essentially semi-arid, periods in the Early to Middle Miocene (Alpers and Brimhall 1988) (Fig. 3). Rapid Andean uplift during the Middle Miocene created a barrier for the westward penetration of moisture from the Amazon; a simultaneous decrease in evaporation from the southern Pacific Ocean was due to a strengthening of the Humboldt current along the Peru–Chile coast and this led to aridification (Alpers and Brimhall 1988). Aridification slowed the process of supergene enrichment, and the consequent and simultaneous decrease in erosion rates helped preserve the supergene enrichment blankets that had formed by the ever-descending water tables (Alpers and Brimhall 1988). Subsequent geochronological studies confirmed that supergene enrichment occurred from ~34 Ma to 14 Ma (Oligocene to Middle Miocene) and that aridification was the most likely cause for the cessation of supergene ore enrichment (Sillitoe and McKee 1996). Dating of Andean supergene alunites, cryptomelanes, and birnessites from El Salvador (Chile) revealed a similar time span (from ~35 Ma to ~11 Ma) for the formation, and then cessation, of exotic copper mineralization, again suggesting that desiccation of the Atacama desert during the Middle Miocene may have stopped the dissolution, transport, and reprecipitation of metals in this supergene system (Mote et al. 2001). A more comprehensive study—which included the  $^{40}\text{Ar}/^{39}\text{Ar}$  analysis of 29 samples of supergene alunites, jarosites, and hollandite-group Mn oxides from the Atacama Desert—confirmed previous conclusions and extended the initiation of hyperaridity to ~5 Ma in the southern region of the Atacama Desert (Arancibia et al. 2006) (Fig. 3). Reich et al. (2008) used U-series geochronology,  $^{36}\text{Cl}$  and  $^{129}\text{I}$  measurements, and fluid inclusion studies, to show that atacamite ( $\text{Cu}_2\text{Cl}(\text{OH})_3$ ), a supergene mineral, precipitated under hyperarid conditions, continued to dissolve and



**FIGURE 3** Schematic representation of supergene enrichment processes during the climatic and tectonic evolution of the Andes. **(REAR PANEL)** A crustal block containing a deeply buried copper ore deposit is progressively exposed to the surface due to tectonic uplift. During exhumation, groundwater flow leaches hypogene copper minerals to form secondary copper assemblages (green) under increasingly oxidizing conditions. Protracted supergene oxidation and enrichment proceeds under a climate-change scenario characterized by transition from wetter,

semi-arid conditions (precipitation rates  $>10$  cm/y) to drier, arid conditions. Under present-day hyperarid climate (precipitation  $<1-4$  mm/y), supergene copper assemblages are modified by upwelling saline waters, leaving  $^{36}\text{Cl}$  signatures that are preserved due to the lack of precipitation. **(CENTER PANEL)** The  $^{40}\text{Ar}/^{39}\text{Ar}$  age spectrum for the last 45 Ma. Vertical scale indicates increasing humidity conditions, reaching a peak at  $\sim 20-15$  Ma in the Atacama Desert. **(FRONT PANEL)** Global changes affecting climate for the last 5 Ma are highlighted.

reprecipitate from  $\sim 2$  Ma to the present; their explanation was that copper could be remobilized by extremely saline solutions, even during the hyperarid stage of supergene enrichment.

Therefore, applying complementary isotopic tools to unravel the different aspects of a weathering history is essential if one wants to extract a complete climatic history from a supergene ore body. There is a wealth of information recorded in these supergene systems.

Whereas the history of mineral dissolution–reprecipitation in the Andes reveals the importance of arid conditions in the preservation of supergene copper deposits, in the adjacent Amazon basin wetter conditions throughout the Cenozoic led to the loss of copper. Several supergene ore deposits are hosted in the Carajás Mountains (Brazil), a series of plateaus at between 600 m to 1000 m and  $\sim 500$  km south of the mouth of the Amazon River (FIG. 2A INSERT). The longevity of the weathering history experienced by these plateaus produced lateritic profiles (i.e. chemically stratified weathering profiles blanketed by a very stable iron duricrust), including Fe, Mn, Al, Au, and Ni laterites (Vasconcelos 1999a). Several of the Cu–Au deposits at the Carajás district (e.g. Salobo, Igarapé Bahia) underwent deep weathering, but supergene Cu enrichment is not prominent. Weathering at the Igarapé Bahia Cu–Au deposit led to the formation of a 100–150 m deep lateritic profile (FIG. 2B). During weathering, Cu was completely leached from the upper parts (0–100 m) of the profile and only partially concentrated as a complex assemblage of cuprite, malachite, azurite, and native Cu at 100–120 m (FIG. 2D). The abrupt transition from Cu-oxide assemblages to hypogene chalcocite  $\pm$  chalcocite  $\pm$  bornite at  $>120$  m, without a signifi-

cant supergene Cu (chalcocite) blanket, suggests that the Cu that had been leached from the upper parts of the profile must have been lost from the system. Fortunately, the leached Cu part of the Igarapé Bahia profile had been enriched in supergene Au (FIG. 2D). During Au mining, supergene Mn oxides were systematically sampled and dated by the  $^{40}\text{Ar}/^{39}\text{Ar}$  method (Vasconcelos, unpublished results), which yielded the weathering history illustrated in FIGURE 2C. The fact that minerals have been precipitating at Carajás for the past  $\sim 70$  Ma (latest Cretaceous) suggests that wet conditions here have been around for a very long time. The humid weathering conditions, most likely intermittent but spanning the entire Cenozoic, did not favor the reprecipitation of Cu. The Cu must have been leached from the system by the active groundwater system that fed local springs emanating from the plateaus. The protracted weathering history interpreted for the Igarapé Bahia profile is corroborated by the record preserved in nearby lateritic Mn and Fe deposits, also dated by the  $^{40}\text{Ar}/^{39}\text{Ar}$  method (Vasconcelos 1999b).

### Dating Climate Changes from South American and Other Supergene Manganese Deposits

The abundance and relative stability of K–Mn oxides in Mn laterites preserves a comprehensive record of weathering. Hollandite ( $\text{Ba}(\text{Mn}_6^{4+}\text{Mn}_2^{3+})\text{O}_{16}$ ) and cryptomelane ( $\text{K}(\text{Mn}_7^{4+}\text{Mn}_3^{3+})\text{O}_{16}$ ), major ore minerals in Mn laterites, yield a detailed history of weathering and continental paleoclimatic evolution (Vasconcelos 1999b) when dated by the  $^{40}\text{Ar}/^{39}\text{Ar}$  method. At the Carajás district (Brazil), supergene Mn-oxide precipitation in the Azul deposit initiated at  $\sim 67$  Ma (Late Cretaceous) and continued intermittently until  $\sim 40$  Ma (Middle Eocene) (Vasconcelos 1999b). A more

recent study, encompassing a larger number of samples from representative areas of the Azul deposit, shows an even more prolonged history, very similar to that obtained for the Igarapé Bahia profile.

Hollandite-group Mn oxides also occur as minor phases in lateritic iron deposits at the Carajás district (Vasconcelos 1999b). An  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology study showed a history of Mn precipitation similar to that obtained from the Azul and Igarapé Bahia profiles. Overall, the Carajás geochronology revealed a history of possibly intermittent, but abundant, rainfall throughout the Cenozoic.

The study of supergene Mn deposits elsewhere in Brazil (de Oliveira Carmo and Vasconcelos 2006; Spier et al. 2006) shows a similarly prolonged history of weathering, starting at ~67 Ma and continuing until the present. This history is intermittent, revealing a close link between the evolution of weathering profiles and global climatic conditions.

Many  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronological studies of Mn deposits in Africa (Beauvais et al. 2008), Australia (Dammer et al. 1999; Li and Vasconcelos 2002; Vasconcelos 2002; Feng and Vasconcelos 2007; Vasconcelos et al. 2013), China (Li et al. 2007; Deng et al. 2014), India (Bonnet et al. 2014), and Europe (Hautmann and Lippolt 2000) now reveal comparable histories, where intermittent weathering and mineral precipitation throughout the entire Cenozoic suggests alternating wet and dry periods that, in turn, reflect global climatic conditions (FIG. 4 A-D). Hautmann and Lippolt (2000) prefer to attribute this intermittent mineral precipitation history to tectonic controls, but a clear mechanism that can link tectonic forces to mineral precipitation in the weathering crust is not clearly identifiable.

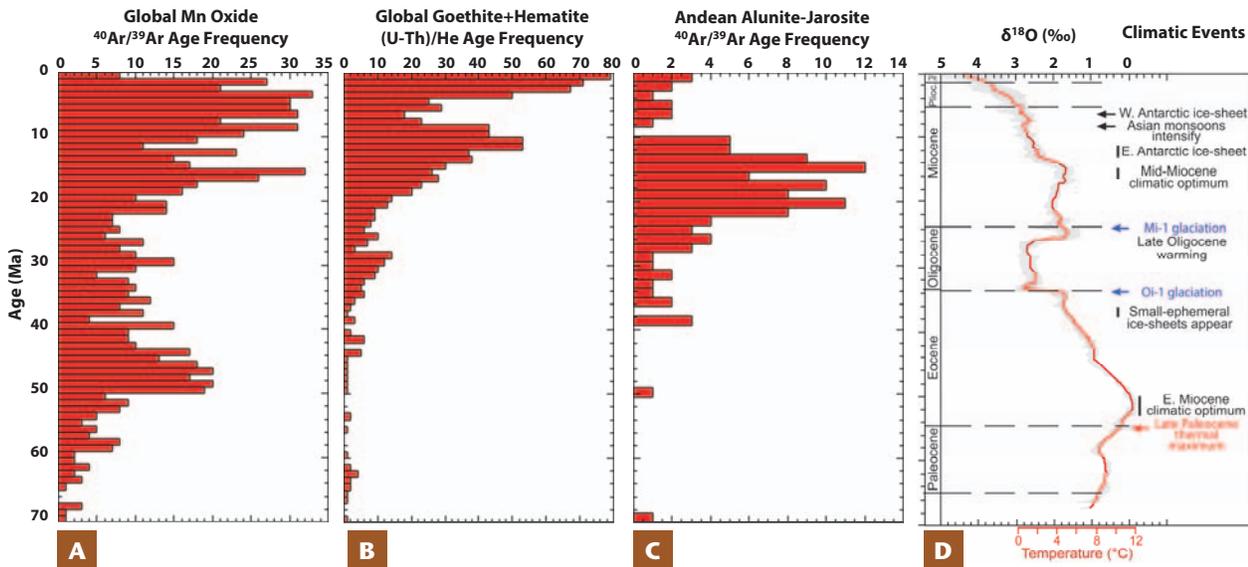
### Climate Inferences from Supergene Iron Deposits

There are two main types of supergene iron deposits: lateritic deposits, where deep stratified profiles overlie weathered banded-iron formations (BIFs); and channel

iron deposits (CIDs), where iron-rich alluvial sediments have undergone ferruginization after river channel aggradation (Heim et al. 2006). Applying  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology to the Mn minerals in these deposits in Australia and Brazil showed that the lateritic deposits span a longer history of weathering than the CIDs (Vasconcelos 1999b; Vasconcelos et al. 2013). Both types of deposits are capped by goethite-cemented crusts, which are amenable to (U–Th)/He geochronology.

Vasconcelos et al. (2013) reported on a (U–Th)/He geochronology study of the Lynn Peak CID (Western Australia) and showed that ancient weathering profiles that overlie the BIFs had been partially eroded, that the transported material had been deposited in river channels, and that the detritus had finally been cemented by goethite shortly after erosion and deposition. The history of weathering derived from the (U–Th)/He method is very similar to that obtained through  $^{40}\text{Ar}/^{39}\text{Ar}$  geochronology of coexisting Mn oxides (Vasconcelos et al. 2013), indicating internal consistency between these independent geochronological systems. Interestingly, (U–Th)/He dating of goethite cements through a vertical profile of the Yandi CID (Western Australia) shows that goethite cements in the channels become younger towards the bottom of the profile. This observation suggests that CID cementation resulted from a descending water table during the aridification of Western Australia throughout the Miocene (Heim et al. 2006).

Contrasting with the tenacity of iron oxyhydroxides in the Australian weathering profiles, studies on the (U–Th)/He geochronology of goethite cements in duricrusts overlying weathered BIFs in Brazil showed that the Brazilian duricrusts at the surface are invariably younger than the saprolites at depth (Monteiro et al. 2014). Iron dissolution–reprecipitation in duricrusts appears to respond to dissolution under reducing conditions that are driven by microorganisms and organic acids exuded from the local vegetation (Monteiro



**FIGURE 4** (A) Histogram illustrating the global distribution of ages for supergene Mn oxides. (B) Histogram illustrating the global distribution of ages for supergene goethites + hematites. (C) Histogram illustrating the distribution of Andean supergene alunite–jarosite ages. The distribution of supergene minerals through time helps to identify periods in the geological past conducive to the dissolution and reprecipitation of ore elements in the weathering environment. Each mineral species records slightly different conditions. For example, Mn oxides record more humid conditions, but also times in the past where abundant vegetation may have exuded the organic acids needed for

the reduction–dissolution processes needed to dissolve and reprecipitate Mn oxides in the weathering environment. In contrast, the formation and preservation of supergene alunite and jarosite requires relatively dry conditions after mineral precipitation, typically achieved by drawdown of the water table during a transition from humid or semi-arid to hyperarid conditions. (D) Graph of global temperature changes from the Paleocene to Recent, including key warm and cold periods. This graph helps explain the weathering conditions reflected in figures A to C. AFTER ZACHOS ET AL. (2001).

et al. 2014). More detailed studies, on a global scale, would help to differentiate between local versus global controls on weathering and supergene ore genesis.

## CONCLUSIONS

By determining which, where, how, and when chemical reactions occur in the weathering crust, we can decipher the tectonic and climatic histories of the Earth during the formation of supergene ore bodies. Probability density distributions of mineral ages through time, obtained from distinct mineral species dated using different, but complementary, isotopic methods, provide a complete weathering and paleoclimatic history for an exposed segment of the weathered crust. A continental paleoclimatic record derived from chemical reactions preserved in supergene ore deposits may complement the record available from ocean

sediments and so yield information that can be very useful in reconciling paleoceanographic and paleocontinental climatic histories.

## ACKNOWLEDGMENTS

The authors thank the editors and reviewers of this manuscript, especially those by H. Bao and an anonymous reviewer. PV thanks the ARC for the construction of the Argon Laboratory at UQ; Vale for access to study sites at Carajás and Minas Gerais; Rio Tinto for access to sites in Western Australia; and ARC and FAPESP for research funding. MR thanks CONICYT funding through Fondecyt and Fondap grants and support from ICM through grant #130065 "Millennium Nucleus for Metal Tracing Along Subduction". DLS acknowledges CONICYT funding through the University of California, Berkeley. ■

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# Copper Isotopic Perspectives on Supergene Processes: Implications for the Global Cu Cycle

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1811-5209/15/0011-0323\$2.50 DOI: 10.2113/gselements.11.5.323

**A compilation of copper isotopic compositions ( $\delta^{65}\text{Cu}$ ) from supergene systems suggests distinct differences in the mean  $\delta^{65}\text{Cu}$  of Cu in leach cap ( $\delta^{65}\text{Cu} = -1.2 \pm 3.5\text{‰}$ ), enrichment zone (mean  $\delta^{65}\text{Cu} = +1.2 \pm 4.2\text{‰}$ ), and fluids (mean  $\delta^{65}\text{Cu} = +0.9 \pm 1.3\text{‰}$ ) relative to the high-temperature sulfides that comprise the primary ore ( $\delta^{65}\text{Cu} = +0.1 \pm 0.6\text{‰}$ ). These isotopic differences can be explained by the oxidative dissolution of primary ore minerals, such as chalcopyrite, and the subsequent precipitation of oxides in the near-surface system and of sulfides at depth. A dynamic mass balance model predicts the observed Cu isotopic compositions of the Cu reservoirs in nature and constrains the temporal isotopic evolution of supergene systems. From the model, these systems isotopically evolve to substantial extents over 500 ka to 5 Ma time scales. In relatively closed systems, percent-level loss of Cu from the solid (with  $\delta^{65}\text{Cu}$  values  $\gg 0\text{‰}$ ) is possible, suggesting that supergene systems are important components of the global Cu cycle.**

**KEYWORDS:** supergene system, copper isotopes, reactive transport model, exploration geology, global Cu cycle

## INTRODUCTION

Copper (Cu) is an element essential to life, cycled during the chemical weathering of rocks, intimately involved in reduction and oxidation (redox) processes, and a valuable economic metal. Supergene systems are important Cu resources because Cu is the principal metal that is redistributed and (re)concentrated (i.e. cycled) during supergene enrichment. Sillitoe (2005) notes that  $>50\%$  of the copper currently mined on Earth is derived from supergene deposits. It is, therefore, important to understand how and why Cu ore deposits form, where they might be found, and which geochemical tools are best for finding them. More broadly, supergene systems cycle a substantial mass of Cu over millions of years, leading to the possibility that supergene systems play an important role in the global Cu cycle.

While Cu is a substantially heavier element than those elements whose isotopes have been traditionally targeted as tracers in natural systems ( $\delta^{13}\text{C}$ ,  $\delta^{18}\text{O}$ ,  $\delta^{15}\text{N}$ , and  $\delta\text{D}$ ), it fractionates isotopically in a mass-dependent manner in nature (Note: Cu isotopic composition is expressed in delta notation as  $\delta^{65}\text{Cu}$  (in permil, ‰, units), which expresses the  $^{65}\text{Cu}/^{63}\text{Cu}$  ratio of a sample relative to the NIST 976 standard). Redox processes are known to fractionate Cu isotopes to significant extents compared to other transition

metals (FIG. 1). Supergene systems cycle Cu via redox processes and, therefore, exhibit a wide range of  $\delta^{65}\text{Cu}$  values in both fluids and rocks that is characteristic of the main Cu reservoirs in the system (e.g. the leach cap, enrichment zone, and primary ore; FIGS. 1 AND 2). Accordingly, Cu isotopes may prove a useful tool for mineral exploration purposes.

Supergene systems have the potential to reveal isotopic variability in the global Cu cycle over time given the amount of copper that is cycled and the large variability in  $\delta^{65}\text{Cu}$  in the supergene system. Understanding Cu isotopic variability in nature is critical to characterizing Cu fluxes in the modern global Cu cycle, identifying the processes that isotopically fractionate Cu, and developing Cu

isotopes as a tool for constraining Cu cycling in the past (i.e. the Cu isotope “proxy”). Therefore, from the perspectives of both mineral exploration and geochemical cycling, Cu isotopes might prove effective tools for elucidating supergene-system processes and constraining how these systems evolve on regional and global scales.

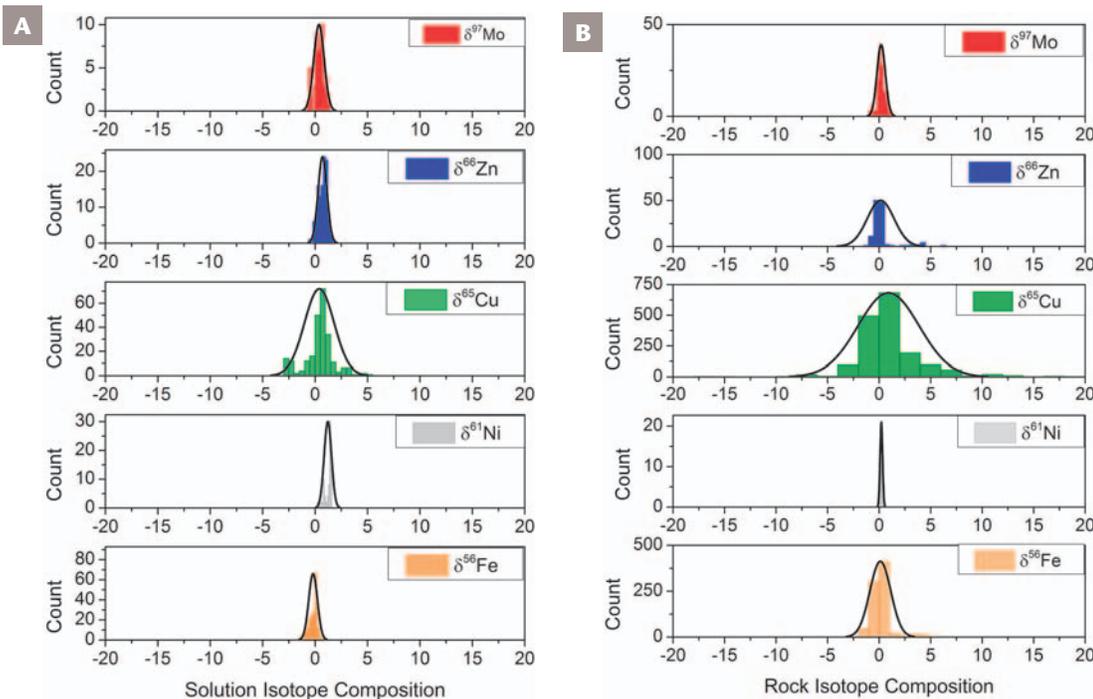
## COPPER CYCLING IN SUPERGENE SYSTEMS

The supergene system is a regional-scale weathering system in which Cu is mobilized in the near surface and transported to depth. The key processes that occur during supergene weathering are the oxidation of primary Cu-rich sulfide minerals, the downward migration of Cu-rich fluids, and the precipitation of secondary Cu-rich minerals at a redox boundary (i.e. the water table). Both oxidative dissolution and precipitation have been shown to fractionate Cu isotopes at low temperatures (see FIGS. 1 AND 2).

Previous studies have focused on understanding how Cu is mobilized and enriched in low-temperature aqueous supergene systems. The specific objectives of such work have been to identify the main mineral dissolution reactions that generate economically relevant Cu deposits, to constrain the temporal and spatial evolution of mineral assemblages and fluid compositions, and to address the extent to which supergene systems are open to the loss of metals and sulfur (Ague and Brimhall 1989; Lichtner and Biino 1992; Chavez 2000). Such work has demonstrated that supergene systems behave as closed systems (with respect to Cu) and that uplift and erosion are important processes for enriching Cu concentrations.

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**FIGURE 1** Histograms of literature-derived transition metal isotopic compositions of natural (A) rocks and (B) fluids, with number of papers utilized noted: Fe ( $n = 35$ ), Ni ( $n = 5$ ), Cu ( $n = 37$ ), Zn ( $n = 14$ ), Mo ( $n = 16$ ). The reference standards are: IRMM 14 (Fe), NIST 986 (Ni), NIST 976 (Cu), and JMC Lyon (Zn). No consistent reference standard has been used across laboratories for Mo, though none of the ICP-MS standards that are currently used appear to vary significantly ( $<0.6\text{‰}$ ) from NIST SRM 3134.

Local supergene activity can also persist over long timescales on the order of  $<10$  Ma (Sillitoe and McKee 1996; Braxton et al. 2012). Supergene systems have sufficient time to be influenced by evolving surface geochemical and/or by geological conditions (e.g. surface Earth oxidation state,  $p\text{CO}_2$ , temperature, uplift rate). As conditions evolve, they can drive multiple cycles of metal mobilization, immobilization, and erosion that are difficult to decipher. Given such long timescales of evolution, supergene systems become potentially important components of the global Cu geochemical cycle and, perhaps, indicators of how surface geochemical conditions have evolved over time.

### COPPER ISOTOPES IN THE SUPERGENE SYSTEM

Within supergene systems, there are distinct differences in  $\delta^{65}\text{Cu}$  between the three reservoirs (i.e. the leach cap, enrichment zone, and primary ore; FIG. 2). Leach caps usually have the lowest  $\delta^{65}\text{Cu}$  values, while the enrichment zone has the highest  $\delta^{65}\text{Cu}$ . From a mass balance perspective, a cyclic (leaching, erosion, recycling) open system dynamic is clearly expressed in supergene enrichment zones, for which Cu enrichments can reach as high as 700%. Such enrichments correspond to  $\delta^{65}\text{Cu}$  values in secondary Cu sulfides that are isotopically heavy (mean:  $+1.2\text{‰}$ ) relative to the primary ore but span a tremendous range ( $\delta^{65}\text{Cu}$  of  $-6$  to  $+8\text{‰}$ ; FIGS. 1 AND 2). Supergene mobilization, transport, and precipitation also results in the generation of soils and leach cap Fe-oxides in which the secondary Cu minerals have modestly low  $\delta^{65}\text{Cu}$  values, yet also cover quite a large range ( $-9\text{‰}$  to  $+2\text{‰}$ ; Mathur et al. 2009; Braxton and Mathur 2011).

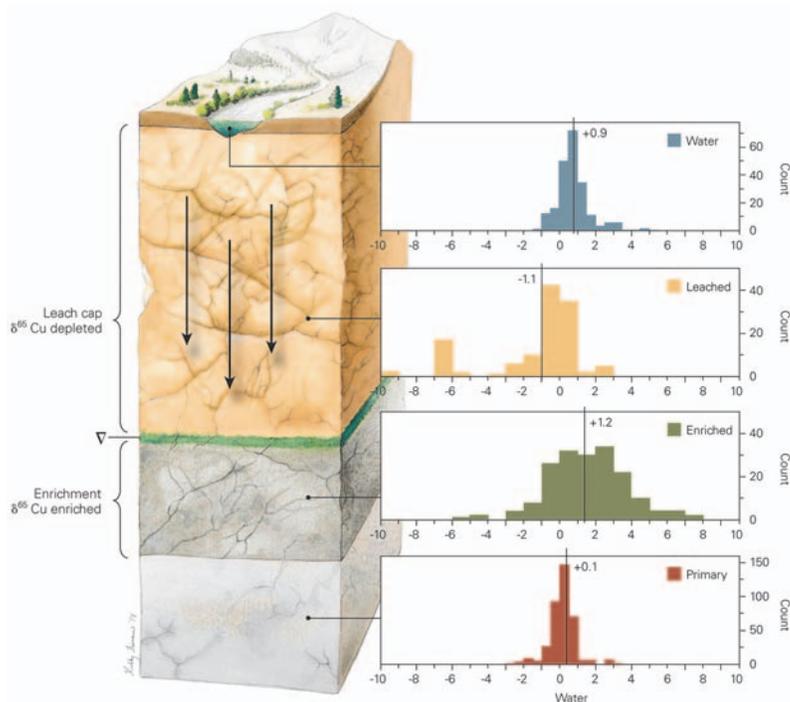
Both oxidative dissolution and precipitation of sulfides can isotopically fractionate Cu. Experimental studies have demonstrated that the oxidation of Cu sulfides (Mathur et al. 2005; Fernandez and Borrok 2009; Kimball et al. 2009), chalcocite, bornite (Wall et al. 2011), and enargite (Kimball et al. 2009) generates solutions that are  $+1\text{‰}$  to  $+3\text{‰}$  relative to the initial reactant. Such values are corroborated by measurements of natural systems in which oxidative dissolution is occurring. (Fernandez and Borrok 2009; Kimball et al. 2009; Mathur et al. 2013a,b).

Experimental studies suggest that considerable isotopic fractionation is associated with sulfide precipitation on preexisting sulfides surfaces (approximately  $-2.6\text{‰}$ ; Pekala et al. 2011), while the precipitation of Cu chlorides results in a much smaller isotopic effect (Ehrlich et al. 2004). Such empirical constraints on isotopic fractionation is generally consistent with theoretically predicted estimates of equilibrium isotope fractionation (Sherman 2013). Interestingly, experimental work demonstrates that the final sulfide precipitates appear to be in isotopic equilibrium with their solutions. This suggests that the bulk solid is capable of isotopic equilibration with its ambient fluid over experimental timescales. Given the slow pace at which equilibrium is achieved in natural geologic systems, this may obviate the need to call upon kinetic isotope effects when interpreting natural sulfide isotopic compositions.

Biological processes can also affect the  $\delta^{65}\text{Cu}$  of solutions and solids in supergene systems, though such effects are going to be best seen close to the surface in the critical zone. Microbes and plants can both fractionate Cu isotopes (Kimball et al. 2009; Navarrete et al. 2011a,b). In most cases, biological material (i.e. cells) sequesters Cu with lower  $\delta^{65}\text{Cu}$  values, though the magnitude of the expressed isotopic fractionation can vary greatly.

### SUPERGENE WEATHERING AND THE GLOBAL COPPER CYCLE

The riverine input flux of dissolved Cu to the global ocean is  $\sim 7.7 \times 10^8 \text{ mol y}^{-1}$  and has a  $\delta^{65}\text{Cu}$  of  $0.63\text{‰}$  (Little et al. 2014). The  $\delta^{65}\text{Cu}$  of rivers is quite heavy, which could be partly explained by the leaching and/or erosion of Cu from supergene systems. Though supergene systems are typically regarded as closed, it is likely that enough Cu leaves them to be relevant to the global Cu cycle. A back-of-the-envelope calculation suggests that the flux of Cu from actively evolving supergene systems is  $\sim 10^8 \text{ mol y}^{-1}$ . This figure assumes a subaerial landmass surface area of  $\sim 1.5 \times 10^8 \text{ km}^2$  (Turcotte and Schubert 1982), supergene activity in the uppermost 100 meters of  $\sim 1\%$  of this crustal area, an average primary ore Cu concentration of  $0.024 \text{ mol Cu/kg rock}$  ( $0.15 \text{ wt\% Cu}$ ), an average rock density of  $3 \text{ g/cm}^3$ , and the loss of  $1\%$  of this mass of Cu over a million-year



**FIGURE 2** (LEFT) Schematic illustrating the spatial relationship between Cu reservoirs in a typical supergene system (leach cap, enrichment zone, and primary ore). ILLUSTRATION BY KELLY FINAN. (RIGHT) Histograms of literature-derived ( $n = 37$ ) Cu isotopic compositions ( $\delta^{65}\text{Cu}$ ) of each reservoir and surface water.

time scale. This estimate is comparable to the total input flux to the modern ocean, which implies that a supergene-related flux is relevant to, and could even dominate, the global Cu cycle. A supergene flux is also relevant to the global Cu cycle from an isotopic perspective, given the significant in  $\delta^{65}\text{Cu}$  variability in supergene systems. Such an estimate does not even consider the weathering flux of Cu from supergene systems after enrichment has ceased, which could generate a comparable mass flux with equally considerable isotopic leverage within the global Cu cycle.

To understand all this better, geochemists need to constrain quantitatively the temporal and spatial evolution of  $\delta^{65}\text{Cu}$  in the output flux from active supergene systems (as a whole) and from distinct portions of the supergene system, because all may influence the global Cu cycle. The motivating questions are: Can supergene systems affect the global Cu cycle? If so, what is the likely  $\delta^{65}\text{Cu}$  of the supergene input flux and how might the  $\delta^{65}\text{Cu}$  of this flux evolve over time?

### REACTIVE TRANSPORT MODEL FOR SUPERGENE PROCESSES

A simple reactive transport model (Fantle and DePaolo, 2006, 2007) can be used to approximate the dominant processes operating in supergene systems. The model simulates a single solid dissolving and reprecipitating such that there is no net change in the solid mass with time; in this case, the evolution of the pore fluid ( $f$ ) is described by:

$$\frac{C_f}{t} = D \frac{\partial^2 C_f}{\partial z^2} - v \frac{\partial C_f}{\partial z} + RM(C_s - KC_f) \quad (1)$$

while the evolution of the bulk, homogeneously reacting solid ( $s$ ) is described by:

$$\frac{C_s}{t} = -R(C_s - KC_f) \quad (2)$$

where  $D$  is the diffusion coefficient of the aqueous species under consideration in a porous medium (i.e. corrected for tortuosity, such that  $D = 0.0114 \text{ m}^2 \text{ y}^{-1}$  for  $\text{Cu}^{2+}$  at  $25^\circ\text{C}$  and a porosity of 0.6),  $v$  is the advection velocity of the pore fluid ( $\text{m y}^{-1}$ ),  $C_s$  is the concentration of Cu in the solid ( $\text{mol kg}^{-1}$ ),  $C_f$  is the concentration of Cu in the fluid ( $\text{mol kg}^{-1}$ ),  $R$  is the rate at which the solid reacts with pore fluid ( $\text{y}^{-1}$ ),  $M$  is the local solid/fluid mass ratio, and  $K$  is the equilibrium distribution coefficient of the element between the solid and the fluid. The one-dimensional spatial reference frame (i.e. the model “column”) is defined with  $z = 0$  at the atmosphere–soil interface, with  $z$  being positive in the downwards direction. The evolution of isotopic composition is simulated by tracking each of the individual stable nuclides of Cu ( $^{63}\text{Cu}$  and  $^{65}\text{Cu}$ ) separately. Fractionation factors, which describe the preference for one nuclide over another during a specific process ( $\alpha = 1$ , for example, indicates no preference), are applied to both the dissolution and precipitation fluxes, as described in the “What do the models of supergene processes tell us?” section below.

The model is designed to run iteratively for up to 10 sequential run cycles, with the results from the previous cycle used as the initial conditions for the subsequent cycle. A length-scale parameter ( $\sim 150 \text{ m}$ ) is applied that resamples the solid concentration and isotopic composition from the bottom up, simulating rapid surface erosion of the model column between cycles. In the simulations, the depth variability in  $K$  is constrained by a logistic function, which varies from low values at shallow depths ( $\rightarrow 0$ ) to higher values at deeper depths ( $\rightarrow 1000$ ). The transition from low to high  $K$  is placed randomly around a mean depth from cycle to cycle to simulate the change in depth to groundwater.

The equations above are solved with a modified centered finite difference approach (e.g. Fantle and DePaolo 2006), with a modified leapfrog approximation utilized for the advection term to enhance stability (Bourchtein and Bourchtein 2012). The spatial resolution of the model ( $dz$ ) is 10 meters, the time step ( $dt$ ) is 0.1 years, the total column height is 300 m, the total time is 500 ka (per cycle), the reaction rate ( $R$ ) is constant with depth and time (on the order of  $5 \times 10^{-6} \text{ y}^{-1}$ , which is a reasonable rate given the observations made of reaction rates in nature (e.g. Maher et al. 2004, 2006; Fantle and DePaolo 2006), and the porosity is constant ( $= 0.6$ ) in all simulations. Advection is assumed to occur only in the downwards (+) direction, and the advection velocity is constrained to be less than  $0.1 \text{ m y}^{-1}$  in all simulations (Ague and Brimhall 1989).

With regard to the fluid at the upper boundary is constrained to be closed to diffusion but open to advection in the positive direction, and the concentration (0.01 mM) and isotopic composition (0‰) of the advecting fluid held constant in time. The lower boundary, however, is technically open, though is more leaky than fully open. The reason for this is the numerical instability that arises in the presence of large concentration gradients in the fluid, even at exceedingly low  $dt$  ( $< 0.005 \text{ y}$ ) and using the modified leapfrog approach. To minimize such gradients, the  $K$  value is varied smoothly over the model space and the reaction rate held constant as a function of depth. Similarly, the lower boundary is constrained to be no more than a few percent lower in concentration than, and identical in isotopic composition as, the lowermost grid point (i.e. lowermost point in the model domain at which the reactive transport equations are solved).

## WHAT DO THE MODELS OF SUPERGENE PROCESSES TELL US?

### Mass and Isotopic Evolution of Supergene Solids

Reactive transport models simulate supergene processes, replicating the gross features of a supergene deposit, including the generation of a leach cap and an enrichment zone over ten successive 500 ka cycles (5 Ma) of leaching, reprecipitation, and erosion (a single representative simulation cycle is shown in Fig. 3). The model results below are discussed relative to the degree to which the system is open or closed, which is expressed herein by the advective length scale,  $L_a (= v/RMK)$  (Fantle et al. 2010). This length scale reflects the relative dominance of the rate of advection compared to the rate of reaction in the model system, and it generally describes the distance ( $\sim 3 \cdot L_a$ ) over which solid and fluid reach local equilibrium (e.g. Maher et al. 2004). For a relatively closed system ( $L_a \approx 20$  m), and assuming a primary ore Cu concentration of  $\sim 0.024$  mol Cu kg<sup>-1</sup> (0.15% Cu), a reaction rate of  $5 \times 10^{-6}$  y<sup>-1</sup>, and a depth-variable  $K$  value, then a single 500 ka cycle can produce a maximum enrichment of up to three times the primary ore Cu concentration at  $\sim 200$  meters depth.

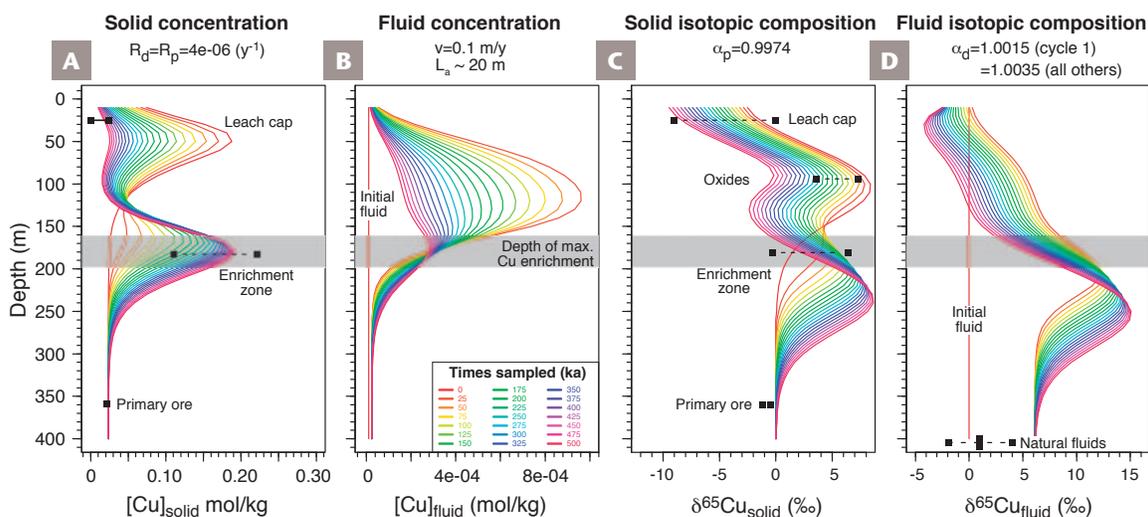
The extent of enrichment increases with each supergene Cu cycle, though not necessarily in a linear manner (Fig. 4A). However, the critical observation, based purely on mass balance constraints, is that a single 500 ka cycle cannot generate the type of enrichments typically observed in supergene systems ( $>0.10$  mol/kg; Titley 1982). In the simulations conducted to date, at least four cycles (2 Ma) are needed to reach the lower range of enrichment values observed in nature. Further, in the relatively closed system scenario presented in FIGURE 3, on the order of 1% to 3% of the Cu is lost from the total solid per cycle (Fig. 4B).

In a more open system ( $L_a = v/RMK \approx 60$  m), the enrichment process is significantly retarded. When the rate is decreased by a factor of three, the cycle 1 (i.e. the first 500 ka) enrichment in the solid is only  $\sim 50\%$ , compared to  $\sim 150\%$  in the relatively closed system scenario (Fig. 4A). If the model system is even more open ( $L_a \approx 200$  m; not shown), the

enrichment is even smaller ( $\sim 10\%$ ). Consequently, over the course of any given cycle in the relatively open system, a significantly larger proportion of Cu is removed from the solid (a fairly constant 3%) compared to that in a closed system (Fig. 4B).

The general Cu isotope systematics of the supergene system are also well characterized by the reactive transport model. The fractionation factor associated with dissolution ( $\alpha_d$ ) is assumed to be consistent with oxidative dissolution of either chalcopyrite ( $\alpha_d = 1.0015$  in cycle 1) or chalcocite ( $\alpha_d = 1.0035$  in cycles  $> 1$ ). The fractionation factor associated with precipitation ( $\alpha_p$ ) is varied between 1.003 and 0.9974, thereby encompassing the maximum range of values one would expect for the precipitation of oxides such as tenorite and cuprite at low temperatures and the precipitation of sulfides on preexisting sulfide surfaces (e.g. Pekala et al. 2011; Sherman 2013). Generally, a single cycle of supergene enrichment has the potential to produce a leach cap that is isotopically light and portions of the enrichment zone that have  $\delta^{65}\text{Cu}$  values that are higher than the primary ore ( $\delta_{\text{enrichment}} - \delta_{\text{primary ore}} \approx +1.5\text{‰}$ ). In both the closed and relatively open system scenarios, the isotopically heavy enrichment zone is initially isotopically mass balanced by isotopically light Cu just below the main enrichment zone. The overall pattern from a single cycle of enrichment, therefore, is consistent with what is observed in nature, where the mean  $\delta^{65}\text{Cu}$  of the leach cap is  $-1.1\text{‰}$  and the mean  $\delta^{65}\text{Cu}$  of the enrichment zone is  $+1.2\text{‰}$ .

Subsequent cycles of erosion and supergene weathering further fractionate the enrichment layer (FIGS. 3 AND 4). Relatively low  $\delta^{65}\text{Cu}$  values in the lower part of the system are gradually overwritten and the maximum  $\delta^{65}\text{Cu}$  of the enrichment zone increases. In the closed system case, the maximum  $\delta^{65}\text{Cu}$  observed in the enrichment zone after 10 cycles (5 Ma) reaches  $\sim +4.5\text{‰}$  ( $\alpha_p = 1.003$ ) to  $+8.5\text{‰}$  ( $\alpha_p = 0.9974$ ). Critically, these relatively high  $\delta^{65}\text{Cu}$  values are displaced relative to the depths of maximum Cu concentrations (Fig. 3), which is a consequence of isotopic distillation (expressed in the depth realm) in the presence of downwards advection. In a relatively open system, the



**FIGURE 3** Representative dynamic mass balance simulation of supergene Cu enrichment for the case in which the system is relatively closed ( $L_a = 20$  m), where  $L_a = v/RMK$  ( $v =$  advection velocity,  $R =$  reaction rate,  $M =$  mass ratio of solid/fluid, and  $K =$  equilibrium partition coefficient,  $C_s/C_f$ ). The (A) solid and (B) fluid Cu concentrations and (C–D)  $\delta^{65}\text{Cu}$  values are sampled as a function of time (sampling interval = 25 ka; total simulation time per cycle = 500 ka). The results shown represent the intracycle

evolution of the supergene system during the last of ten cycles of mobilization, transport, and precipitation (i.e. the final 500 ka of 5 Ma of evolution). Between each cycle (i.e. every 500 ka), the column is resampled to simulate relatively rapid erosion at the top of the section and the resampled data used as the starting solid in the next cycle. Isotopic fractionation factors are denoted by  $\alpha_i$ , where  $i$  refers to either precipitation ( $p$ ) or dissolution ( $d$ ).

solid evolves more slowly and does not develop enrichment zones with the high  $\delta^{65}\text{Cu}$  values observed in the closed system scenario.

### Mass and Isotopic Evolution of Supergene Fluids

The models of supergene processes suggest that supergene processes can generate fluids with a wide range of Cu concentrations and  $\delta^{65}\text{Cu}$  values. Fluid concentrations are generally low in the model simulations, but this depends on the advective length scale ( $L_a$ ): as the advective length scale increases, fluid concentrations decrease. At relatively small  $L_a$  (~20 m), fluid Cu concentrations are on the order of hundreds of  $\mu\text{M}$  in the early stages but can increase to mM levels as the enrichment zone evolves. By comparison, at  $L_a$  of ~60 m, fluid Cu concentrations are consistently less than 100  $\mu\text{M}$  through the early stages, a consequence of the relative dominance of advection over reaction in such systems.

Similarly, the patterns of fluid  $\delta^{65}\text{Cu}$  in the model column vary between open and closed systems. The simulated values are generally consistent with the data from natural systems, in which fluid  $\delta^{65}\text{Cu}$  values are between -2 and +4‰ (mean = 0.9‰; FIG. 2). The model suggests that the  $\delta^{65}\text{Cu}$  values of shallow fluids are distinct at any given point in time and can evolve over time to significant extents. For instance, in a given cycle, shallow fluids tend to have  $\delta^{65}\text{Cu}$  values that are a few permil higher than the parent. With time, shallow fluid  $\delta^{65}\text{Cu}$  values decrease, reflecting the isotopic evolution of the solid due to fractionation during oxidative dissolution ( $\alpha_d = 1.0015$  to 1.0035). Consequently, shallow fluids can attain relatively low deep fluid  $\delta^{65}\text{Cu}$  values. Such an evolution is somewhat buffered in more open systems, resulting in relatively invariant fluid  $\delta^{65}\text{Cu}$  in the early stages of supergene enrichment and, ultimately,  $\delta^{65}\text{Cu}$  values that are ~3‰ higher than to primary ore.

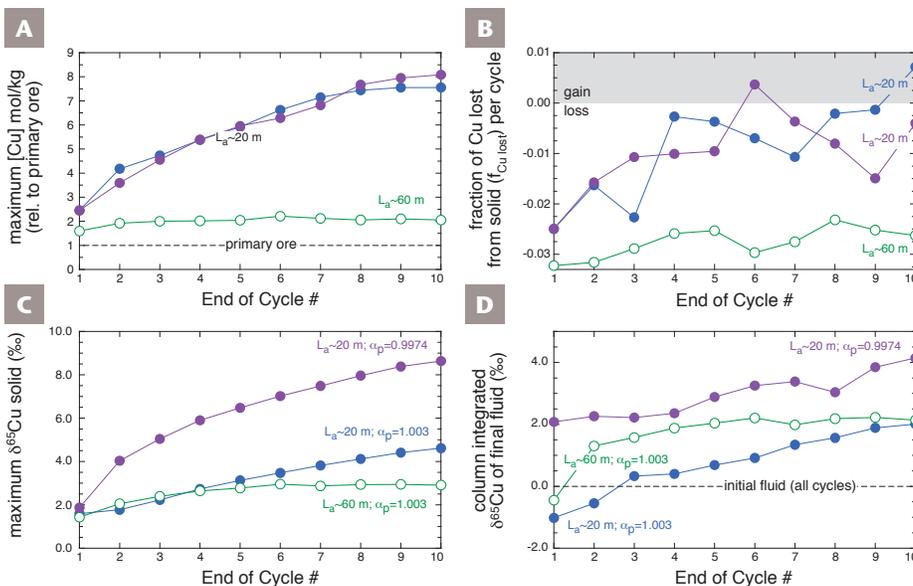
By contrast, in a relatively closed supergene system, deep fluid  $\delta^{65}\text{Cu}$  values generally vary over a more restricted range than do shallow fluids. Even so, there is potentially a ~4‰ to 5‰ range in deep fluids, both in space and time. If the fractionation factor associated with precipitation ( $\alpha_p$ ) is made to be consistent with experimental data ( $\alpha_p = 0.9974$ ), then deep fluids can be driven to extremely high  $\delta^{65}\text{Cu}$  values (~+15‰; FIG. 3D). For the case where  $\alpha_p = 1.003$ , relatively low deep fluid  $\delta^{65}\text{Cu}$  values reflect distillation of the fluids caused by enrichment early in the cycle, whereas

the increase in  $\delta^{65}\text{Cu}$  values later in the cycle reflect the increasing contribution of the dissolution flux from the enrichment zone (high  $\delta^{65}\text{Cu}$  values). In the latter case, the mass of Cu being supplied from above is extremely low so that the fluid is much more affected by continued reaction with the solid at depth than by either distillation or the supply of isotopically light Cu from the leach cap above. It is this late-stage fluid that is generally consistent with measured fluid  $\delta^{65}\text{Cu}$  values (~+0.9‰; FIG. 2), though there are indications of low  $\delta^{65}\text{Cu}$  fluids (0 to -1‰) that may reflect either the early stages of supergene evolution or simply fluids influenced by dissolution of the leach cap.

### RELATING THE MODEL SUPERGENE SYSTEM TO REAL SYSTEMS

Assuming reasonable fractionation factors associated with dissolution ( $\alpha_d = 1.0015$  and 1.0035) and precipitation ( $\alpha_p = 0.9974$  and 1.003) in supergene systems, the dynamic mass balance model generates isotopically fractionated leach caps and enrichment zones that are comparable in magnitude to the  $\delta^{65}\text{Cu}$  values measured in natural systems. The fractionation factors of 0.9974 and 1.003 are broadly consistent with both experimental and theoretical constraints on the fractionation factors associated with sulfide and oxide precipitation, respectively, while recognizing the considerable uncertainty in these values (e.g. Pekala et al. 2011; Sherman 2013). The simple approach to modeling supergene systematics described above is only an initial attempt; however, the relative mass balance between Cu immobilization in the shallow (small mass flux) and deep (large mass flux) supergene environment suggests that more complex simulations may not yield substantially different conclusions. Such a hypothesis is supported by simulations (not shown), in which distinct  $\alpha_p$  are assigned to oxide precipitation in the shallow system ( $\alpha_p = 1.0014$ ) and sulfide precipitation at depth ( $\alpha_p = 0.9974$ ), whose results do not vary markedly from the depth-invariant  $\alpha_p = 0.9974$  scenario (FIG. 4).

The simulations highlight a few important points regarding the spatial and temporal development of supergene systems. As has been suggested previously (Cook 1988), multiple cycles of Cu mobilization and immobilization, punctuated by erosive episodes, are required to generate the magnitude of Cu concentrations observed in supergene enrichment



**FIGURE 4** Summary of dynamic mass balance simulations: (A) maximum Cu concentration, (B) fraction of initial Cu lost from solid within each cycle, (C) maximum solid  $\delta^{65}\text{Cu}$ , and (D) column integrated  $\delta^{65}\text{Cu}$  of the final fluid over the course of ten cycles,  $\delta_{\text{fluid}}^{\text{total}} = \sum_n C_{\text{fluid}}^n \delta_{\text{fluid}}^n / \sum_n C_{\text{fluid}}^n$ ,

for  $n$  grid points where  $C$  is the Cu concentration at each grid point, and the porosity is assumed constant over all  $n$ . Each point represents the value culled, or calculated, from the simulation result at the end of any given cycle. Stochastic behavior illustrated in panel (C) is attributable to the randomly selected depth to groundwater (~150–250 meters depth). Erosion is simulated between cycles by resampling the model section from the bottom up (~upper 150 m removed); this process is the source of considerable intercycle Cu loss from the supergene system.

zones (Fig. 4A). The only ways around this requirement are to increase the mass of initial primary ore leached and/or allow lateral transport of Cu into the system.

Additionally, assuming that the fractionation factors used are valid, a single cycle of enrichment can quite easily satisfy the Cu isotopic requirements of a mean leach cap  $\delta^{65}\text{Cu}$  of  $-1\text{‰}$  and a mean enrichment zone  $\delta^{65}\text{Cu}$  of  $1\text{‰}$ . However, if further processing is required from a mass balance point-of-view, then the isotopic evolution of the supergene system will continue, resulting in substantially fractionated leach caps and enrichment zones (Fig. 4C). Such a possibility highlights (1) the importance of thoroughly characterizing what is probably an isotopically heterogeneous system, and (2) the utility of modeling to provide clear expectations that place field data in context. Further, the requirement for subsequent cycling from a mass perspective suggests that Cu isotopes may then be useful for constraining the advective reaction length scales appropriate for a given supergene system, given reasonable constraints on process-specific fractionation factors. In other words, the Cu isotopic compositions of aqueous Cu in solution, leach cap minerals, and/or enrichment minerals can be used in conjunction with simple models to constrain the degree to which Cu has been recycled in the system. As discussed below, constraining advective length scales is fundamental to evaluating the role of supergene systems in the global Cu cycle.

The reactive transport modeling also points out that high spatial resolution mass and isotopic patterns with depth in supergene systems convey useful information regarding supergene isotope systematics. In particular, it is possible to constrain the fractionation factor associated with precipitation by considering where the maximum  $\delta^{65}\text{Cu}$  value falls in the enrichment zone relative to the maximum Cu concentration (e.g. Fig. 3). The diagnostic patterns, which simply reflect distillation in a vertically mobile system, imply that preferential precipitation of the heavy Cu nuclide should generate a profile in which the maximum  $\delta^{65}\text{Cu}$  and Cu concentrations generally co-occur (depth offset  $\sim 0 \pm 2$  meters). Such a pattern has been observed in the Ray and Silver Bell porphyry Cu deposits in southern Arizona, where chalcocites with higher  $\delta^{65}\text{Cu}$  values covary with total Cu content (Mathur et al. 2010). By contrast, fractionation factors less than 1 suggests a sizeable vertical displacement between the maximum  $\delta^{65}\text{Cu}$  and maximum Cu concentration in the enrichment zone (where the maximum  $\delta^{65}\text{Cu}$  is  $\sim 50$  meters deeper than the maximum Cu concentration;  $L_a \sim 20$  m).

The simulations also indicate a noticeable difference in the temporal evolution of supergene  $\delta^{65}\text{Cu}$  values over a rather restricted range of advective reaction length scales ( $L_a = 20$  and  $60$  m). More open systems ( $L_a \sim 60$  m) evolve much more slowly from both mass and isotopic perspectives (Fig. 4), and generally feature less in-cycle variability than the more closed system case ( $L_a \sim 20$  m). As expected, considerably more Cu is lost from the more open system, and the difference generally scales with the advective length scale.

Finally, it should be noted that the model simulates a homogeneous solid reservoir, which does not necessarily explain or account for small-scale mineralogical heterogeneities. Such an approach does appear quite useful, however, for constraining the evolution of fluid  $\delta^{65}\text{Cu}$  values within the supergene system, which may serve as a valuable reference for interpreting small-scale isotopic heterogeneities.

## IMPLICATIONS FOR EXPLORATION GEOLOGY

Although the Cu isotopic compositions of chalcocite and the overall concentration of Cu in supergene systems are important to explain, the exploration geologist has slightly different priorities, and (s)he does not have the luxury of seeing enrichment zones in outcrop. Nearly all significant enrichment zones occur at depth, so developing a means of detecting enrichment requires a way of utilizing exposed, or easily accessible, geological materials, such as Fe-oxides and surface waters.

The use of Fe-oxides is complicated by the inability to isolate the weathering products of sulfide oxidation (Blanchard 1968) and, potentially, by the interactions between Cu and Fe-oxide surfaces. Desorption of Cu can isotopically fractionate Cu, making it unclear if the  $\delta^{65}\text{Cu}$  of the Fe-oxides directly reflects weathered primary ore. Theoretically, the pH in supergene systems is low enough to inhibit adsorption of Cu onto Fe-oxide surfaces. From the standpoint of avoiding the effects of sorption, therefore, hematite (i.e. the residual of chalcocite weathering) and martite (i.e. the residual of chalcopyrite and chalcocite weathering) are ideal minerals to target for exploration, whereas jarosite (i.e. the residual of pyrite weathering that contains low concentrations of copper) is less ideal.

Iron-oxides with higher  $\delta^{65}\text{Cu}$  values tend to correlate with enrichment at depth (Braxton and Mathur 2011), suggesting that high  $\delta^{65}\text{Cu}$  values in the leach cap Fe-oxides are evidence of chalcocite weathering, thereby making high  $\delta^{65}\text{Cu}$  Fe-oxides an ideal exploration tool. Model simulations support the concept that Cu cycling at shallow depths can generate Fe-oxides with consistently high  $\delta^{65}\text{Cu}$  values compared to the leach cap above. Early in a given cycle, oxide  $\delta^{65}\text{Cu}$  is even comparable to the enrichment zone, because it represents the enrichment zone from the previous cycle that has been brought to the surface by erosion. If this hypothesis is valid, the  $\delta^{65}\text{Cu}$  of Fe-oxides exposed at the Earth's surface may prove to be an excellent exploration tool.

Surface waters are one of the most accessible targets for exploration purposes. Fluids that have been impacted by oxidative dissolution of sulfide minerals should have relatively high  $\delta^{65}\text{Cu}$  values (Kimball et al. 2009; Mathur et al. 2013). In addition, fluids can integrate both laterally and vertically in space, making them unique probes of supergene systems. However, no published studies have, to date, presented the sort of district-scale studies of Cu isotopic variability in fluids that are needed to develop this tool.

## IMPLICATIONS FOR THE GLOBAL COPPER CYCLE

A key observation of the model simulations is that the relatively closed-system dynamics of the supergene system as a whole has the potential to generate isotopically fractionated fluids, as well as a substantial mass flux of Cu out of the system (Fig. 4B). Though the proportion of Cu that is lost is minimal from the standpoint of supergene enrichment ( $\sim 1\text{--}3\%$  for the scenarios investigated), such a loss corresponds to Cu mass fluxes out of a supergene deposit of  $\sim 10^{-9}$  mol Cu/kg/y. Assuming the mass of rock impacted by supergene processes is  $>10^{17}$  kg (i.e.  $>0.1\%$  of the current subaerial continental area down to 200 m depth), then the total flux out of supergene systems is on par with the total input flux of dissolved Cu that has been estimated for the modern ocean (Little et al. 2013).

A supergene-related Cu output flux is likely to have a  $\delta^{65}\text{Cu}$  value that is substantially greater than 0‰ (Fig. 4D). In fact, loss of Cu either from active supergene systems or from weathering supergene enrichment zones will have tremendous leverage (~2 to 8‰, depending on the source) by which to alter riverine input to the ocean. An isotopically heavy weathering flux has been hypothesized to exist in low-order streams impacted by acid mine drainage and/or the weathering of sulfides (Fernandez and Borrok 2009; Kimball et al. 2009; Mathur et al. 2013). Such a heavy flux is not necessarily balanced by the isotopically light material lost (as inferred in Fig. 4C), because this material is lost mainly by erosion at the top of the supergene system (at least in the model). If lost as relatively insoluble particles, isotopically light material may not reach the ocean in the dissolved phase. This minimizes the ability of this isotopi-

cally light flux to balance the isotopically heavy flux and increases the leverage of supergene-derived Cu to affect the temporal evolution of seawater  $\delta^{65}\text{Cu}$ .

Ultimately, supergene systems have the potential to account for the relatively high  $\delta^{65}\text{Cu}$  of the global riverine flux (0.63‰). Further, variations in supergene activity and the abundance of supergene deposits at the Earth's surface over time could account for temporal variations in seawater  $\delta^{65}\text{Cu}$ .

## ACKNOWLEDGMENTS

The authors thank LA Munk, D Braxton, A Mathews, and M Reich for constructive reviews of the initial manuscript, as well as M Reich for the invitation to submit the manuscript. We also thank Kelly Finan for the watercolor artwork provided in Figure 2. ■

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# Predicting Geologic Corrosion with Electrodes

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1811-5209/15/0011-0331\$2.50 DOI: 10.2113/gselements.11.5.331

**E**ver since humans discovered how to separate metal from its ore mineral, preserving its metallic luster has been a driving force in the advancement of materials science. In modern times, developing materials that will contain and isolate nuclear waste has pushed corrosion science to new limits. We must now predict corrosion rates over geologic time scales, upwards of a million years. This article reviews the electrochemical basics that underpin metal and mineral corrosion and uses that to understand the case study of copper corrosion in nuclear-waste containers. Electrochemistry can also explain electron-transfer processes on mineral surfaces and so offer insight into weathering and environmentally relevant natural redox processes, such as those forming supergene metal deposits.

**KEYWORDS:** electrochemistry, corrosion, nuclear waste, analogues, geologic repository

## GEOLOGIC CORROSION

Corrosion, like death and taxes, is an unavoidable consequence of living on a watery, oxidizing planet. As geologists, we understand that corrosion processes on Earth were jump-started by the Great Oxidation Event (starting ~2.4 Ga), even though biology had developed the machinery for harvesting energy from sunlight and expelling molecular oxygen as a waste product long before (perhaps as early as 3.5 Ga) (Holland 2006). The first significant “rusts” to form on Earth’s crust, which were the result of increased levels of O<sub>2</sub> in the atmosphere, were the banded iron formations (BIFs) of the Paleoproterozoic, especially between 2.4 and 1.8 Ga (Klein 2005). In addition to the formation of BIFs, rising O<sub>2</sub> levels initiated the formation of supergene mineral deposits along reduction–oxidation (redox) boundaries at shallow crustal depths: these boundaries were, and are, a major mechanism for metal enrichment in crustal rocks. Unique examples of redox-driven processes in the Precambrian are the set of Oklo natural fission reactors in Gabon (~2 Ga), which are evidence of uranium being moved and concentrated by supergene (corrosion) processes in the uppermost crust. Between the formation of BIFs, natural nuclear reactors, and supergene deposits, redox reactions have been transforming the surface of the planet for billions of years.

## CORROSION AND SOCIETY

Most redox reactions are overwhelmingly energetically favorable. For example, the oxidation of ferrous iron (Fe<sup>2+</sup>) by O<sub>2</sub> to produce ferric iron (Fe<sup>3+</sup>) has a Gibbs free energy value of –27 kJ/mol at a pH of 2.5 (Erlich and Newman 2009). And where there was energy to be had, primitive life developed the catalytic machinery to harvest it. Within the fluids at ancient redox boundaries, aerobic and anaerobic microorganisms evolved ways to harvest the energy stored in chemical bonds.

Flash forward a few billion years and human civilization advanced along these ancient redox boundaries as well. It began between 6500 BC and 5000 BC with the smelting of silver, gold, tin, mercury, lead, and copper from their mineral ores. The energy produced in the Old World smelters and kilns went into liberating metals from their native compounds, be they oxide, sulfide, or carbonate ores. The discovery that copper alloyed with tin, which was mainly from cassiterite (SnO<sub>2</sub>) ore, produces a harder and more durable material marked the beginning of the Bronze Age around 3000 BC. The technically more difficult smelting of iron followed a millenium later, and the quality of life and the rate of technological progress would never be the same again. It was Greek philosopher and natural historian Pliny the Elder (AD 23–79) who first documented the propensity for these metals to return to their native states when he wrote, in his essay “Ferrum Corruptar,” of the “spoiling” of iron metal. Now, we understand that the driving force for all material corrosion—be it metals, minerals, or any other material—is the lowering of a system’s Gibbs free energy (the energy available for doing work). The large amount of energy required by smelting relates to the strong thermodynamic driving force to return a metal to ore by corrosion reactions (symbolically illustrated in Fig. 1). Despite the uphill thermodynamic struggle, humans have always been consumed with trying to slow the rate of Pliny’s observed “spoiling”. Both Pliny and the Greek historian Herodotus (fifth century BC) suggested using tin to protect iron. Alchemists throughout history have played a role in advancing the knowledge of corrosion science through their attempts to transform base metals into noble metals. However, it was Michael Faraday in 1833 who established the first quantitative relationships between electric current and the amount of metal that was

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**FIGURE 1** This abandoned early 1900s copper blast furnace in the New World Mining District (Montana, USA) is symbolic of the full thermodynamic cycle: energy was once inputted to liberate Cu from its native minerals, whereas the iron furnace itself is now corroding back to its native oxides. PHOTO COURTESY OF EDWARD MEYER (DARTMOUTH COLLEGE, USA).

deposited on, or gas that was evolved at, a metal electrode. From then on, corrosion science became firmly grounded in electrochemistry.

Faraday provided the relation between the current measured at an electrode and the reaction rate by the formula

$$\text{Reaction Rate} = \frac{dN}{dt} = \frac{1}{nF} \frac{dQ}{dt} = \frac{I}{nF} \quad (1)$$

where  $N$  is the number of moles formed,  $t$  is reaction duration,  $Q$  is the electrical charge in coulombs (C),  $n$  is the number of electrons transferred,  $F$  is Faraday's constant (96,485 C/mol) and  $I$  is current in amperes (A) or in coulombs per second (C/s). Faraday's first and second laws of electrolysis became the basis for determining the corrosion rates of metals. We suspect that Pliny and Faraday would be amazed at how keenly interested our modern society is in controlling corrosion rates, particularly when the annual direct cost of corrosion to utilities, transportation, and infrastructure in the United States alone is estimated to be over US\$276 billion per year (Koch 2002).

Electrochemistry is a common language among Earth scientists and materials scientists in areas as diverse as metallurgy and corrosion, metal extraction from ore minerals, geological weathering, leaching processes, and elemental cycling. The timescales over which corrosion processes are assessed in these areas are variable. Material scientists who estimate the rates of steel corrosion and service life of, say, modern bridges are interested in a 50–100-year timescale. Geologists assess natural corrosion (or weathering) processes over timescales that can span millions of years.

There is a significant and established body of literature on the corrosion of metals and alloys by electrochemical techniques. Electrochemical studies of minerals have played an important role in developing mineral processing techniques that are used to liberate a metal from its ore. However, the use of electrochemical techniques to determine the fundamental corrosion parameters for minerals is less widely established.

This article will review the basic electrochemistry needed to understand corrosion and also discuss an area where materials scientists and Earth scientists have a mutual vested interest—the assessment of the corrosion resistance of materials designed to isolate and contain nuclear waste in long-term geologic repositories. This is an ideal

example to illustrate how models utilizing electrochemical data are employed to assess corrosion processes over geologic timescales. We intend for this review to provide a framework for how electrochemical techniques, although inherently challenging, can be applied to explain mineral weathering processes, or redox cycling, in natural or engineered environments.

## THE ELECTROCHEMICAL BASICS

The process of natural metal corrosion is driven by the coupling of two redox half-reactions occurring at the same rate. The anodic reaction, which results in oxidation, releases electrons into the metal. The cathodic reaction—in which an oxidant species such as  $O_2$ ,  $Fe^{3+}$ , or  $H^+$  is reduced—removes electrons from the metal. The two reactions can take place simultaneously on one metal or on two dissimilar metals that are in electrical contact. Mixed potential theory, established by Wagner and Traud (1938) and mathematically refined by Stern and Geary (1957), states that corrosion occurs on a metal as a result of localized anodic and cathodic reactions occurring simultaneously on the surface. For a naturally occurring corrosion process, the sum of the rate(s) of the oxidation half-reaction(s) at anodic sites must be equal to the sum of the rate(s) of the reduction half-reaction(s) at cathodic sites. That is, there should be no accumulation of charge on the metal's surface. The potential at which anodic and cathodic reaction rates are equal is called the “mixed” or “corrosion” potential,  $E_{corr}$ . At  $E_{corr}$ , the surface of the material corrodes as a consequence of the kinetic (i.e. rate) balance between anodic and cathodic reactions. The  $E_{corr}$  lies somewhere between the equilibrium potentials of the oxidation and reduction half reactions. The equilibrium potential,  $E_{eq}$ , can be determined for a given set of environmental conditions by the well-known Nernst relationship, here shown for the reduction of ferric ions:

$$E_{eq} = E^0 + \frac{2.3RT}{F} \log \left\{ \frac{(a_{Fe^{3+}})}{(a_{Fe^{2+}})} \right\} \quad (2)$$

for the reaction  $Fe^{3+} + e^- \leftrightarrow Fe^{2+}$

where  $E^0$  is the standard reduction potential,  $R$  is the molar gas constant,  $T$  is the absolute temperature,  $F$  is the Faraday constant, and  $a_{Fe^{3+}}$  and  $a_{Fe^{2+}}$  are the activities of ferric iron and ferrous iron, respectively.

Corrosion of mineral surfaces is also described by electrochemical mechanisms. For example, the overall reaction for the well-studied oxidative dissolution of pyrite ( $FeS_2$ ) is written in terms of the redox half-reactions for the oxidation of pyrite and the reduction of  $O_2$ :

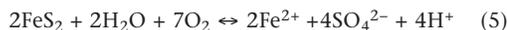
Oxidation half reaction:



Reduction half reaction:



Overall reaction:

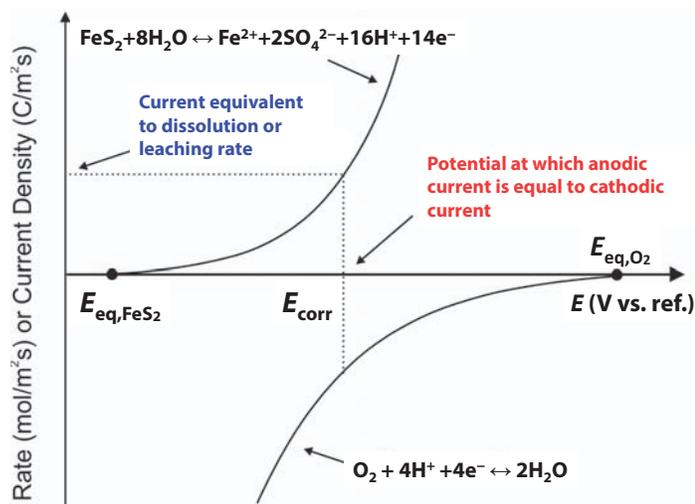


The electrochemical dissolution of pyrite by the reactions above is illustrated schematically in FIGURE 2. Validation of the electrochemical mechanism came from studies showing that oxygen in the sulfate product came from  $H_2O$ , rather than the oxidant,  $O_2$  (Bailey and Peters 1976; Taylor et al. 1984; Holmes and Crundwell 2000; Usher et al. 2004). Molecular modeling showed that the dissociation of water at Fe sites and the subsequent nucleophilic attack by hydroxyls at surface S sites was an energetically favorable pathway (Rosso et al. 1999). The rate of oxidative dissolution of pyrite is the same magnitude as either the

rate of oxidation of pyrite (to form sulfuric acid) or the rate of  $O_2$  reduction occurring at  $E_{\text{corr}}$  (FIG. 2). In natural environments, the surface of the metal or the mineral in question will dissolve and/or become covered with corrosion products, depending on environmental Eh–pH (redox and acid/basic) conditions. The  $E_{\text{corr}}$  evolves due to changes in the composition of the material surface.

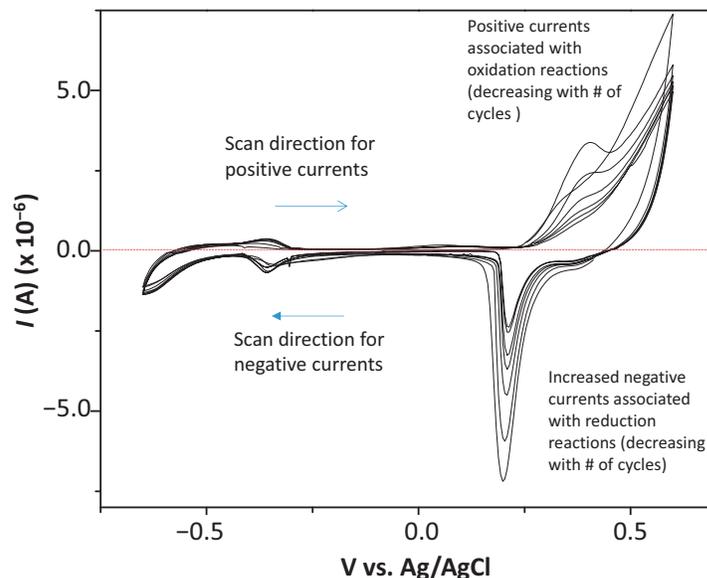
From a practical standpoint,  $E_{\text{corr}}$  can be determined by making a working electrode out of the metal or mineral of interest and measuring the potential that develops between the working electrode and a stable reference electrode (commonly a silver/silver chloride electrode, Ag/AgCl) using a high-impedance voltmeter. This type of electrochemical experiment is called a potentiometric technique. Fabricating an electrode out of a metal is straightforward; however, a mineral electrode must satisfy the condition of having either a metallic or a semiconductor degree of conductivity (e.g. sulfides and semiconducting oxides). A bulk mineral electrode is fashioned by cutting or cleaving the bulk mineral into a wafer, polishing the surface, and attaching a conductive wire. Alternatively, minerals can be evaluated by packing mineral powders into a micron-sized cavity at the tip of a Pt microelectrode (see Renock et al. 2013) or immobilizing the mineral particles on an inert electrode surface (or within a thin layer) using a conductive binder, such as graphite powder mixed with paraffin.

Metal or mineral electrodes can be polarized by making the electrode be the so-called “working electrode” in a three-electrode electrochemical cell. An instrument called a potentiostat is used to maintain the potential between the working electrode and the reference electrode. The third electrode is called the “counter electrode” and is typically made of a Pt wire mesh. These types of experiments are known generally as amperometric techniques, which involve measuring the current,  $I$ , flowing between the working electrode and the counter electrode. For example, if the working electrode potential is negatively polarized relative to  $E_{\text{corr}}$ , the rate of cathodic reaction(s) will increase at the expense of the anodic reaction(s) ( $|I_c| > |I_a|$ ) as  $E$  is polarized to the left of  $E_{\text{corr}}$  in FIG. 2), and the net current



**FIGURE 2** A schematic diagram showing the reaction rate–potential relationship for the electrochemical dissolution of pyrite. The rate of oxidation of pyrite and the rate of reduction of molecular oxygen,  $O_2$ , are both exponentially dependent on the potential at the mineral–water interface.  $E_{\text{corr}}$  takes on a value where the (sum of) cathodic and anodic rates (or currents) are equal. The thermodynamic driving force for the reaction is the potential difference between the equilibrium redox potentials for the anodic and cathodic reactions ( $E_{\text{eq, FeS}_2}$  and  $E_{\text{eq, O}_2}$ , respectively). FIGURE ADAPTED FROM HOLMES AND CRUNDWELL, (2000) WITH PERMISSION.

will be negative by convention. The current response of the working electrode is measured by the potentiostat. The various stages of oxidation and reduction can be assessed by cyclic voltammetry experiments in which the electrode potential is swept linearly between two potential limits through one or more cycles (hence “cyclic” voltammetry). Peaks in current that appear on the positive-going scan correspond to oxidation reactions and peaks that appear on the negative-going scan correspond to reduction reactions occurring on the electrode surface. An example is shown in FIGURE 3 for chalcopyrite ( $\text{CuFeS}_2$ ). Peak currents that increase or decrease over the course of multiple cycles indicate dynamic processes occurring on the surface of the working electrode. For the chalcopyrite example, decreasing currents on the positive-going scan are due to the formation of a partially protective oxide layer on the



**FIGURE 3** Cyclic voltammogram (see text for details) of chalcopyrite ( $\text{CuFeS}_2$ ) using a mineral powder microelectrode (pH 7, 25°C). Peaks in current that appear on the positive-going scan correspond to oxidation reactions and peaks that appear on the negative-going scan correspond to reduction reactions occurring on the electrode surface. By convention, anodic current is given a positive sign and cathodic current a negative sign. The # symbol means “number”.

mineral electrode that increases in thickness with subsequent cycles. In addition, the formation of a cathodic peak at low potentials (e.g. peak occurring at about  $-0.35$  V in FIG. 3) may be accompanied by the formation of an anodic peak on the subsequent cycle. This occurs when soluble redox species generated at low potentials are re-oxidized on the electrode surface during the sweep to higher potentials. Much can be learned about the energetics, kinetics, and mechanisms of corrosion and other redox processes from cyclic voltammograms, and readers are referred to the classic text by Bard and Faulkner (1980).

In terms of current,  $E_{\text{corr}}$  is the electrode potential where the anodic current,  $I_a$ , is equal and opposite in sign to the cathodic current,  $I_c$  (i.e.  $|I_a| = |I_c| = I_{\text{corr}}$  at  $E_{\text{corr}}$ ). Both  $I_a$  and  $I_c$  are equal to the sum of all currents associated with oxidation reactions and reduction reactions occurring on the electrode surface, respectively. Thus, by measuring  $I_{\text{corr}}$ , the overall corrosion rate of the material can be calculated. The corrosion scientist, armed with an electrode and Faraday’s laws, can then determine the mass loss of a material due to corrosion by

$$\frac{W}{t} = \frac{I_{\text{corr}} MW}{nF} \quad (6)$$

where  $W$  is the mass loss in grams,  $t$  is the duration of corrosion, and  $MW$  is the molecular weight of the corroding material. The mass loss can be converted into a value that is more useful, like the rate of penetration into the surface (e.g. millimeters per year), if the density and surface area of the material is known. However, the practical application of Equation (6) is not straightforward. Accurate determination of  $I_{\text{corr}}$  is technically challenging, though several methods can be employed in this regard (e.g. Tafel extrapolation, linear polarization resistance measurements, and impedance spectroscopy measurements). Bard and Faulkner (1980) is an excellent resource for understanding the different methods that are used to estimate  $I_{\text{corr}}$ .

It should be noted that determining redox kinetics using these methods has limitations when applied to semiconductor mineral electrodes. Charge depletion in semiconductor surface electronic states during polarization can affect the kinetic values obtained for redox reactions on the surface. Thus, care should be taken before assessing the kinetics of oxide and sulfide electrodes (Xu and Schoonen 2000; Meitl et al. 2009; Renock et al. 2013).

## ELECTROCHEMISTRY TO STUDY NUCLEAR WASTE DISPOSAL

The main issue with radioactive waste disposal is that the waste remains a risk to environmental and human health for, potentially, millions of years. For many repository risk assessments, the target life of the waste canisters ranges from tens of thousands of years to one million years; this ensures that the radioactivity of the waste has decayed to levels below acceptable risk should the containment fail (NWTRB 2009). Repository design proposals vary from country to country based on the composition of the spent fuel and the geologic (and geochemical) conditions of the repository site. The spent fuel itself consists of a matrix of irradiated uranium dioxide ( $\text{UO}_2$ ) containing fission products and activation products from the reactor. Due to the uncertainties inherent in the repository environment, the corrosion resistance of the waste package itself (i.e. spent fuel + metal package enclosing the spent fuel) is a significant focus for ensuring overall repository performance (Ewing and Macfarlane 2006). Radionuclide release into the environment may occur when the waste package is breached because of corrosion of the metallic canister and subsequent corrosion of the enclosed  $\text{UO}_2$  fuel matrix. Therefore, the waste-package design must account for biogeochemical attack from oxidants within the near-field environment of the waste package.

The environmental conditions of repositories are classified based on the chemistry of the groundwater that may come into contact with the enclosed nuclear waste. Whether the repository conditions are expected to be oxidizing (e.g. due to emplacement above the water table) or reducing, will dictate the possible corrosion mechanism(s) and, thus, the waste-package design. Most repository designs, except for the proposed (and now tabled) United States repository at Yucca Mountain in Nevada, call for emplacement of the waste package in reducing conditions. For example, Canadian, Finnish, and Swedish design concepts for the waste package assume predominantly reducing conditions during the service life of the repository deep underground (> 400 m deep) in granitic rocks (NWTRB 2009). For our case study, we will focus on a proposed, but not yet active, Swedish and Finnish repository design developed using Cu metal waste canisters.

An important feature of the Swedish and Finnish design is that the waste containers will be emplaced within boreholes in crystalline rock and then surrounded by compacted

bentonite clay, which has a low hydraulic permeability (KBS 1978; SBK 2012). Initially, the water in the repository is expected to be oxidizing due to trapped  $\text{O}_2$  in the tight pore spaces of the clay backfill. Over time,  $\text{O}_2$  will be consumed in reactions with oxidizable material within the repository, and the redox potential (or Eh) will drop. After the initial oxidizing interval, the groundwater that penetrates the clay buffer is expected to be predominantly anoxic (low Eh). Groundwater may also be saline (up to 15,000 mg/L  $\text{Cl}^-$ ), and contain sulfides ( $10^{-7}$ – $10^{-4}$  mol/L) with the primary oxidant being  $\text{H}^+/\text{H}_2\text{O}$  in the presence of sulfide (King et al. 2013). The Eh of the repository environment can be calculated from thermodynamic modeling of the redox species that are expected to be present in the groundwater over the service life of the repository. However, it is the  $E_{\text{corr}}$  value of the Cu containment material that determines the corrosion rate as illustrated by the corrosion current density  $I_{\text{corr}}$  versus  $E_{\text{corr}}$  relationship in FIGURE 2.

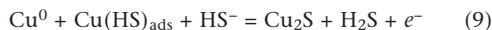
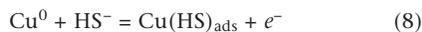
The time dependence of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  over the service life of the repository can be predicted from reactive transport models that utilize electrochemical data. Briefly, reactive transport equations that take into account the diffusion of oxidants and soluble redox species to and from the waste package are solved using finite-difference methods subject to a set of initial and boundary conditions. These boundary conditions are defined by electrochemical rate expressions for all of the possible anodic and cathodic reactions that are expected to occur at the surface of the waste container. Rate constants and reaction orders for each kinetic expression come from extensive electrochemical studies done under experimental conditions that best represent the geochemical environment of the repository. In addition, a condition is imposed that the sum of the rates of the anodic reactions must equal the sum of the rates of the cathodic reactions, and this serves as the basis for a mixed potential model (reviewed in Shoesmith et al. 2003, 2004; King et al. 2011, 2013). Ultimately, predicting the time dependence of  $E_{\text{corr}}$  and  $I_{\text{corr}}$  allows for the estimation of the extent of corrosion (e.g. penetration into metal) over time by a relationship such as Equation (6).

### Copper as a Waste Container and its Resistance to Corrosion

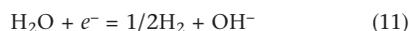
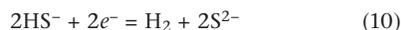
In 1978, the Swedish Corrosion Institute first proposed copper metal as a nuclear waste container material. Containers sheathed in Cu metal were predicted to exceed the 100,000 year service lifetime criteria (KBS 1978). Generally, copper metal is known to be particularly resistant to corrosion in underground environments because it is shielded by supergene minerals that form on the exposed surface. For example, you may have noticed the formation of brightly colored solids forming on the surface of exposed Cu pipes: reddish-brown cuprous oxide ( $\text{Cu}_2\text{O}$ ), green copper carbonates, green sulfates or oxychlorides, or black copper sulfides. Evidence of copper's exceptional corrosion resistance in oxidizing environments also comes from many archeological analogues. For example, underground copper pipes that carried water in Egypt nearly 5,000 years ago are still in existence (Schweitzer 1996). Furthermore, copper is one of the few metals that exist on Earth in its natural (native) form. Modern electrochemical studies using Cu electrodes, an analogue of sorts, predict that the rate of corrosion during the initial oxidizing condition in a repository is limited by the availability and rate of supply of  $\text{O}_2$  to the container, as shown in FIGURE 4A (King et al. 2013). Both the clay backfill and mineral passivation layers on the pure  $\text{Cu}^0$  act as diffusion barriers that limit the transport of  $\text{O}_2$  to electroactive sites on the  $\text{Cu}^0$  surface. In addition, mass transport of redox products away from the corroded surface must also be considered. For

example,  $\text{Cl}^-$  from saline pore water in the surrounding clay backfill enhances corrosion rates via the formation of soluble anions, such as  $\text{CuCl}_2^-$ , that can diffuse away from the container. Under these conditions, diffusion of  $\text{CuCl}_2^-$  away from the surface is rate limiting, as shown in FIGURE 4B.

After all of the  $\text{O}_2$  in the repository is consumed (about 200 years according to some models; King et al. 2013), corrosion will be controlled by hydrogen sulfide,  $\text{HS}^-$ , which may diffuse to the container surface from anaerobic dissolution of sulfides present in the surrounding clay or from possible microbial sulfate reduction. The anodic reactions that occur in the presence of hydrogen sulfide include:



and result in the precipitation of a chalcocite ( $\text{Cu}_2\text{S}$ ) layer on the  $\text{Cu}^0$  surface. The cathodic reactions probably include:



The rate of corrosion of  $\text{Cu}^0$  is not limited by the kinetics of the half reactions but by diffusion of  $\text{HS}^-$  through the  $\text{Cu}_2\text{S}$  layer (Chen et al. 2011, 2014; King and Lilja 2011). Because diffusion of  $\text{HS}^-$  through the surrounding clay barrier is orders of magnitude smaller than diffusion through the porous passivation layers formed on the  $\text{Cu}^0$ , the rate of corrosion of a copper canister in the repository will ultimately be limited by the rate of transport of  $\text{HS}^-$  through the clay barrier (Fig. 4C).

Reactive transport models that incorporate the conditions present during the relatively brief oxic period, as well as the anoxic period, have predicted  $E_{\text{corr}}$  of the canister to drop from  $\sim -0.2$  V to  $\sim -1.0$  V (vs Ag/AgCl) after a few hundred years, and, after depleting the initially trapped  $\text{O}_2$ , remain at these extremely low potentials for  $10^6$  years (King et al. 2011). A brief interval in between the oxic and anoxic periods with an undefined  $E_{\text{corr}}$  indicates a period in which the waste canister heats up to temperatures that dry out the

surrounding clays and effectively shut down aqueous corrosion. Integration of  $I_{\text{corr}}$  over time gives the charge density, which can then be used to determine the depth of corrosion (King et al. 2011). Models generally show  $< 1$  mm of uniform penetration into the Cu after  $10^6$  years suggesting a service lifetime well within the established criteria (King et al. 2013). Model predictions like this are cited as evidence of copper's suitability for nuclear-waste containment designs.

### The Debate about Anaerobic Corrosion Mechanisms

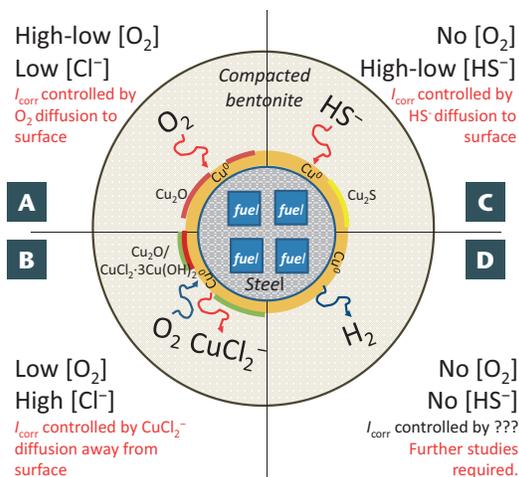
Despite the hopeful predictions above, there remains a question as to whether  $\text{Cu}^0$  will anaerobically corrode by a reaction mechanism(s) that is not considered in the mixed potential models. Specifically, experimental studies have demonstrated the production of  $\text{H}_2$  gas from  $\text{Cu}^0$  that has been immersed in pure anoxic water that does not contain  $\text{HS}^-$  (Hultquist 1986). Though no experimentally verifiable corrosion mechanism has been put forward to explain the production of  $\text{H}_2$ , Åkermark (2013) suggests that these findings are sufficiently provocative to warrant further study (see Fig. 4D). A lack of a comprehensive understanding of all the possible mechanisms of  $\text{Cu}^0$  corrosion would have implications for moving forward with present designs because it could mean the difference between corrosion rates on the order of nanometers per year versus rates as high as micrometers per year (King et al. 2011; Åkermark 2013). Though the debate remains unresolved, both sides agree that more fundamental electrochemical experiments are required to explore all possible mechanisms of  $\text{Cu}^0$  corrosion in anaerobic environments.

### CONCLUSIONS

Corrosion is a fundamental and integral process to the geology that controls the geochemical makeup of the Earth. Corrosion processes have likely played a central role in the origin of life, have been a major factor in the migration and spread of civilization, and will certainly help society (both through the natural production of supergene metal deposits and man's own understanding of corrosive processes) to technologically advance. Electrochemical methods enable geologists and materials scientists to better understand the fundamentals of corrosion and redox reactions through the determination of two fundamental parameters: the corrosion potential, and the corrosion current. Mixed potential models that predict how the corrosion current and corrosion potential vary over geologic time have been applied to  $\text{Cu}^0$  metal proposed to be used in containing and isolating spent nuclear fuel from the environment. This nuclear-waste containment case study, which details  $\text{Cu}^0$  corrosion, provides a framework for understanding how fundamental electrochemical methods and mixed potential models can be used to assess the dissolution of minerals. Electrochemical methods, in combination with surface-sensitive spectroscopy and microscopy techniques, as well as molecular modeling of redox reactions, will help us understand and improve hydrometallurgical processing of minerals and could potentially be used to assess geologic processes involved in the formation and long-term corrosion (weathering) of minerals themselves.

### ACKNOWLEDGMENTS

The authors would like to thank Frank Crundwell and Theodore Bornhorst for their contributions to the manuscript, as well as Rodney Ewing and an anonymous reviewer for invaluable constructive criticism. DR thanks National Science Foundation grant (EAR-1223600). LSN was supported by the US Nuclear Regulatory Commission Junior Faculty Award (#NRC-38-10-921) to Clemson University. ■



**FIGURE 4** Schematic showing four generalized examples (A–D) of geochemical conditions that a Cu waste container may experience over the lifetime of a geologic nuclear-waste repository, where the corrosion rate-limiting mechanisms change depending on the evolution of the conditions within the repository. (A) For high-low  $[\text{O}_2]$  and low  $[\text{Cl}^-]$  conditions, the rate-limiting process is  $\text{O}_2$  diffusion through a  $\text{Cu}_2\text{O}$  layer to the metal surface. (B) For low  $[\text{O}_2]$  and high  $[\text{Cl}^-]$  conditions, the rate-limiting process is  $\text{CuCl}_2^-$  diffusion from surface. (C) For no  $[\text{O}_2]$  and high-low  $[\text{HS}^-]$ , the rate-limiting process is  $\text{HS}^-$  diffusion through a  $\text{Cu}_2\text{S}$  layer to the metal surface. (D) Further studies are necessary to confirm the corrosion rate-limiting process(es) in the absence of both  $[\text{O}_2]$  and  $[\text{HS}^-]$ .

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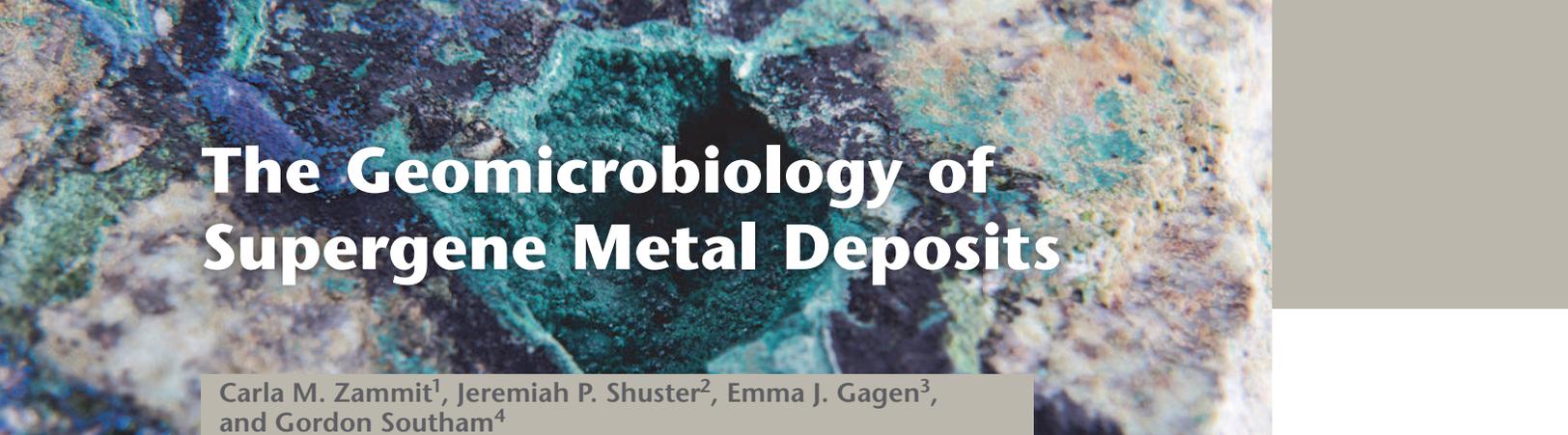


A crude crystal of djurleite on natrolite and crossite matrix with minor benitoite from the Gem Mine, San Benito Co., California. Image by Dr. J. Weissman from *Excalibur's Photographic Guide to Mineral Species CD*.

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# The Geomicrobiology of Supergene Metal Deposits

Carla M. Zammit<sup>1</sup>, Jeremiah P. Shuster<sup>2</sup>, Emma J. Gagen<sup>3</sup>,  
and Gordon Southam<sup>4</sup>

1811-5209/15/0011-0337\$2.50 DOI: 10.2113/gselements.11.5.337

**M**icrobe-catalyzed redistribution of metals in the Earth's crust can produce remarkable, and often economic, metal enrichments. These catalytic processes rely on redox transformations to produce secondary-mineral assemblages. Classic supergene systems relate to copper, where weathering is driven by microbial activity. Roll-front uranium deposits represent a similar, albeit lateral, evolution from aerobic weathering to anaerobic enrichment. Gold is generally resistant to oxidation but a remarkable biogeochemical cycle can produce secondary gold. Finally, banded iron formations, which are microbially catalysed sedimentary deposits, can be further weathered to form high-grade ore. Metals are as important to enzyme catalysts as these catalysts are to metal enrichment.

**KEYWORDS:** prokaryotes, mineral dissolution, mineral precipitation, supergene processes, metal deposits

## INTRODUCTION

Microorganisms interact with minerals in the Earth's crust by catalysing weathering processes. This means that minerals are often subjected to reduction–oxidation (redox) reactions that alter the chemical and physical state of the metals they contain (Ehrlich and Newman 2008). To promote cellular growth and sustain metabolic activity, all microorganisms require major and trace metal nutrients, which can be acquired from metal-bearing minerals. Essential metals for metabolism include magnesium, sodium, potassium, iron, cobalt, copper, molybdenum, nickel and zinc (Ehrlich and Newman 2008). Metals such as iron, arsenic, magnesium, vanadium, selenium and uranium can also be used by microorganisms to generate energy (Ehrlich and Newman 2008). Some metals have no known function within a cell's metabolic pathways and just accumulate over time, leading to the biomineralisation of the cell membrane during fossilisation (Silver 2003). From the perspective of an individual microorganism, biogeochemical reactions occur on spatial and temporal scales of micrometres and seconds, respectively. However, when microbial populations 'work' over geological time scales, biogeochemical processes can have profound local to global effects, such as the oxygenation of Earth's atmosphere which promotes weathering and the formation of supergene metal deposits. We must never underestimate the importance of microorganisms.

The oxidation or reduction of metals by microorganisms can occur via direct and/or indirect mechanisms – direct mechanisms involve microbial enzymes, whereas indirect mechanisms involve by-products of microbial metabolism (e.g. acid, oxidising agents and ligands). Rapid developments in molecular biology techniques have advanced our understanding of the role of microorganisms in metal solubility, mobility and precipitation. Here, we discuss the impact of the biosphere on the evolution of supergene copper, uranium, gold

and iron deposits, highlighting the often over looked role that microorganisms play in the formation of such deposits.

## THE ROLE OF MICROORGANISMS IN SUPERGENE COPPER DEPOSITS

An example of a supergene copper deposit that has been influenced/developed by microorganisms is that of the Morenci copper mine (Arizona, USA). Here, oxidation and enrichment processes have produced a classic example of a supergene profile of an original copper porphyry system (Fig. 1). This profile is characterised by an increase in copper grade with depth (Enders et al. 2006). The profile contains a limonitic leached cap containing hematite that overlies an enriched 'blanket' of high-grade chalcocite with occasional covellite as replacements and coatings on primary pyrite and chalcopyrite. Weathering and alteration cycles of copper enrichment correspond to the lowering of the local water table, which resulted in copper being leached from the cap, transported downward and finally concentrated at depth (Enders et al. 2006).

The surfaces of metal sulphide minerals are ideal substrates for the attachment of iron- and/or sulphur-oxidising microorganisms that catalyse biogeochemical processes and that have contributed to the formation of the Morenci copper deposit. *Acidithiobacillus ferrooxidans* is a microorganism capable of oxidising both iron and sulphur and is associated with bioleaching operations and acid mine drainage environments. A microorganism closely related to *A. ferrooxidans* was recovered from samples of sulphide minerals at Morenci under near-neutral environmental pH conditions. This microorganism forms microenvironments on sulphide mineral surfaces (Fig. 2) and oxidises the iron and/or sulphur in the rock, which results in acidification (Mielke et al. 2003; Dockrey et al. 2014).

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**FIGURE 1** (A) View of the Metcalf Pit, Morenci Copper Mine (Arizona, USA) showing the weathering profile studied by Enders et al. (2006). Arrow indicates the position of close-up

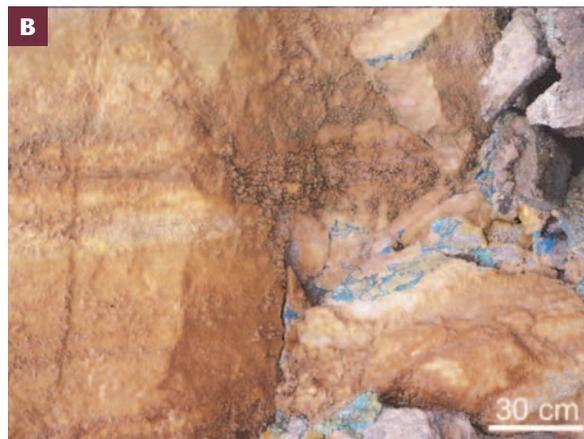
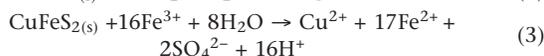
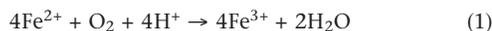


photo in B. (B) Jarosite (brown crystals) and chalcocite (blue crystals), the latter being a very soluble copper mineral.

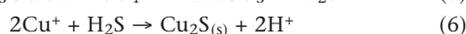
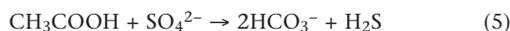
In general, near-surface oxidation of metal sulphide minerals is attributed to microorganisms (re)generating ferric iron and acidity (reactions 1 and 2). As a result, ferric iron acts as an oxidising agent that contributes to the mobilisation of cupric ions from the dissolution of metal sulphide minerals (reaction 3). Singer and Stumm (1970) noted that although oxidation of metal sulphide minerals can be perceived in abiotic mechanistic terms, microorganisms catalyse sulphide mineral oxidation  $10^5$  times faster than the abiotic rate.



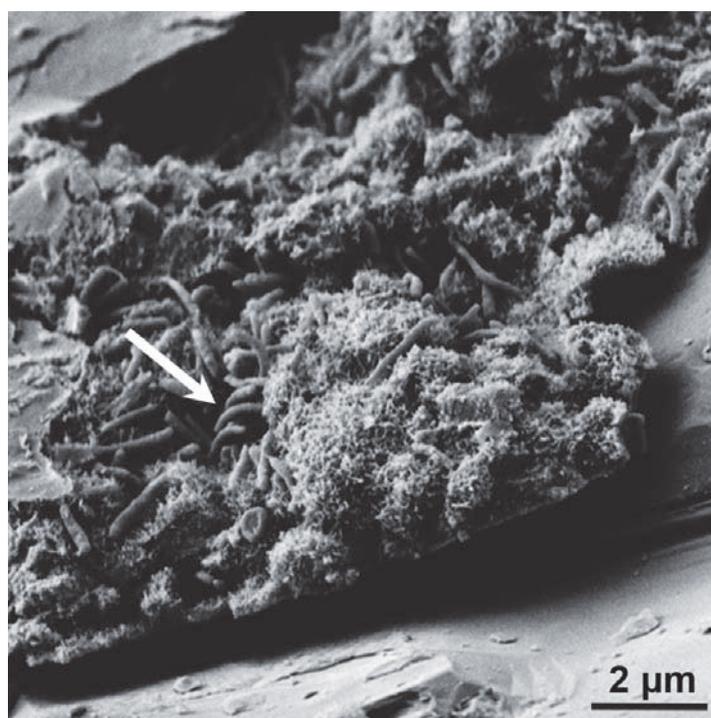
Copper enrichment in supergene deposits is generally considered to occur through the abiotic replacement of chalcocite with covellite (reaction 4)



However, the activity of sulphate-reducing bacteria in natural environments has been used to provide a model/example of how metal sulphide ores are deposited (Labrenz et al. 2000; Druschel et al. 2002). Sulphate-reducing bacteria oxidise low-molecular-weight environmental organic compounds. A by-product of their active metabolism is the formation of hydrogen sulphide. This gas is then released into the surrounding environment (Donald and Southam 1999) and may contribute to metal enrichment (Southam and Saunders 2006). For example, Alpers and Brimhall (1989) proposed that sulphate-reducing bacteria activity might explain a thin zone of massive chalcocite at the top of the enrichment blanket at La Escondida (Chile) (reactions 5 and 6)



Mathematical modelling by Lichtner and Biino (1992) suggests that sulphate-reducing bacteria are involved in the precipitation of pyrite, bornite and chalcocite in the lower blanket of supergene enrichment zones. In a related study, sulphur isotopes were used to demonstrate the involvement of sulphate-reducing bacteria in sulphide enrichment blankets in the Mike gold deposit in the Carlin Trend (Nevada, USA) (Bawden et al. 2003). While sulphate-reducing bacteria occur naturally in weathering profiles at Morenci, their populations are too small to have produced significant enrichment (Enders et al. 2006).



**FIGURE 2** Field emission scanning electron microscope secondary electron micrograph of a bacterially colonized weathered pyrrhotite grain encased within secondary Fe(III) (oxy)hydroxysulphate precipitates at the sulphide–mineral surface. Image reproduced with permission from Dockrey et al. (2014).

Contemporaneous biotic and abiotic factors contribute to in situ leaching and are, almost certainly, responsible for the formation of worldwide economic accumulations of supergene copper (Enders et al. 2006).

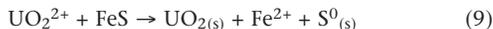
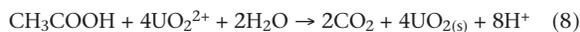
## THE ROLE OF MICROORGANISMS IN SUPERGENE URANIUM DEPOSITS

In roll-front uranium deposits, soluble uranyl complexes (e.g. rutherfordine and  $\text{UO}_2\text{CO}_3$ ), along with other mobile metals, are transported away from a mineralised source via hydrological processes. Under aerobic conditions, microorganisms are capable of solubilising uranium through direct oxidation, thereby enabling mobilisation of uranium as

a soluble uranyl complex. Acid-generating reactions (e.g. reactions 2 and 3) can also indirectly enhance uranium solubilisation (reaction 7)



By contrast, soluble uranyl complexes can be reduced under anaerobic conditions by microorganisms (reaction 8) and by microbially produced by-products (reaction 9)



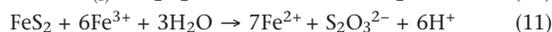
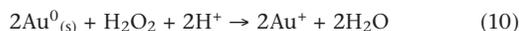
which leads to the immobilisation and enrichment of uranium (Zammit et al. 2014; Fig. 3).

In roll-front deposits, uranium is mobilised from a nearby source and transported until it meets reducing ground waters where it is then deposited at the redox boundary. When anaerobic microbial communities come into contact with oxidising uranium-bearing groundwaters, they metabolically reduce  $\text{Fe}^{3+}$  to  $\text{Fe}^{2+}$ , reduce  $\text{UO}_2^{2+}$  to  $\text{UO}_{2(s)}$  (reaction 8), and reduce  $\text{SO}_4^{2-}$  to  $\text{H}_2\text{S}$  (reaction 5), leading to the immobilisation and enrichment of uranium (Angiboust et al. 2012; Zammit et al. 2014; Fig. 3). A study on uraninite and coffinite from a sandstone-hosted roll-front deposit in Xinjiang, northwest China, showed that these minerals are indeed precipitated by microorganisms (Min et al. 2005). Another study of coffinite at the Beverly uranium deposit in South Australia suggested that bacterial reduction may have been the primary ore-forming process (Wülser et al. 2011). Indirect uranium reduction via iron sulphide oxidation also produces enrichments of uranium (reaction 9; Angiboust et al. 2012; Ingham et al. 2014).

## THE ROLE OF MICROORGANISMS IN SUPERGENE GOLD DEPOSITS

The biogeochemical cycling of gold is well established through studies on bacteria–gold interactions, which highlight microbial contributions to gold weathering and precipitation (Reith et al. 2007). Though gold is not readily maintained as a soluble complex, rapid gold dissolution–reprecipitation processes occur much faster than geological time scales.

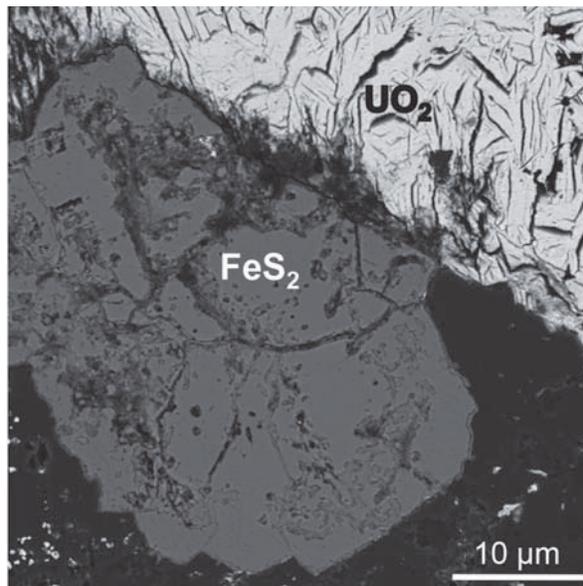
The exposure of electrum (naturally occurring gold alloys) and gold-bearing metal–sulphide minerals to oxidising conditions can release gold from the host mineral matrix. This is thought to promote the oxidation of  $\text{Au}^0$  to  $\text{Au}^+$ , which results in the formation  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  (reactions 10–12).



When considering gold complexation in the absence of thiosulphate ligands,  $\text{AuCl}_4^-$  complexes could form, depending on the availability of chloride ions (reaction 13) (Mann 1984; Gammons et al. 1997).

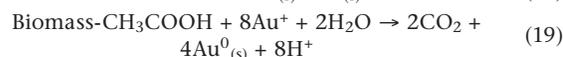
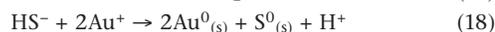
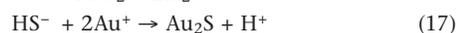
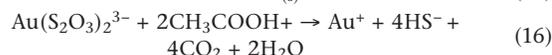
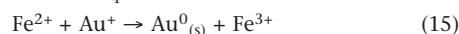
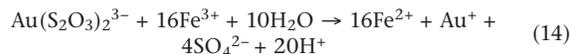


The biogeochemical conditions of surface to near-surface environments and the availability of anionic ligands are the primary factors that determine the formation of soluble gold complexes (Mann 1984; Benedetti and Boulegue 1991) and the mobility of gold. However, the mobility of  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and  $\text{AuCl}_4^-$  within hydrological systems is likely affected by an array of biogeochemical processes that could destabilise these gold complexes.



**FIGURE 3** Back scattered electron, field emission scanning electron microscope image of a ‘biogenic’ uraninite (Sierra Peña Blanca, Mexico) possessing structural and isotopic evidence of dissimilatory sulphate reduction (Angiboust et al. 2012). Biogenic pyrite ( $\text{FeS}_2$ ) is closely associated with uranophane ( $\text{UO}_2$ ).

While mobility occurs under aerobic conditions, acidophilic iron- and sulphur-oxidising bacteria can destabilise  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  complexes and so produce elemental gold (Southam and Saunders 2005). In the laboratory, the resulting biomineralisation of gold under both oxidising and reducing conditions formed nanometre-size gold colloid particles within bacterial cell envelopes and in association with the secondary mineral precipitates formed by the bacteria. Under aerobic conditions, ferric iron (maintained through bioleaching; reaction 1) has been found to be a particularly important biogeochemical reactant contributing to the destabilisation of  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  and to the subsequent reduction to  $\text{Au}^0$  (reactions 14, 15; see Shuster et al. 2014). The substitution of biogenic jarosite (acicular iron oxyhydroxide) minerals by colloidal gold links the biogeochemical cycling of iron to that of gold. Specifically, iron reduction (see canga section, below) would release colloidal gold, which would thereby increase gold mobility and potential reactivity. Under anaerobic conditions, sulphate-reducing bacteria can substitute  $\text{Au}(\text{S}_2\text{O}_3)_2^{3-}$  as an electron acceptor (reaction 16) promoting the formation of gold sulphide (reaction 17) and elemental gold (reactions 18 and 19).



Gold(III) chloride is even less stable than gold(I) thiosulphate in the presence of bacteria. Heterotrophic soil bacteria (e.g. *Bacillus subtilis*; Southam and Beveridge, 1994) or cyanobacteria (e.g. *Plectonema boryanum*) and dissimilatory sulphate-reducing bacteria directly reduce  $\text{AuCl}_4^-$  to  $\text{Au}^0$  even under halophilic conditions and possessing excess chloride ions (Shuster et al. 2013). Like the biogeochemical gold reactions in acidic and oxidised weathering environ-

ments, the presence of reduced iron and/or sulphur (as  $\text{Fe}^{2+}$  or  $\text{FeS}$ ) can immobilise elemental gold from  $\text{AuCl}_4^-$  (similar to reactions 15 and 18).

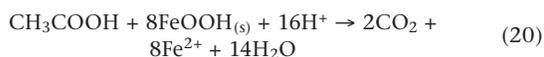
When assessing the limited stability of inorganic gold complexes in the presence of a wide range of bacteria, it is essential to consider the importance of gold mobility as complexes, as nanophases and as secondary gold particles (colloidal suspensions) within surface to near-surface hydrological regimes. The overall result of weathering (oxidation), complexation, and microbial 'degradation' of gold complexes that form nanometre-scale colloidal to micrometre-scale octahedral gold (Fig. 4) is the movement of gold downward in supergene systems (or laterally in placers). The subsequent biological enrichment of gold at the redox boundary (reactions 14–19; Lengke and Southam 2007) can produce economic accumulations of secondary gold.

### THE ROLE OF MICROORGANISMS IN CANGA-TYPE IRON DEPOSITS

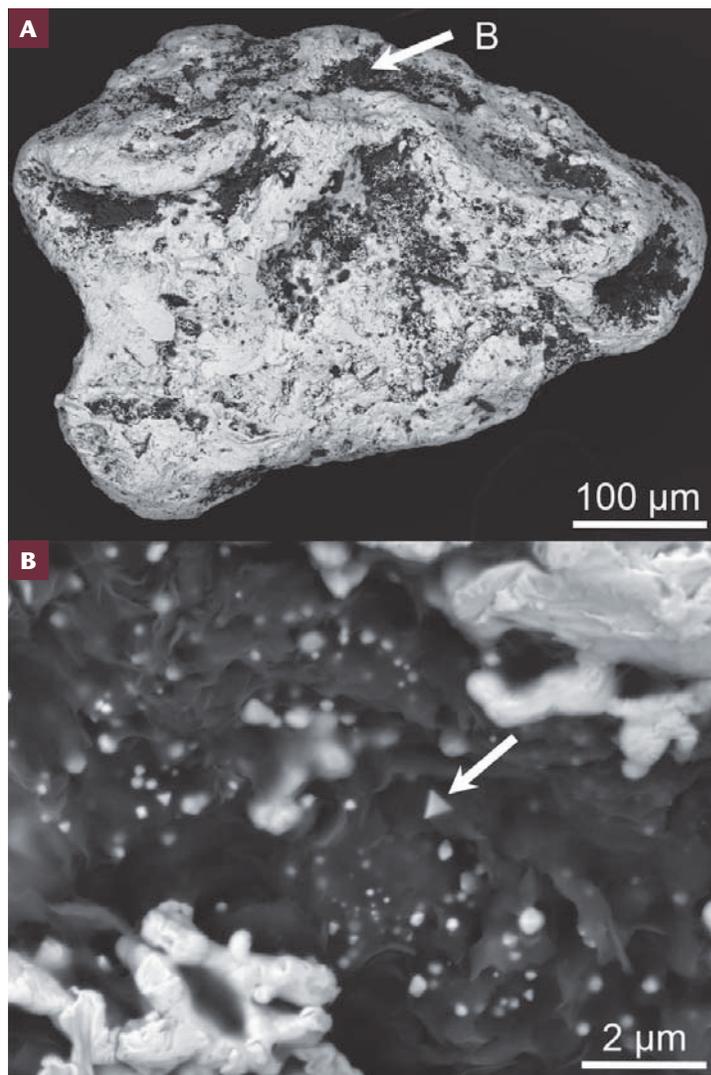
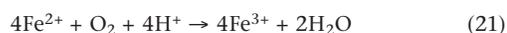
High-grade iron-ore reserves contain more than 60% iron, which generally occurs as iron (oxyhydr)oxides, such as hematite, magnetite and goethite. Some of the world's largest iron-ore deposits are located in South America and Australia and are the result of supergene lateritic weathering acting on banded iron formations (BIFs). During supergene lateritic weathering of BIFs, gangue minerals are leached, resulting in a relative enrichment of iron; note that iron oxide minerals also undergo multiple phases of dissolution and precipitation (Ramanaidou and Morris 2010). This is particularly evident in the ferruginous duricrust known as *canga*, which caps supergene lateritic iron ores in wet tropical conditions (Figs. 5A, B).

Dorr (1964) was the first to propose that geomicrobiological cycling of iron occurs in *canga*. Monteiro et al. (2014) later described *canga* as 'self-healing' because recurrent goethite dissolution and re-precipitation give it the capacity to re-form. The only reasonable reducing agent capable of 'driving' the frequent and repeated dissolution of iron oxides in *canga* must come from the biosphere, either indirectly from plants that exude organic acids around their roots, or directly by microorganisms that are involved in iron reduction as part of their metabolism. In addition to the evidence for bacteriological iron reduction in *canga*, electron microscopy has revealed that ferruginous stromatolite-like textures (Fig. 5C) possess microfossils reminiscent of iron-oxidising bacteria (Fig. 5D). These observations suggest that biological iron oxidation may also play a role in *canga* formation (see Monteiro et al. 2014).

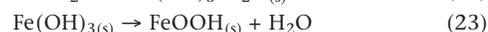
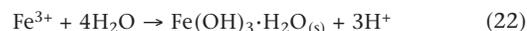
Biological iron reduction is an anaerobic process that is important in iron-rich soils and sediments worldwide (e.g. Lovley 1991). Biological iron reduction occurs when microorganisms use ferric iron as a terminal electron acceptor during metabolic oxidation of either hydrogen or various carbon compounds (e.g. goethite reduction with acetate; reaction 20).



The ferrous iron produced by iron reduction is unstable in the presence of oxygen and readily oxidises to ferric iron (reaction 21), or hydrolyses to form ferrihydrite (reaction 22), or can dehydrate to form goethite (reaction 23) abiotically or biologically, indicating that these processes are regenerative.

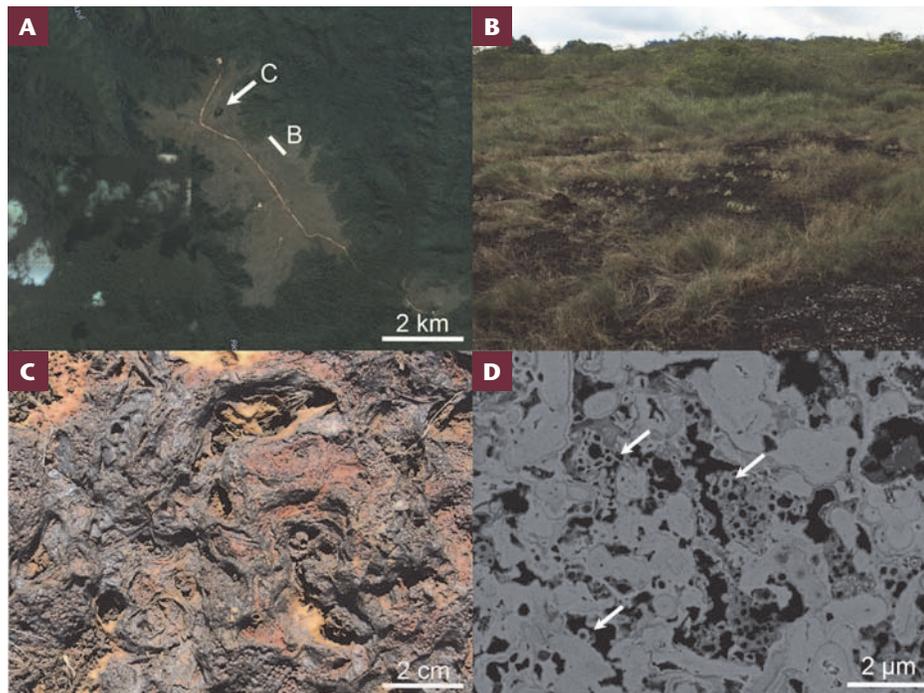


**FIGURE 4** (A) Back scattered electron, field emission scanning electron microscope image of a gold grain collected from West Coast Creek, Queensland, Australia. Location of photo in B is indicated by arrow. (B) High magnification scanning electron micrograph of one of the soil-covered, dark regions in (A), demonstrating the presence of colloidal (spherical particles) and octahedral secondary gold crystals (arrow).



In acidic aerobic environments or under near-surface low-oxygen conditions, microorganisms can oxidise ferrous iron (reaction 21). Biological iron reduction and biological iron oxidation both appear to occur in *canga* deposits (Monteiro et al. 2014); therefore, either spatial or temporal separation of environmental conditions suitable for both microbial groups must be present. This means that anaerobic microenvironments co-exist alongside aerobic and microaerophilic environments within *canga*. Furthermore, seasonal changes may be responsible for changes between aerobic and anaerobic conditions. During rainy periods, subsurface environments receive an influx of organic compounds, which contribute to the generation of anaerobic conditions. In dry months, evaporation will lead to aerobic and microaerobic conditions. Understanding the factors that control geomicrobiological iron cycling in *canga* is important for a more complete understanding of supergene lateritic iron-ore systems. Furthermore,

**FIGURE 5** (A) Google map image showing a kilometre-scale canga deposit in Carajás, Brazil (B) Field photograph of ridge within (A), highlighting the arid landscape and the scrub vegetation that grows on the iron oxide. (C) Photograph of stromatolite-like texture observed along an ephemeral lake (see arrow in A). (D) Back scattered electron, field emission–scanning electron microscope image of polished canga. Arrows indicate the bacteria-scale microfossils (dark spots) within the iron oxide matrix (light grey) (see also, Monteiro et al. 2014).



stimulating the natural geomicrobiological processes that occur in canga could be a useful strategy for rehabilitating iron-ore areas after mining activities have ceased.

## THE FUTURE OF BIOTECHNOLOGY IN MINING

Bioleaching processes liberate a wide range of metals under experimental conditions (Ehrlich and Newman 2008), suggesting that microorganisms could play an important role in the formation of supergene deposits. These processes are fundamentally interesting, but they also have commercial applications to the mining industry, as well as offering potential routes for mine remediation. Molecular biology is opening up a tremendous opportunity for researching the role that microorganisms play in metal mobility. For example, relatively little work has been done on the interaction between microorganisms and chalcopyrite. Chalcopyrite accounts for approximately 70% of the world's copper reserves; however, copper from low-grade chalcopyrite is not currently economically extractable using traditional mining methods. Because biotechnology offers a potentially cost-effective alternative to traditional mining techniques, further research into the interactions between microorganisms and chalcopyrite could have enormous commercial value.

In the case of gold, the discovery of new, large, and easily accessible deposits is becoming increasingly rare, and mining companies are pressured into locating economic deposits under increasingly deeper cover. Research into

microbe–gold interactions presents a range of new opportunities in developing novel techniques for gold exploration, processing and mine remediation.

The role that microorganisms play in the oxidation and reduction of iron has served as the cornerstone to geomicrobiological research. There is increasing evidence that certain microorganisms play a critical role in the cycling of iron and the formation of iron duricrusts within supergene lateritic iron-ore systems. A thorough understanding of the factors affecting microbial processes in these systems will be critical to artificially accelerating the re-formation of canga and, therefore, for the remediation of post-mining iron-ore sites.

In summary, understanding the role that microorganisms play in the turnover of metals is fundamental to developing new biotechnologies and will help shape the future of the minerals industry.

## ACKNOWLEDGMENTS

Electron microscopy was performed in the Nanofabrication Laboratory at Western University (Canada) and in the Centre for Microscopy & Microanalysis at the University of Queensland (Australia). Funding was provided through a Natural Sciences and Engineering Research Council (NSERC) of Canada Discovery and Accelerator Grants, through ARC Discovery support, and by Vale Technology Institute, Vale SA. We would like to thank the reviewers for their valuable suggestions and support. ■

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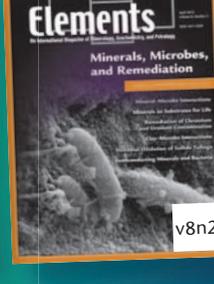


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## NAC+ 2016

### *The North Atlantic Craton and Surrounding Belts: A Craton-Specific Approach to Exploration Targeting'*

Following on from the successful first North Atlantic Craton (NAC) meeting in St Andrews (Scotland) in March 2014, the organizing committee invites you to attend the second meeting in Edinburgh (Scotland) that will be held 21–23 March 2016.

The North Atlantic Craton (NAC) stretches from Canada, through Greenland, Scotland and into Norway. The 2016 meeting welcomes contributions that develop our understanding of the NAC, its surrounding mobile belts, and their mineral resource potential.

Science themes:

- Formation and cratonization of the NAC: from micro-continents to craton
- Proterozoic orogens: the mobile belts surrounding the NAC
- The NAC margin in Canada and its mineralization
- Metallogensis and links to geodynamic setting
- Mineral resources of the NAC and adjacent Palaeoproterozoic mobile belts



Visit [bgs.ac.uk/NAC2016/home.html](http://bgs.ac.uk/NAC2016/home.html) for information as plans develop.

As in 2014, there will be a post-conference fieldtrip which will run from 24–28 March 2016 and will visit the Outer Hebrides (Scotland). The focus will be on Archaean gneisses of the NAC, Palaeoproterozoic belts formed at the craton margins, and a range of younger intrusions including the Loch Roag dyke, a mantle and lower crustal xenolith locality. There will also be spectacular coastal scenery and the chance to visit some stunning heritage sites.

The cost of the field trip is to be confirmed, but likely to be ~£500 including all travel, hotel accommodation, meals and field guidebook. A maximum of 15 places will be available. Please email [NACworkshop@gmail.com](mailto:NACworkshop@gmail.com) to express interest.



## GEOMICROBIOLOGY NETWORK – FOCUSED MEETING

The Geomicrobiology Network, a joint group of the Mineralogical Society and the Society for General Microbiology, will be holding its third Focused Meeting 'The Industrial Applications of Metal–Microbe Applications' on 9–10 November 2015 at Charles Darwin House, London (UK). It is part of the 2015 Focused Meeting series.

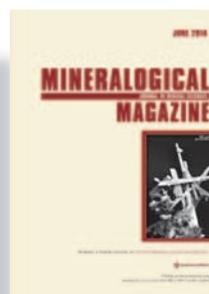
Metals are key components of life and play crucial roles in many areas of science and technology. Metal–microbe interactions, therefore, underpin many areas of industry: the mining sector that relies on 'biomining' for extracting valuable metals from low grade ores and 'biorecovery' for metal processing; and the water companies and contaminated-land stakeholders who rely on 'bioremediation' for the sustainable clean-up of contaminated land. Metal–microbe interactions are also key to many high-technology applications. These include the correct processing of metal cofactors, which are required for a large range of pharmaceuticals and fine chemicals; and novel biofabrication strategies, which are required for new nanotechnological applications, including the synthesis of quantum dots, catalysts, nanomagnets and other high-value products (often from wastes).



The meeting will have ~100 participants, with representatives from industry and academia. The Geomicrobiology Network/Mineralogical Society will support a session on bioprocessing of e-tech elements and will subsidize an evening social event; the Metals in Biology Networks of Industrial Biotechnology and Bioenergy will support the attendance of key industrialists. Participants will be drawn from a broad range of sources, including the Society for General Microbiology, the Geomicrobiology Network and those signed up to the Metals in Biology NIBB. Key European Union groups will also be targeted to enhance UK participation in future European Commission Horizon2020 (H2020) programmes. The organizers aim to have a 50:50 blend of industrial and academic invited speakers, with additional oral and poster presentations offered to younger researchers.

Register at [tinyurl.com/pq6mf5e](http://tinyurl.com/pq6mf5e).

## IMPACT FACTORS



The latest Thomson-Reuters impact factors (for 2014) were released in June 2015. *Mineralogical Magazine* has maintained its very good showing, having an impact factor (IF) for 2014 of 2.03, which is up 7% from 2013 and indicates that the increased rate of citation per article over

the past couple of years has continued. The IF for *Clay Minerals* has increased to 0.969, which is up since 2013, but still not quite as high as the editors would like. We are working on improving this rating.

The editors of both journals and the society's council have worked hard to secure good quality content, to have it reviewed thoroughly, fairly (and quickly) and to publish it as soon as possible after acceptance. They have also worked to secure content from authors new to the



# Italian Society of Mineralogy and Petrology

[www.socminpet.it](http://www.socminpet.it)

Congratulations to **Luca Bindi**, Professor of Mineralogy and Crystallography at the University of Florence (Italy), who received the 2015 President of the Republic Prize from the Accademia Nazionale dei Lincei (founded in 1603 and the oldest academy in the world). This prize is Italy's highest national achievement for science. The prize is awarded to outstanding scientists who have made distinguished contributions to the fields of physics, mathematics and the natural sciences. Professor Bindi's prize citation was as follows: "For the contribution Luca Bindi gave to mineralogy in general and in particular for the discovery of icosahedrite, the first natural quasicrystal, and the recent discovery of decagonite, the second natural quasicrystal with decagonal symmetry. His work has opened new challenges in solid-state chemistry, geology, astrophysics and cosmochemistry and changed our understanding of condensed matter." The prize was presented to Prof. Bindi by Sergio Mattarella, the President of Italy.



Luca Bindi (right) being congratulated by Sergio Mattarella, the President of Italy (left).



Chiara Anzolini (right) being congratulated by Sergio Mattarella, the President of Italy (left).

Congratulations also go to **Chiara Anzolini**, currently a PhD student at the Department of Geosciences in the University of Padova who received the 2015 Giuseppe Schiavinato Prize from the Accademia Nazionale dei Lincei for having produced the best master's thesis in mineralogy (with applications to petrology) completed in an Italian university. Her thesis, "Thermoelastic Parameters of Coesite: Implications for Diamond Geobarometry," was supervised by Prof. Fabrizio Nestola and was selected by the Physics, Mathematics and Natural Sciences Commission. The prize was presented to Chiara by the President Sergio Mattarella.

For more information see [www.socminpet.it/](http://www.socminpet.it/).

## MSGBI *Cont'd from page 344*

respective journals, by publishing papers from specific conferences, e.g. on radioactive waste management, or on mineral deposits. Watch out for these issues – we publicize them via the MSGBI member *E-Bulletin*, and occasionally on MSA-Talk. Our hybrid funding model means that we can offer some of these special issues as open access, alongside the regular, subscription-model issues. We will continue to push hard on all fronts and welcome offers from individual authors and from groups interested in publishing high-quality science in journals with good reputations and strong editing and production values.

## EUROCLAY

At the time of writing, we have just completed the mammoth Euroclay 2015 meeting in Edinburgh. This event ran for seven days in early July and included five field trips, a workshop, a short-course, a range of social events (including a superb banquet at 'Our Dynamic Earth'), five parallel sessions and two poster sessions. Some 520 delegates, including 128 students, attended.

The conference was organized by Prof. Steve Hillier of the Hutton Institute in Aberdeen (Scotland) and was supported by a large team that included the programme and finance committees, session chairs and the staff of the Mineralogical Society (Russell Rajendra, Anna Lofts, Martin Hughes and Kevin Murphy).



From left to right: Ed Grew, Frances Wall, Simon Harley, Stuart Mills

Three society awards were made during the end-of-conference Awards Ceremony. Ed Grew received the Collins Medal, Simon Harley received the Schlumberger Medal, and Stuart Mills received the Hey Medal.

Make a nomination for the 2017 awards now (closing date 22 April 2016). Visit [www.minersoc.org/Awards.html](http://www.minersoc.org/Awards.html) for more information.



The Hey, Schlumberger and Collins medals, respectively.

A fuller report of the meeting will be published online shortly.



# Sociedad Española de Mineralogía

[www.ehu.es/sem](http://www.ehu.es/sem)

## SEM 2015: 35<sup>th</sup> MEETING OF THE SPANISH MINERALOGICAL SOCIETY

The 35<sup>th</sup> Annual Meeting of the Spanish Mineralogical Society (SEM 2015) was held 30 June–03 July 2015, in Huelva (Spain). The meeting was organized by the University of Huelva and was coordinated by José Miguel Nieto. The program and abstracts, which can be downloaded from the conference website ([www.uhu.es/fexp/sem2015/](http://www.uhu.es/fexp/sem2015/)), included a one-day workshop, posters and oral presentations, and a one-day field trip to the Rio Tinto mining district.

### Workshop Seminar

The *Rare Earth Elements: Mineralogy, Geochemistry, Ore Deposits and Metallurgy* seminar took place 30 June 2015. The aim of the seminar was to present and discuss new perspectives and ideas about the rare earth elements, particularly for young scientists. The speakers were scientists and professionals of international prestige in this field. The program consisted of 5 lectures:

- “Geochemistry of the lanthanide elements” by F. Bea Barredo (University of Granada, Spain)
- “Elementos de las tierras raras: depósitos convencionales y no convencionales” by J.C. Melgarejo Draper (University of Barcelona, Spain)
- “Rare earth elements in acid mine drainage” by C. Ayora Ibañez (Institute of Environmental Assessment and Water Research at the CSIC, Barcelona, Spain)
- “Innovative recovery strategies of rare earth and other critical metals from electric and electronic waste” by J. Hobohm (University of Hamburg, Germany)
- “Progress in hydrometallurgy for selective extraction and recycling of strategic metals” by S. Pellet-Rostaing (Marcoule Institute for Separative Chemistry, Lyon, France).

The lectures will be published in volume 12 (2015) of the journal *Seminarios de la Sociedad Española de Mineralogía* ([www.ehu.es/sem/revista/seminarios.htm](http://www.ehu.es/sem/revista/seminarios.htm)).

### Posters and Oral Presentations

The scientific sessions took place 1–2 July. In all, nearly 200 scientists were involved in the 67 presentations, 37 of which were oral and 30 were posters. Contributions included topics on mineralogy, petrology, geochemistry, mineral deposits, conservation of historical heritage, synthesis and crystal growth, and clay minerals. The main objective was to hold high-quality scientific sessions that would become a platform for debate, a means to exchange ideas, and a way to establish new scientific collaborations. A program of grants and awards encouraged the participation of young researchers.

The SEM 2015 program included two plenary lectures: “Estudio de los mecanismos de disolución y precipitación a escala de poro mediante el uso de experimentos de percolación y microtomografía de Rayos-X” (Linda Luquot) and “Mineralogía y geoquímica de Ni, Co, EGP, Sc, REE en yacimientos lateríticos” (Joaquín A. Proenza). All these scientific contributions have been published in volume 20 of *Macla*, the journal of the SEM.

### Awards for Young Researchers

Two awards were given to the best oral presentations at the conference. The winners were: Didac Navarro-Ciurana (University Autònoma of Barcelona) for “C and O isotopes of the Riópar non-sulfide Zn ores (Albacete, SE Spain)”; and Cristina Ruiz-Agudo (University of Münster) for “Mecanismos de precipitación de BaSO<sub>4</sub> y el efecto de aditivos”.



Winners of the young researchers award were Cristina Ruiz-Agudo and Didac Navarro-Ciurana, with Juan Jiménez-Millán (SEM President, left) and José Miguel Nieto (SEM meeting coordinator, right).

### ENCIENDE-SEM Award



Mª José Mayayo

The 2015 ENCIENDE-SEM Award is sponsored by the SEM and recognizes the best educational initiative or innovative action that promotes scientific careers among children and young students at the primary and high school levels in the field of the Earth sciences, especially in mineralogy, petrology and geochemistry. The 2015 award has gone to the project “3D-SYM, descubriendo la simetría de los cristales” carried out by Mª José Mayayo, Ester Mateo and Felipe Barbed. As the leader of this project, Mª José Mayayo (University of Zaragoza) received the award.

### Field Trip to the Rio Tinto Mining District

A geological excursion to the Rio Tinto mining district was held on 03 July. Participants visited the source area of the Tinto River and learned about the geology of the Rio Tinto ore deposits, environmental mining impact, new mining projects, and the acid mine drainage generation and transport processes.



Participants of the trip enjoyed a geological overview of the Cerro Colorado open pit.

### Other Scientific Activities



Poster of the exhibition “Cristales: A World to Discover”.

During the SEM meeting, the exhibition “Cristales: A World to Discover” by Manuel García-Ruiz and Fermín Otorola was on display in the hall of the Faculty of Experimental Sciences (University of Huelva). The exhibition comprised 14 posters and was designed to reach school or college students. The goals of this exhibition were to increase awareness of the importance of crystallography and its role in everyday life in modern society, motivate young people, and promote education and research in crystallography ([https://cristales.fundaciondescubre.es/?page\\_id=1769](https://cristales.fundaciondescubre.es/?page_id=1769)).



# Association of Applied Geochemists

[www.appliedgeochemists.org](http://www.appliedgeochemists.org)

## IN MEMORIAM: ERIC HOFFMAN

It is with great sadness that the AAG marks the passing of Dr. Eric Hoffman in July of this year. Eric was a Fellow of the Association and a Gold Medal recipient in 2013. He began his working career in 1978 at McMaster University (Canada) where he helped develop one of the first commercial instrumental neutron activation analysis (INAA) laboratories in the world. This endeavour led to the formation of his own company in 1987: Activation Laboratories Ltd, or Actlabs,



which provided commercial analyses to the mineral exploration industry. Actlabs diversified into materials testing in 1994, forensic applications in 1996, pharmaceuticals in 2003 and, more recently, geometalurgy, petroleum exploration and refining, and environmental/occupational health and agriculture. Eric was an innovator. He began with the development of new INAA techniques, successfully adopted inductively coupled plasma mass spectrometry (ICPMS) and high-resolution ICPMS in a commercial

laboratory, and introduced proprietary analytical services, such as Enzyme Leach and Soil Gas Hydrocarbons (SGH), for mineral exploration. Actlabs has grown a single facility to an international company with 30 laboratories operating in 12 countries while remaining a business his family is deeply involved in. Eric will be sorely missed by his friends and colleagues. More information can be found on the Actlabs website ([www.actlabs.com](http://www.actlabs.com)) and a more extensive summary of Eric's many achievements will be published in the *Explore* magazine and on the AAG web site.

**Dale Sutherland** ([DaleSutherland@actlabs.com](mailto:DaleSutherland@actlabs.com))  
Director of Research, Activation Laboratories Ltd.

## AAG MEDAL RECIPIENTS

The AAG awarded three medals at its 2015 International Applied Geochemistry Symposium held in Tucson, Arizona (USA). The Gold Medal is awarded for outstanding scientific achievement in applied geochemistry, and the Silver Medal is awarded to an AAG member for dedicated service to the association.

### Colin Dunn Citation for AAG 2014 Gold Medal

Dr. Colin Dunn has worked tirelessly for decades in advancing the field of biogeochemistry applied to exploration. In this field, he is the preeminent world leader. Many geoscientists have been mentored by Colin over the last several decades. His work has been documented through over 200 peer-reviewed publications, as well as presentations at international venues, short courses, and informal conversations with many prospectors, geologists, and geochemists, and through the publication of his definitive book on the subject, *Biogeochemistry in Mineral Exploration* (2007; Elsevier). Colin has assisted commercial analytical laboratories in the development of analytical techniques and in the establishment of analytical control materials. Furthermore, he has been a long-standing member and fellow of the AAG, a past AAG councillor, and has volunteered on numerous AAG committees. As an applied geochemist, Colin has been a stalwart for the geochemistry profession in general and for biogeochemistry in particular.

### Ravi Anand Citation for AAG 2015 Gold Medal

Dr. Ravi Anand has developed a vast knowledge on regolith geochemistry processes, landscape evolution, and secondary dispersion in deeply weathered terranes, and he has applied this knowledge to mineral exploration. Understanding the regolith is critical for correctly interpreting soil geochemistry, and Ravi's research on the subject has involved numerous empirical field studies combined with extensive laboratory experiments. His research has resulted in significant and lasting changes to the philosophy and practice of geochemical exploration in the deeply weathered terranes of Australia and elsewhere and has contributed directly to major mineral discoveries. A fellow of the AAG, Dr. Anand served as the association's Distinguished Lecturer in 2013–2014, giving presentations on several continents. Dr. Anand is presently a chief research scientist at CSIRO Mineral Resources Flagship and an adjunct professor at Curtin University (Australia).



From left to right: Matt Leybourne, AAG President; Colin Dunn; Beth McClenaghan in center; Ravi Anand; Ryan Noble, AAG Vice-president.

### Beth McClenaghan Citation for AAG 2015 Silver Medal

This year's Silver Medallist is Beth McClenaghan, who thoroughly deserves this reward. Beth has been an AAG Fellow for some 23 years. During this time, she has served the association as a councillor; has organized numerous workshops in conjunction with our IAGS symposia, including this present one; has served on IAGS organizing committees; and has chaired sessions for same. She is currently Editor of the association's newsletter, *EXPLORE*, a position Beth has held since 2005. This newsletter is extremely important for promoting the association, as a vehicle for disseminating information to AAG members, and for promoting the science of applied geochemistry. Under Beth, the newsletter has been enhanced on several fronts. Beth was instrumental in getting all of the association newsletters—from the earliest 1970s to the present—digitized, on-line, and available for download from the AAG website. Beth is also an accomplished scientist with the Geological Survey of Canada, specializing in the use of indicator minerals in exploration. Having known her professionally for some 20 years, it is a true honor for me to present the 2015 AAG Silver Medal to Beth McClenaghan.

**Robert G. Eppinger**  
Chair, AAG Awards and Medals Committee



web

www.minsocam.org

## PRESIDENT'S LETTER

### *Diamond — Premier Mineral for Understanding the Geology of the Deep Earth*

The following is a summary of my Mineralogical Society of America presidential address that will be delivered at the next Geological Society of America meeting, which is to take place 1–4 November 2015 in Baltimore (Maryland, USA). Such addresses are normally the time for the MSA President to present some aspect of his/her research, especially if it has mineralogical relevance. For almost 20 years, I have been working on radiogenic isotopic dating of diamonds by analyzing their sulfide inclusions using the Re–Os system. What started as a geochronological tool for single diamonds, has expanded into a broader field of study that attempts to understand various geological aspects of the mantle at depths far below the region of basaltic magma generation.

Diamond provides extraordinary information about Earth's interior. Diamond is the only mineral that can trap other phases growing in the mantle (at depths to 800 km) and then can fully isolate the included minerals from chemically reacting with any surrounding fluids, melts or solids. These diamond “capsules” themselves crystallize from highly mobile C–O–H-bearing fluids or melts and display remarkable growth textures. A diamond's preserved growth history can be used to track carbon sources and carbon mobility in the deep mantle. Information about fluid sources, host lithologies, diamond ages, mantle mineralogy, diamond-forming reactions, and the reduction–oxidation (redox) state of the mantle can all be obtained via the fortuitous co-crystallization or entrapment of silicate, sulfide, metal, and carbide inclusions.

Information on diamond ages, C and N isotopic compositions, and inclusion mineralogy gleaned from many single diamonds can be combined into large-scale patterns that reveal continental-scale geological structures and/or remote aspects of mantle geodynamics. Because diamonds from the continental lithospheric mantle are of great antiquity (in some cases up to 3.5 Ga), their study allows one to look back into the ancient geologic past. Direct studies on diamond, as well as theoretical studies that consider its role in mantle mineralogy, have helped us to pinpoint the initiation of subduction, to trace recycled crustal components (including water) into the mantle transition zone, to record the passage of fluids into the continental lithosphere, to see the preserved signature of carbonatitic fluids that trigger deep mantle melting, and to reveal the change in mantle redox state with depth. In the future, a better knowledge of fluid compositions, of diamond-forming reactions, of C and N isotopic fractionation factors, plus analyzing new suites of sublithospheric (superdeep) diamonds, all hold the promise of changing our understanding of the geology of the deep Earth.

**Steven B. Shirey**

2015 Mineralogical Society of America President  
Carnegie Institution of Washington  
sshirey@carnegiescience.edu



EVEN IF YOUR INTERESTS ARE DIFFERENT THAN THOSE AROUND YOU, THERE IS A PLACE FOR YOU IN MSA. JOIN MSA ONLINE AT WWW.MINSOCAM.ORG.

## NOTES FROM CHANTILLY

- 2015 election results** – the 2016 MSA President is Rebecca Lange, the MSA Vice President is George E. Harlow, and the MSA Past President is Steven B. Shirey. Bryan Chakoumakos was elected secretary. Howard W. Day remains in office as treasurer. Rajdeep Dasgupta and Peter Nabelek join as new councilors, while Edward S. Grew, Wendy Panero, Abby Kavner, and Matthew J. (Matt) Kohn remain as continuing councilors. Our outgoing councilors are Isabelle Daniel and Kirsten Nicolaysen, and the outgoing secretary is Andrea Koziol.
- MSA 2016 membership renewals** will start early October 2015, with notices sent electronically, followed by several electronic reminders before a paper copy is sent to those who do not renew online by the end of October. Members who renew and pay online before 31 October 2015 will receive a \$5 dues discount; the discount reflects cost savings to MSA from members who renew early online.
- Members and Fellows who are in the senior, honorary, and life categories are sent renewal notices. They need not pay dues, but are, nevertheless, sent notices as the best way to prompt an update of membership information, particularly mail and e-mail addresses.
- If you subscribe to other journals through MSA—*Gems & Gemology*, *Journal of Petrology*, *Mineral News*, *Physics and Chemistry of Minerals*, *Mineralogy and Petrology*, or *Rocks & Minerals*—please renew early. MSA needs to forward your renewal to those publishers before your subscription runs out.
- The 2015 MSA Awards Lunch will be held in Holiday Ballroom number 4 of the Hilton Baltimore Hotel (Baltimore, Maryland, USA) on Tuesday, 3 November 2015, at 12:15–2:30 p.m. At the lunch, **Rodney C. Ewing** (Stanford University) will receive the Roebing Medal, **Nicholas J. Tosca** (University of Oxford) the MSA Award, and MSA's own **J. Alex Speer** the Distinguished Public Service Medal. There is also recognition of the 2013–14 MSA Lecturers: Bethany Ehlmann, Colleen Hansel, and Lutz Nasdala, as well as Timothy W. Grover, the outgoing MSA Lecture Administrator.
- The MSA Awards Lectures, Annual Business Meeting, and Presidential Address at the 2015 GSA Annual Meeting are on Tuesday, 3 November 2015, 3:00–5:30 p.m., at the Baltimore Convention Center (BCC 317). Rodney C. Ewing will deliver the “MSA Roebing Medal Lecture: The Science-Policy Interface”; Nicholas J. Tosca gives his “MSA Award Lecture: Mineralogy as a Bridge between Geochemistry and Earth History”; and Steve Shirey his “MSA Presidential Address: Diamond: Premier Mineral for Understanding the Geology of the Deep Earth”. The Annual Business Meeting will follow the lectures, then there will be the MSA/GS/MGPV Joint Reception.
- During the Annual Meeting there are topical sessions for the two MSA awardees. Session T134: “Radiation Effects, Mineralogy, and Materials Science of Actinides: In Honor of Rodney C. Ewing, 2015 Roebing Medalist,” with both oral (Sunday, 1 November 2015: 8:00 a.m.–5:00 p.m.; BCC 317) and poster (Monday, 2 November 2015: 9:00 a.m.–6:30 p.m.; Exhibit Hall) sessions. Session T132: “Mineralogy of Diagenesis on Earth and Mars: In Honor of Nicholas J. Tosca, 2015 MSA Awardee” (Monday, 2 November 2015: 8:00 a.m.–12:00 p.m.; BCC 342). There are also sessions honoring MSA members: Session T133: “Mineralogy Writ Small: A Tribute to the Distinguished Career of **David R. Veblen**” (Monday, 2 November 2015: 8:00 a.m.–12:00 p.m.; BCC 317); Session T168: “Subduction, Fluids, Accessory Minerals, and Trace Elements: A Celebration of **Sorena Sorensen's** Career” with both oral (Monday, 2 November 2015: 1:30–5:30 p.m.; BCC 341) and poster (Wednesday, 4 November 2015: 9:00 a.m.–6:30 p.m.; Exhibit Hall) sessions. Session T165: “Zen and Now: Honoring the Legacy of **E-an Zen's** Contributions to Geology” (Tuesday, 3 November 2015: 8:00 a.m.–12:00 p.m. BCC 317).

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

## NEW TITLE

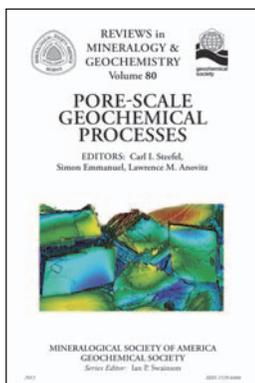
## Reviews in Mineralogy and Geochemistry

Mineralogical Society of America  
and The Geochemical Society

Volume 80: **Pore-Scale Geochemical Processes**,  
Carl I. Steefel, Simon Emmanuel, Lawrence M. Anovitz,  
editors. i-xiv + 491 pages. ISBN 978-0-939950-96-6

This volume reviews the experimental, characterization, and modeling advances in our understanding of pore-scale geochemical processes. The pore scale is a distinct scale and environment associated with its own set of questions and challenges. The scale is important because it accounts for the pore architecture within which such diverse processes as multi mineral reaction networks, microbial community interaction, and transport play out, giving rise to new geochemical behavior that might not be understood or predicted by considering smaller or larger scales alone.

Description and ordering online at [www.minsocam.org](http://www.minsocam.org) or contact Mineralogical Society of America, 3635 Concorde Pkwy Ste 500, Chantilly, VA 20151-1110 USA phone: +1 (703) 9950 fax: +1 (703) 652-9951 e-mail: [business@minsocam.org](mailto:business@minsocam.org) Cost is \$50 (\$37.50 members MSA, GS, CMS).



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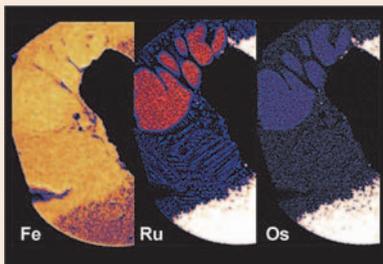
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## SHORT COURSE ANNOUNCEMENT

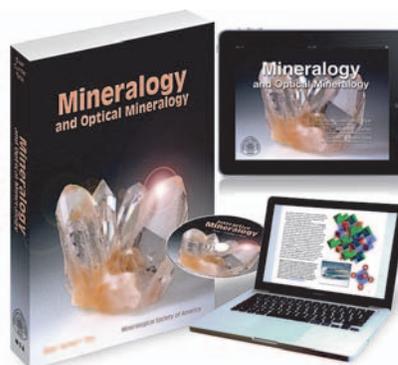
## Siderophile and Chalcophile Elements

ORGANIZERS: JASON HARVEY and JAMES DAY  
14-18 December 2015, Scripps Oceanographic Institute  
San Diego, CA, US

The strongly chalcophile (sulfur-loving) elements include Se and Te, while the highly siderophile (iron-loving) elements are the platinum-group elements (PGEs: Ir, Os, Pt, Pd, Rh, Ru), Re, and Au, and include the long-lived isotope systems based on the decay of Re and Pt to isotopes of Os ( $^{187}\text{Re}$ – $^{187}\text{Os}$  and  $^{190}\text{Pt}$ – $^{186}\text{Os}$ , respectively). As a result of the strong partitioning of siderophile and chalcophile elements into metals, alloys, and sulfides, the study of the distribution and behavior of the siderophile and chalcophile elements, and of the phases that host them, may provide a unique perspective on how the major geochemical reservoirs of the Earth and other rocky planets formed and developed.



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# EUROPEAN ASSOCIATION OF GEOCHEMISTRY



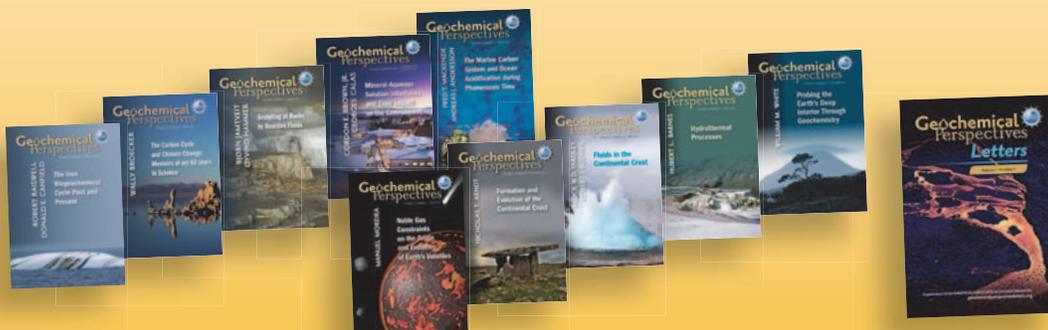
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# Geochemical Society

[www.geochemsoc.org](http://www.geochemsoc.org)

## FROM THE PRESIDENT



Barbara Sherwood Lollar

I write this shortly after returning from this year's 25<sup>th</sup> V.M. Goldschmidt Conference. This wonderful conference was held in Prague (Czech Republic) and was jointly sponsored by the European Association of Geochemistry (EAG) and the Geochemical Society (GS), with the Geochemical Society of Japan as principal co-sponsor. We extend thanks and congratulations to our EAG colleagues; to all the many scientists and colleagues who contributed to the organization, program and, spirit of this year's gathering; and to Cambridge Publications for their expert execution of the meeting.

The 25<sup>th</sup> meeting was a special one. It integrated the traditional aspects of the Goldschmidt spirit, which stretches back to the very first meeting in Baltimore (Maryland, USA) in 1988, while seamlessly incorporating new initiatives and activities—particularly those designed to introduce, support, and mentor the next generation of young scientists. Once again, significant support was committed to subsidizing the registration and/or travel for students and for international attendees from low-income countries. Special 25<sup>th</sup> anniversary initiatives were included this year, such as the “25 + 25” student ambassadors, professionals who volunteered their talents to energize audiences and to participate in the plenaries. The successful mentoring program first introduced last year in Sacramento (California, USA) was again very popular and active. A new initiative was “Meet the Plenary”: this allowed students in particular to participate in a sponsored lunch after a plenary lecture and have a one-on-one interaction (in some cases for hours!) with a plenary speaker.

Our societies, such as the GS, take very seriously their mission to lead in community building. We know we need to pay special attention to the group that is the foundation and future of geochemistry: students and early career scientists. The 25<sup>th</sup> Goldschmidt continued the tradition of free seminars and events that focused on themes as diverse as innovations in teaching; publishing and reviewing manuscripts; fellowship and grant writing; employment and career options; and research workshops on emerging research areas. A very special thanks goes out to those academics and meeting partners who volunteered their time, expertise, and insights in developing and running these workshops. If you have ideas or particular talents to bring forward to future workshops at a Goldschmidt conference then be sure to get in touch with us! The success of these events is a credit to the creativity and enthusiasm of the entire Goldschmidt community.

It was a great pleasure to inaugurate another new tradition at this meeting: the Geochemical Society Business Meeting and Reception, which was held on Wednesday evening and open to all GS members (and friends). This year's meeting gave us an opportunity to offer a warm welcome to our colleagues and friends from the Geochemical Society of Japan,



Hodaka Kawahata, President, Geochemical Society of Japan; Barbara Sherwood Lollar, President of GS; Harue Masuda, Chair, 2016 Goldschmidt Local Organizing Committee; Naohiro Yoshida, Past President, Geochemical Society of Japan; and Naomi Harada, Geochemical Society of Japan at the GS Business Meeting and Reception.

and to the Local Organizing Committee, and to highlight and convey the excitement that we all feel for the upcoming 2016 Goldschmidt to be held in Yokohama (Japan). Decorations and sushi were provided, as well as information on the exciting activities planned for this meeting. Be sure to visit [goldschmidt.info/2016/](http://goldschmidt.info/2016/) for the latest on the scientific program, field trips, student programs, and more. You can also find information on the wide range of extremely reasonable housing and accommodation. Located less than half-an-hour from Tokyo's Haneda airport, the Yokohama Goldschmidt promises not only exceptional scientific and professional activities but also a cultural, historical and scenic Goldschmidt of extraordinary beauty and distinction.

**Barbara Sherwood Lollar**  
President, The Geochemical Society

## STAY IN TOUCH WITH GS EVERY WEEK

Membership in the Geochemical Society includes a subscription to the weekly email newsbrief *Geochemical News*. Reading it is a great way to stay in touch with the latest published research in the field and with the society's activities. Check your inbox on Tuesdays (or early Wednesdays in Asia-Pacific) for *Geochemical News*. If you are not receiving it, please contact us ([gsoffice@geochemsoc.org](mailto:gsoffice@geochemsoc.org)) to make sure that we have your current email address.

## GEOCHEMICAL SOCIETY BUSINESS OFFICE

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# Japan Association of Mineralogical Sciences

<http://jams.la.coocan.jp>

## JAPAN ASSOCIATION OF MINERALOGICAL SCIENCES AWARDEES

The Japan Association of Mineralogical Sciences (JAMS) is proud to announce the recipients of its 2015 society awards. The **Japan Association of Mineralogical Sciences Award** is presented to a maximum of two scientists in any one year for exceptional contributions to mineralogical and related sciences. The **Manjiro Watanabe Award**—named in honor of Professor Manjiro Watanabe, a well-known Japanese mineralogist, and founded at his bequest—is awarded every year to a scientist who has contributed significantly to mineralogy, or a related science, over his or her entire career. The **Sakurai Medal**—named in honor of Dr. Kin-ichi Sakurai, who discovered many new minerals—is awarded to a scientist who has made a lasting contribution to the study of new minerals.

### Japan Association of Mineralogical Sciences Award to Masaaki Obata



Masaaki Obata is a Professor Emeritus at Kyoto University. He graduated from Kyoto University, obtained his Master of Science degree from Kanazawa University under the supervision of the late Prof. S. Banno, and obtained his PhD in 1977 in geochemistry from the Massachusetts Institute of Technology (MIT; USA) under the supervision of Prof. John Dickey. Following postdoctoral tenures at MIT and

ETH Zurich (Switzerland), Prof. Obata has been a professor (associate and/or full) at Toyama University, Kumamoto University, and Kyoto University. Following petrological work on the Ronda peridotite (Spain), which was the subject of his thesis work at MIT, he collaborated with others to investigate the Ultental garnet peridotite (Italy) and the Horoman peridotite in Hokkaido (Japan), all within the context of magma genesis and metamorphic reactions in the upper mantle. Prof. Obata extended his investigations into magma genesis by analyzing the problem of how magma forms in the lower crust, which he did through the study of migmatites and high-grade metamorphic rocks. He also developed an interest in magmatic fractionation processes that produce layered igneous rocks. Prof. Obata and his co-workers continue to research kelyphite and symplectite formation and how ultramafic pseudotachylytes form, for which he employs high-pressure shock-compression melting experiments using olivine modeled on seismic processes in the upper mantle.

### Manjiro Watanabe Award to Kosuke Onuma



Kosuke Onuma received his doctor of science degree in 1964 from Hokkaido University: his thesis was "The systems  $\text{NaAlSiO}_4\text{-Ca}_2\text{MgSi}_2\text{O}_7$  and  $\text{CaMgSi}_2\text{O}_6\text{-Ca}_2\text{MgSi}_2\text{O}_7\text{-NaAlSiO}_4$ , and their petrologic application", which was supervised by Prof. Kenzo Yagi. While at the University of Pittsburgh (January 1965 to May 1968), Hokkaido University (May 1968 to September 1983), and at Tohoku University, (October 1983 to February 1997), Dr. Onuma advanced his research on phase equilibrium in multi component silicate systems at atmospheric and high pressures; the stability fields and crystal chemistry of rock-forming minerals; and the evolution of alkaline magma. Dr. Onuma devoted his effort to the experimental studies of clinopyroxene–melilite–nepheline-bearing systems in order to clarify the general crystallization behavior of alkaline rocks and to establish a differentiation scheme for nephelinitic rocks. His experimental studies have helped to define the impacts of oxygen fugacity on differentiation trends in alkaline magmas and also elucidate the role of minor transition elements in the stability of rock-forming minerals. In addition to these investigations, Dr. Onuma

has also engaged in research on ionic substitutions in Fe–Ti–Al-rich silicates and the effects such substitutions have on these silicates' stability and crystal chemistry. Examples of this research include the phase relations and crystal chemistry of clinopyroxene in the join  $\text{CaMgSi}_2\text{O}_6\text{-CaFeAlSiO}_6\text{-CaAl}_2\text{SiO}_6\text{-CaTiAl}_2\text{O}_6$  at atmospheric pressure and at high pressure; the substitution of  $\text{Fe}^{3+}$  for Al in nepheline and its effect on crystal structure; and nonstoichiometric solid solution in the nepheline–aegirine system. Dr. Onuma's influential studies offer valuable insights into the crystallization behavior of alkaline rocks, the crystal chemistry of rock-forming minerals, and the crystallization processes of high-temperature products in meteorites. His studies have significantly advanced the field of mineralogy and petrology.

### Sakurai Medal to Mariko Nagashima



The Sakurai Medal has been awarded to associate professor Mariko Nagashima, of the Department of Earth Science at Yamaguchi University, for her discovery of ferriakasaite-(La) (IMA CNMNC #2013-126). Prof. Nagashima's overarching interest is to systematically and completely understand the relationship between a transition-metal elements' oxidation state and the associated hydrogen-bonding system. Her investigations aim to establish a general rule for the relationship between cation substitution and structural variation and to determine the influence that formation conditions (e.g.  $P$ ,  $T$ , and  $f\text{O}_2$ ) have on cation distribution and associated structural variation. To approach these goals, she studies both natural and synthetic minerals using single-crystal and powder diffraction methods, plus spectroscopic techniques.

Prof. Nagashima has, to date, undertaken systematic studies on epidotes and pumpellyites, and related minerals such as sursassite, and worked on the hydroxyroxenoids babingtonite and nambulite. Her expertise and knowledge of the epidote supergroup enabled her to contribute to the discovery of ferriakasaite-(La), which has the crystallochemical formula of  $^{\text{A1}}\text{Ca}^{\text{A2}}\text{La}^{\text{M1}}\text{Fe}^{3+\text{M2}}\text{Al}^{\text{M3}}\text{Mn}^{2+}(\text{SiO}_4)(\text{Si}_2\text{O}_7)\text{O}(\text{OH})$ . This new mineral was discovered in tephroite  $\pm$  calcite veinlets (< 2 mm in width) that cut the stratiform ferromanganese deposit at Shobu, Ise (Japan). Euhedral to subhedral prismatic crystals (up to 150  $\mu\text{m}$  long) represent the most common appearance of the mineral. Ferriakasaite-(La) is named in honor of Masahide Akasaka (b. 1950) for his outstanding contributions to mineralogy, especially to the study of rock-forming minerals occurring in Mn–Fe ore deposits and the natural and synthetic epidote-supergroup minerals.

## JOURNAL OF MINERALOGICAL AND PETROLOGICAL SCIENCES

Vol. 110, No. 4, August 2015

### Original articles

**Structural rationale for the occurrence of the elbow twins in cassiterite and rutile** Massimo NESPOLO and Bernd SOUVIGNIER

**Geochemical behavior of zirconium during Cl-rich fluid or melt infiltration under upper amphibolite facies metamorphism — A case study from Brattnipene, Sør Rondane Mountains, East Antarctica** Fumiko HIGASHINO, Tetsuo KAWAKAMI, Noriyoshi TSUCHIYA, M. SATISH-KUMAR, Masahiro ISHIKAWA, Geoffrey H. GRANTHAM, Shuhei SAKATA, Kentaro HATTORI and Takafumi HIRATA

**Decarbonation and melting in  $\text{MgCO}_3\text{-SiO}_2$  system at high temperature and high pressure** Sho KAKIZAWA, Toru INOUE, Hideki SUENAMI and Takumi KIKEGAWA

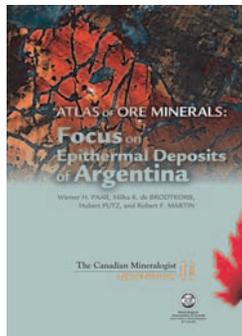
**EDS quantification of light elements using osmium surface coating** Hiroaki OHFUJI and Masashi YAMAMOTO



# Mineralogical Association of Canada

[www.mineralogicalassociation.ca](http://www.mineralogicalassociation.ca)

## PUBLICATION NEWS



*Coming Soon!*

### Special Publication 11

This atlas of ore minerals focuses on the mineral species encountered in ore deposits of Argentina, many of them of epithermal type. The authors describe 210 ore minerals, illustrate their associations, both with macro-photos and in reflected light, and document their chemical composition.

## THE CANADIAN MINERALOGIST

Over the last two years, there have been significant changes in the way *The Canadian Mineralogist* is produced. These include the introduction of an online submission and tracking system, changing the first issue in a year to January from February, and introduction of "online-first" publication (see [www.canmin.org/content/early/recent](http://www.canmin.org/content/early/recent)). Unfortunately, this last change resulted in a major delay due to unexpected problems with one of the journal's subcontractors. We are happy to report that the problem has been resolved and that subscribers will be receiving their issues at the rate of one per month until we are caught up at the end of the year. Upcoming issues include:

- A thematic issue in honor of Edward S. Grew
- A thematic issue in honor of John L. Jambor
- A thematic issue to accompany the 12<sup>th</sup> International Platinum Symposium

## 2016 MAC AWARDS – CALL FOR NOMINATIONS

### Peacock Medal

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

### Young Scientist Award

This award is given to a young scientist who has made a significant international research contribution during the early part of their developing scientific career. The scientist will have received his/her PhD not more than 15 years before the award. He or she must be a Canadian working anywhere in the world or a scientist of any nationality working in Canada. The research areas include mineralogy, crystallography, petrology, geochemistry, mineral deposits, or related fields of study.

### Leonard G. Berry Medal

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

Please submit your nominations by 31 December 2015. Check our website, [www.mineralogicalassociation.ca](http://www.mineralogicalassociation.ca), for additional details.

## STUDENT TRAVEL/RESEARCH GRANTS

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

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

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

Quotations and receipts may be requested for any equipment purchased.

For more information, see [www.mineralogicalassociation.ca](http://www.mineralogicalassociation.ca).

**Deadline to apply: 15 January 2016**



**Special Sessions**  
*Rodinia to Laurentia in NW North America*  
*Geology and tectonics of orogenic belts*  
*Remediation and mine closure in cold climates*

## Whitehorse 2016

### GAC®-MAC Joint Annual Meeting

### L'AGC®-AMC Congrès Annuel

June 1–3, 2016

Join us for the first GAC®-MAC annual meeting to be held in Yukon! The conference theme, "From Laurentia to Beringia: Margins through time", reflects a wide array of technical sessions and field trips sure to cover topics of interest to geologists of all kinds.

[www.whitehorse2016.ca](http://www.whitehorse2016.ca)



**Séances Spéciales**  
*De la Rodinie à la Laurentie dans le Nord-Ouest de l'Amérique du Nord*  
*Géologie et tectonique des chaînes orogéniques*  
*Remédiation des sites miniers sous climats froids*

Joignez-vous à nous pour le congrès annuel de l'AGC®-AMC 2015 qui se tiendra pour la première fois au Yukon. Le thème de la conférence: "De la Laurentie à la Beringie : les marges au fil du temps", comprend une large variété de séances techniques et d'excursions qui couvriront sûrement les sujets d'intérêt des géologues de tout genre.



## Meteoritical Society

<http://meteoriticalsociety.org>

### 2016 ANNUAL MEETING INVITATION

You are cordially invited to attend the 79<sup>th</sup> Annual Meeting of the Meteoritical Society, which will take place 7–12 August 2016 in Berlin (Germany). The annual meeting is jointly organized by the Museum für Naturkunde (MfN) Berlin and the Geosciences Department of Freie Universität Berlin (FUB). It will be held on the Dahlem Campus of FUB in the modern Henry-Ford-Bau conference center. Oral sessions will take place in the state-of-the-art auditoria; plenary sessions will be in the main auditorium, which seats 1,000 and where the public Barringer Invitational Lecture will be presented. Poster sessions will also take place on the Dahlem Campus. Conference registration starts Sunday, 7 August 2016, and will be arranged at the historic Thae Saal of the Humboldt Universität zu Berlin in Berlin-Mitte, directly adjacent to the Museum für Naturkunde. From 6 p.m. that Sunday, the welcome party will be held at the MfN itself. Participants who attended the 1996 MetSoc meeting in Berlin will be able to judge how this museum, which was situated in the former GDR, has changed since Germany's reunification. Like the museum, the city of Berlin has also dramatically changed since reunification and has become one of the premium travel destinations worldwide.

One of the highlights will take place on Wednesday (10 August) when the awards ceremonies will take place. That will be followed by several enjoyable excursions (e.g. "Historical Potsdam" or "Cultural Berlin") before the conference banquet. The banquet will take place in the Wasserwerk, and although this was the former location of Berlin's sewage works, participants are assured that this venue lacks for nothing when it comes to comfort and has a distinct, somewhat unique, charm.

The conference program will include two scientific workshops, both of which will precede the conference. A two-day workshop on "Shock Metamorphism and High-Pressure Phases in Meteorites and Terrestrial Impactites" will be organized by Tom Sharp, Dieter Stoeffler, and Oliver Tschauer; and a one-day workshop entitled "Microstructure and Geochronology of Shocked Accessory Phases" will be organized by Aaron Cavosie and Nicholas Timms. This latter workshop will comprise a day of preconference presentations on the state-of-the-art in this field, covering everything from sample preparation to data reduction. This will be followed-up by SEM sessions scheduled during the week for live data collection.

There are a number of excursions being prepared, including a 5-day postconference excursion to the Gardnos and Ritland impact structures in Norway. Other excursions include the Nördlinger, Ries, and Steinheim impact craters in southern Germany (3 days); a two-day excursion to the Morasko impact-crater field near Poznan in Poland. There also will be two excursions dedicated to historical geology and mining in the scenic parts of the Ore Mountains: the first will be to the Reiche Zeche mine and the Terra Mineralia in Freiberg, plus the Zinnwald visitors' mine; the second to the Harz Mountains for an unforgettable World Heritage experience where participants will visit the Rammelsberg mine, the historic city of Goslar, and the exceptionally preserved medieval town of Quedlinburg.

Our official housing agency for the 79<sup>th</sup> Annual Meeting of the Meteoritical Society has reserved hotel rooms in different price categories either close to the conference venue or in the Western and Eastern parts of the city center, with easy access to the public transportation system. Reservations will soon be possible via the conference website.

The city of Berlin is vibrant and internationally renowned for its cultural attractions. Both airports (Tegel and Schönefeld) are located close to the city, and there are excellent public transport options to access the hotels. The weather in early August in Berlin is likely to be hot: 25–30°C during the day and 15–18°C at night; some humidity

## THE METEORITICAL SOCIETY 79<sup>th</sup> ANNUAL MEETING

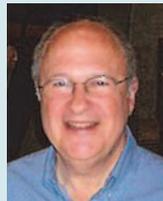
BERLIN · GERMANY · 7–12 AUGUST 2016



may occur, and summer thunderstorms cannot be ruled out. Further information about Berlin and its environs can be obtained at [www.berlin.de/en/](http://www.berlin.de/en/) or at [www.visitberlin.de/en](http://www.visitberlin.de/en).

The conference website is [www.metsoc-berlin.de](http://www.metsoc-berlin.de), which will be updated as further information becomes available. For specific information please contact the Organizing Committee at [MetSoc2016@mfn-berlin.de](mailto:MetSoc2016@mfn-berlin.de)

### IN MEMORIAM – JOE GOLDSTEIN



Dr. Joseph I. Goldstein passed away at home on Saturday, 27 June 2015. He was born 6 January 1939 in Syracuse, New York and obtained his bachelor's, master's, and doctorate degrees from the Massachusetts Institute of Technology in 1960, 1962, and 1964, respectively. Upon completing his doctorate, he worked for NASA at the Goddard Space Flight Center in Greenbelt (Maryland, USA) until 1968. From 1968–1993, he was a professor of metallurgy and materials science at Lehigh University (Pennsylvania, USA). Dr. Goldstein provided research and teaching leadership for over 20 years as Vice President for Research at Lehigh (1983–1990) and as Dean of Engineering at the University of Massachusetts (UMass) in Boston (1993–2004). He led the development of several major research and applied research centers, including two National Science Foundation engineering research centers and a Ben Franklin center at Lehigh University, and he improved the undergraduate engineering curriculum at UMass. In addition, he played a major role in increasing diversity in the College of Engineering at UMass. After ending his term as Dean of Engineering at UMass, Joe remained on the UMass faculty until his retirement in 2014.

Dr. Goldstein received a great many awards during his career, including the Presidential Science Award of the Microbeam Analysis Society in 1991; the Leonard Medal of the Meteoritical Society in 2005 for outstanding contributions to the science of meteoritics and closely allied fields; and the Chancellor's Medal at UMass in 2007. In 2000, an asteroid was named Joegoldstein in honor of his research work. In 2015, the Microbeam Analysis Society and the Meteoritical Society together established an early career development award in honor of Dr. Goldstein "to recognize his exceptional contributions to training multiple generations of microanalytic experts."

Joe was an active member of Congregation B'nai Israel of Northampton, where he served on the board of directors. He was also on the board at UMass Hillel and sang in Mak'hela, the Jewish Chorus of Western Massachusetts. He is survived by his wife of 52 years, Barbara; his daughter, Anne Goldstein-Factor; and his grandchildren, Sophie and Dov.

Donations in Dr. Goldstein's memory can be sent to Congregation B'nai Israel, 253 Prospect St., Northampton, MA 01060, USA; the Meteoritical Society, care of Candace Kohl, 294 Torrey Pines Terrace, Del Mar, CA 92014, USA; or the ALS Association, [www.alsa.org](http://www.alsa.org). Obituaries can be found at the *Daily Hampshire Gazette* and the UMass websites\*.

\* [www.legacy.com/obituaries/gazettenet/obituary.aspx?n=joseph-goldstein&pid=175216254&fhid=15522#sthash.T1TCDb19.dpuf](http://www.legacy.com/obituaries/gazettenet/obituary.aspx?n=joseph-goldstein&pid=175216254&fhid=15522#sthash.T1TCDb19.dpuf)  
[www.umass.edu/newsoffice/article/obituary-joseph-i-goldstein-distinguished](http://www.umass.edu/newsoffice/article/obituary-joseph-i-goldstein-distinguished)

## TRAVEL AWARDS

This year, 44 of the students and researchers who attended the annual meeting of the society in Berkeley (California, USA) received travel grants. Student travel grants and travel grants for scientists from countries with limited financial resources are generously sponsored by the Barringer Crater Company, the Planetary Studies Foundation, NASA, the Meteoritical Society Endowment Fund, the International Mineral Collectors Association (Brian Mason Award), the National Institute for Polar Research (NIPR)/Japan Polar Research Association (JPRA), and the Japan Aerospace Exploration Agency (JAXA)/Institute of Space and Astronautical Science (ISAS). On behalf of the students and researchers, we thank all these institutions and organizations for their generosity. Persons who received specific grants or awards are noted below:

### Meteoritical Society Endowment Fund

#### POST-DOCTORAL AWARD

Edivaldo Dos Santos (Centro Brasileiro de Pesquisas Físicas, Rio De Janeiro, Brazil)  
 Noriyuki Kawasaki (Hokkaido University, Japan)  
 Agata Krzesinska (Polish Academy of Sciences, Poland)  
 Millarca Valenzuela (Pontificia Universidad Católica De Chile, Chile)  
 Mehmet Yesiltas (State University of New York at Stonybrook, USA)

#### LOW-INCOME COUNTRY AWARD

Houda El Kerni (Hassan II University, Morocco)  
 S. V. S. Murty (Physical Research Lab, India)

### Barringer Crater Company Fund

Natasha Vasiliki Almeida (Natural History Museum, London, UK)  
 Moritz Barth (University of Jena, Germany)  
 Helene Breton (University of Glasgow, UK)  
 Y. Chang (University of Tokyo, Japan)  
 Daniel Dunlap (Arizona State University, USA)  
 Matthias Ebert (Museum of Natural History – Berlin, Germany)  
 Lucy Forman (Curtin University, Australia)  
 Cosette Gilmour (University of Alberta, Canada)  
 Timothy Hahn (University of Tennessee, USA)  
 Christopher Hamann (Museum für Naturkunde Berlin, Germany)  
 Sakawat Hossain (Technical University Munich, Germany)  
 Christine Jilly-Rehak (University of Hawaii, USA)  
 Emily Pringle (Institut de Physique du Globe de Paris, France)  
 My Riebe (Eidgenössische Technische Hochschule (ETH) Zürich, Switzerland)  
 Ratiba Sahoui (University of Science and Technology Houari Boumediene/  
 Mouloud Mammari University of Tizi-Ouzou, Algiers, Algeria)  
 Epifanio Vaccaro (Natural History Museum, London, UK)

### NASA Award

Carolyn Crow (University of California, Los Angeles, USA)  
 Brendan Haas (Washington University in St. Louis, USA)  
 Pierre Haenecour (Washington University in St. Louis, USA)  
 Romy Hanna (University of Texas, USA)  
 Jonathan Lewis (University of New Mexico, USA)  
 Josiah Lewis (Washington University in St. Louis, USA)  
 Nicole Lunning (University of Tennessee, USA)  
 Prajka Mane (Arizona State University, USA)  
 Morgan Martinez (University of California, San Diego, USA)  
 Christopher Snead (University of California, Los Angeles, USA)  
 Michelle Thompson (University of Arizona, USA)  
 Reto Trappitsch (University of Chicago, USA)  
 Chris Wetteland (University of Tennessee, USA)

### NASA Mars Program Award

Jennifer Caseres (California Institute of Technology, USA)

### International Meteorite Collectors Association – Brian Mason Award

Ellen Crapster-Pregont (Columbia University/American Museum of Natural History, USA)

### Planetary Studies Foundation

Emilie Dunham (Arizona State University, USA)  
 Steven Jaret (State University of New York at Stonybrook, USA)

### NIPR/JPRA Award

Junko Isa (University of California, Los Angeles, USA)  
 Atsushi Takenouchi (University of Tokyo, Japan)

### JAXA/ISAS Award

Sayuri Yamashita (Tohoku University, Japan)  
 Daiki Yamamoto (Hokudai University, Japan)

### International Meteorite Collectors Association: Brian Mason Award

In 1997, Joel Schiff, the first editor of the popular *Meteorite* magazine, created a travel award in honor of Brian Mason, who was born in New Zealand but spent the majority of his career as a curator at the Smithsonian Institution. The award is given to a student attending the annual meeting of the Meteoritical Society who submits an abstract that clearly explains some exciting results that are of particular interest to readers of *Meteorite* magazine. The recipient is required to write a popular account of their work for the magazine. Since 2008, the award has been generously funded by the International Meteorite Collectors Association.



This year the Program Committee for the Berkeley (California) meeting selected **Ellen Crapster-Pregont** to win the Brian Mason Award. Ellen is a graduate student at Columbia University. She submitted an abstract entitled “Insights on Chondrule Formation from Electron Backscattered Diffraction of Chondrule Metal Layers in Acfer 139 (CR2).” The full author list was E J Crapster-Pregont, W H Towbin, and D S Ebel.

## CALL FOR AWARD NOMINATIONS

Please consider nominating a colleague for one of the Society’s awards. Nominations should be sent to Secretary Mike Weisberg (metsosec@gmail.com) by 15 January (31 January for the Service Award and for the Paul Pellas–Graham Ryder Award). For more information and details on how to submit a nomination for any of these awards, please see the latest newsletter at the society website or email the secretary.

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



[www.dmg-home.de](http://www.dmg-home.de)

### DMG WORKING GROUP: MINERALOGICAL MUSEUMS AND COLLECTIONS

The Mineralogical Museums and Collections working group of the DMG meets once every two years. The 2015 meeting took place last spring in Würzburg. More than 30 museum representatives and curators from across the country thanked **Jochen Schlüter** (Hamburg University) who resigned after serving as spokesperson of the group for more than 10 years. **Birgit Kreher-Hartmann** (Jena University) is the new spokesperson for the German curators. **Dorothee Kleinschrot** (Würzburg University), who was this year's meeting host, was elected as vice spokesperson. Info: [mineralogische-sammlungen-dmg.userweb.mwn.de/index-eng.htm](http://mineralogische-sammlungen-dmg.userweb.mwn.de/index-eng.htm).



More than 30 German curators held their biennial meeting in Würzburg. Among those present were J. Schlüter (first row, middle), outgoing group spokesperson; and B. Kreher-Hartmann (next to last row, middle) incoming group spokesperson.

### DMG SECTIONS: GEOCHEMISTRY AND PETROLOGY/PETROPHYSICS

The traditional joint annual meeting of the DMG Petrology/Petrophysics and Geochemistry sections was held 26–27 June 2015 in the GeoForschungsZentrum in Potsdam. More than 70 participants, including international visitors from Australia, Canada, the UK and the USA, participated in lab tours and listened to 22 talks in the recently renovated lecture room. The wide variety of topics ranged from thermodynamic modelling and crystallization of pegmatites to the timescales of magma evolution at mid-ocean ridges and the determination of denudation rates from cosmogenic nuclides. Several talks specifically focused on high-pressure experiments and mantle geochemistry/petrology. Every speaker was awarded with a glass of honey from the local beehive on the Telegrafenberg by Prof. Wilhelm Heinrich.

Although the schedule was not too tightly packed, there was not always enough time for the lively audience discussions. Nevertheless, generous coffee breaks (or beer and wine in the evening) allowed for further dialogue and exchange of ideas with colleagues and friends. These breaks were combined with poster sessions spanning the same variety of topics as the talks. It was a pleasure to have had so many contributions from young scientists and MSc students.



DMG sections Geochemistry and Petrology/Petrophysics at GFZ Potsdam

The meeting ended on Saturday night with the traditional barbecue at the Forsthaus Templin. At this point, we would like to thank Monika Koch-Müller, Max Wilke and Hella Wittmann-Oelze, and their team of assistants, for this exceptionally well-organized event. The much-anticipated 2016 meeting will take place in Bremen.

**Tobias Grützner, Stephan Taetz** (Münster)

### 15<sup>th</sup> NUCLEAR MAGNETIC RESONANCE DMG SHORT COURSE

Nuclear magnetic resonance (NMR) spectroscopy is used in mineralogical and geoscientific research as a method to determine mineral structures on a very local scale. Applications of NMR include supporting analyses for Rietveld refinements, characterizing dynamic processes, and research into crystalline and amorphous ceramics. Furthermore, the NMR-method can be used to solve geochemical and petrological problems, such as element diffusion in liquefied materials or the analysis of local structures in glasses or melts.



Participants of the 15<sup>th</sup> nuclear magnetic resonance DMG short course. Dr. Michael Fechtelkord (Ruhr University Bochum) is at the front.

In order to offer interested students and postgraduates of mineralogy and geosciences an insight into the wide field of solid-state NMR spectroscopy, on 26–29 May 2015, the Institute for Geology, Mineralogy and Geophysics of the Ruhr-University Bochum hosted the 15<sup>th</sup> DMG

NMR short course, this one entitled "Applications of Solid-State NMR Spectroscopy in Mineralogical and Geoscientific Research". The event was supported by the DMG and the DGK (German Society of Crystallography, "Spectroscopy" subsection), was organised by Dr. Michael Fechtelkord, and was attended by 15 postgraduate students and postdoctoral researchers from cities including Berlin, Bochum, Halle (Saale), Jena and Jülich.

The days were split, with theory in the morning and a practical in the afternoon. This latter included preparing samples, operating the hardware and software of the BRUKER ASX 400 spectrometer, and evaluating the data collected.

On the first day, the participants were introduced to the theoretical basics of NMR spectroscopy, learned of possible NMR applications, were shown how to set-up the NMR spectrometer, and were taught about  $^1\text{H}$  spin-lattice relaxation. In the practical part of the first day, the spin-lattice relaxation times of tetramethylammonium iodide at different temperatures were measured. The corresponding activation energies of the rotation of the methyl groups in  $(\text{CH}_3)_4\text{I}$  were estimated by hand using semi-logarithmic graph paper. The second day focused on magnetic dipolar interactions, chemical shifts, the magic angle spinning (MAS) method, and an introduction to the interpretation of spectra using the freeware program DMFIT. The magic angle spinning method was then directly applied to make a plot of the spectra of  $^1\text{H}$ ,  $^{19}\text{F}$  and  $^{29}\text{Si}$  from a synthetic phlogopite. The third day concentrated on the basics of the spin echo, the cross polarization magic angle spinning technique (CPMAS) and its application to a kaolinite sample, where the participants measured the  $^1\text{H}$  and  $^{29}\text{Si}$  spectra, making their final interpretation using Excel. On the last day, the students were introduced

to measuring techniques for nuclei with a spin value  $> \frac{1}{2}$  and to NMR methods such as double rotation (DOR), multiple quantum magic angle spinning (MQMAS), and satellite transition spectroscopy (SATRAS). The final practical was on making measurements of the quadrupole nuclei for  $^{23}\text{Na}$  and  $^{27}\text{Al}$  using samples of  $\text{NaCl}$ ,  $\text{Na}_2\text{SO}_4$  and  $\alpha\text{-Al}_2\text{O}_3$ . The data were interpreted with DMFIT and the quadrupole coupling constant of  $\alpha\text{-Al}_2\text{O}_3$  was determined.

Keeping this excellent short course on schedule was only possible because of Dr. Michael Fechtelkord's excellent preparation and organization, as well as his personal engagement and helpfulness. The script, which was handed out at the beginning of the course, was extremely useful for the theoretical lessons.

This short course is suitable for every masters and postgraduate student with an interest in solid-state NMR spectroscopy and, ideally, who already possesses a good knowledge of mineralogy and quantum mechanics. And by taking a faculty exam, master's students will have the opportunity of earning three credit points (ECTS).

Thank you, Dr. Fechtelkord!

**Achim Schaller, Tobias Linke,  
Karen Maria Dietmann** (Halle / Saale)

The 2<sup>nd</sup> European Mineralogical Conference will be held at the Palacongressi of Rimini, Italy, 11-15 September 2016

**emc<sup>2016</sup>**  
11 - 15 September  
European Mineralogical Conference

**Minerals, rocks and fluids:  
alphabet and words of planet Earth**

WEB: [emc2016.socminpet.it](http://emc2016.socminpet.it)

Contributing societies are:

**DMG** Deutsche Mineralogische Gesellschaft  
**MinSoc** Mineralogical Society of Great Britain & Ireland  
**MinSocFin** Mineralogical Society of Finland  
**ÖMG** Österreichische Mineralogische Gesellschaft  
**PTMin** Mineralogical Society of Poland  
**RMS** Russian Mineralogical Society  
**SEM** Sociedad Española de Mineralogía  
**SFMC** Société Française de Minéralogie et de Cristallographie  
**SIMP** Società Italiana di Mineralogia e Petrologia  
**SSMP** Swiss Society of Mineralogy and Petrology

With participation of:

**EMU** European Mineralogical Union

Main themes will be: Mantle petrology and geochemistry • Magmatism and volcanology • Metamorphism • Applied mineralogy • Mineral physics • Mineralogical crystallography • Mineral diversity and evolution • Planetary materials and processes • Mineral deposits and raw materials • Low-T geochemistry • Geochronology • Geomicrobiology and biomineralogy • Mineralogical sciences for climate change • Environmental and medical mineralogy • Advanced analytical techniques • Archaeometry, care and preservation

There will be a series of invited plenary lectures, including the acceptance speech of the recipient of the IMA medal award. Chairmen: Giuseppe Cruciani and Bernardo Cesare on behalf of SIMP. Email: [info@emc2016.socminpet.it](mailto:info@emc2016.socminpet.it)



# International Association of GeoChemistry

[www.iagc-society.org](http://www.iagc-society.org)

## DISTINGUISH SERVICE AWARD RENAMED

### *Russell S. Harmon Distinguished Service Award*



The IAGC is pleased to announce that the society's Distinguished Service Award has been renamed the IAGC Russell S. Harmon Distinguished Service Award in honor of Russell Harmon as a tribute to his exemplary service to the IAGC over several decades. Dr. Harmon first became a member of the IAGC in 1983 and was a council

member from 1992 until 2004 when he was elected vice president. He served as president from 2007–2010 and past-president from 2010–2012. He has helped the IAGC in many other ways as well, including as the Chair of the Publications Committee, and he was instrumental in helping to negotiate IAGC–Elsevier contracts over the past decade. He helped to modernize the IAGC through leading the revision of our statutes and the development of an official operations manual, and he is still serving the society currently as Chair of the Strategic Planning Committee. Dr. Harmon earned the Distinguished Service award

himself in 2014, but he has done so much for the organization that the IAGC Executive saw fit to name the award after him. He has inspired and motivated many to join and to serve in the IAGC, and he has earned respect and gratitude from everyone with whom he has served.

Dr. Harmon is currently based in London (UK) as Director of the International Research Office (IRO), where he undertakes international science and technology engagement for the US Army Corps of Engineers' Engineer Research and Development Center (ERDC). Prior to joining ERDC-IRO in September 2011, Dr. Harmon was a program manager at the US Army Research Development and Engineering Command–Army Research Laboratory's Army Research Office, where he managed the extramural basic research program in terrestrial sciences. He is a geochemist who has worked at NASA's Lyndon B. Johnson Space Center (aka the Manned Spacecraft Center) in Houston, Texas (USA), the Scottish Universities Research and Reactor Centre (Scotland), and the Natural Environment Research Council (NERC) Isotope Geosciences Laboratory at the British Geological Survey (UK). Dr. Harmon has also held faculty positions at Michigan State University (USA) and the Southern Methodist University (USA). He is presently an adjunct faculty member in the Department of Marine, Earth and Atmospheric Sciences at North Carolina State University (USA). He is a Fellow of the Geological Society of America, the National Speleological Society, and the Army Research Laboratory. He edited/coedited more than 30 books and journal special issues, authored or coauthored more than 220 peer-reviewed publications, and remains actively engaged in geochemical

## 15<sup>th</sup> WATER–ROCK INTERACTION INTERNATIONAL SYMPOSIUM (WRI-15)

16–21 October 2016 at Évora, Portugal  
<http://wri15portugal.org/>

**Abstract deadline:** 29 January 2016

**Early registration deadline:** 31 May 2016

**Regular registration deadline:** 11 October 2016

There will be three main scientific topics at this symposium.

### *Essentials of water–rock interactions*

1. Recent developments in groundwater reactive transport modeling in fractured and porous media
2. Future challenges for aqueous geochemistry and biogeochemistry: from nano- to basin-scale approaches
3. New trends on isotope hydrology, isotopologues (i.e. molecules that differ only in their isotopic composition) and noble gases
4. New insights into thermodynamics and kinetics of water–rock interactions
5. Developments in water–gas–rock interactions
6. Advances and technological challenges in experimental design for laboratory and field investigations of water–rock interactions

### *Particular environments*

1. Water–rock interaction in volcanic systems and natural hazards
2. High- and low-enthalpy geothermal systems
3. Organic geochemistry and pore-water chemistry of sediments and sedimentary basins
4. The origins and special challenges of high-salinity continental fluids
5. Emerging issues related with ore deposits and ore-forming processes
6. Geochemical controls and influences on the genesis of conventional and unconventional oil and gas fields
7. Insights into the evolution of karst water systems and global climate changes
8. Improvements in water–rock interaction and ecohydrology of arid and semiarid environments
9. Advances in water–rock interactions for tropical and subtropical settings
10. Developments in water–rock interactions applied to astrobiology

### *Case studies and applications*

1. Emerging issues in water–rock interactions applied to energy resources
2. Water–energy nexus: special challenges of shale gas and other low-permeability reservoirs
3. Controls and impacts on groundwater quality and quantity
4. Challenges of water–rock interactions at high temperatures and pressures
5. Alternatives for deep geological repositories for nuclear waste
6. Updating gas–water–rock interaction processes for CO<sub>2</sub> geological sequestration
7. Water quality at active and abandoned mines
8. Transport, fate and tracers of contaminants in shallow and deep aquifers
9. Tracer isotopes for tracking processes and contamination: advances in stable and radiogenic isotope methods
10. Recent approaches in water–rock interactions and the impact on human health
11. Water–rock interaction versus stone decay and conservation, as applied to cultural heritage
12. Geomicrobiology in groundwater environments: microbe–mineral–water interactions

and spectroscopic research. Dr. Harmon holds a BA from the University of Texas, an MS from the Pennsylvania State University (USA), and a PhD from McMaster University (Canada).

**2016 AWARD NOMINATIONS**

Now is the time for 2016 IAGC award nominations! The window of opportunity for nomination submission will extend through 1 December 2015. Awards available for nomination in 2016 are the Vernadsky Medal, the Kharaka Award, the IAGC Russell S. Harmon Distinguished Service Award, IAGC Fellow, and the Certificate of Recognition. For a summary of the awards and instructions on how to submit your nomination, visit [www.iagc-society.org/awards.html](http://www.iagc-society.org/awards.html).

**ELSEVIER PHD STUDENT RESEARCH GRANTS: CALL FOR PROPOSALS**

Generously supported by Elsevier, the PhD Student Research Grants help support the cost of the analytical needs of geochemistry PhD students. PhD Student Research Grants of up to \$3,000 (US) may be awarded annually, based upon receipt of deserving proposals, as determined by the grant committee.

The closing date for applications for Student Research Grants for 2016 is 1 December 2015. Funds will be dispersed to winning applicants before 1 May 2016. The recipients of each Student Research Grant will be profiled in *Elements*, on the IAGC website, and in the spring edition of the *IAGC Newsletter*. Recipients will also receive a one-year complimentary IAGC membership. For application instructions and to download the necessary forms, please visit [www.iagc-society.org/phd\\_grants.html](http://www.iagc-society.org/phd_grants.html).

**IAGC COSPONSORED SESSIONS AT THE GSA ANNUAL MEETING**

The IAGC is cosponsoring three sessions at the Geological Society of America (GSA) Annual Meeting, 1–4 November 2015 in Baltimore (Maryland, USA).

**T32. Urban Geochemistry**

W. Berry Lyons, David T. Long

This session encourages presentations that qualify and quantify the geochemical and biogeochemical impacts (temporal and spatial) of urbanization and urban activities on soil, water, and air resources, as well as on human and ecosystem health.

**T35. Honoring the Diverse Career of Dr. W. Berry Lyons: Geochemistry from Polar Deserts to Tropical Watersheds**

Sarah K. Fortner, Carolyn B. Dowling, Karen Johannesson, Klaus Neumann, Carmen A. Nezat

This session honors W. Berry Lyons and his many contributions to geochemistry. Dr. Lyons has investigated polar to tropical settings. His research, collaborative abilities, and leadership continues to inspire many and has laid the foundations for new directions in geochemistry.

**T39. Sources, Transport, Fate, and Toxicology of Trace Elements and Organics in the Environment**

LeeAnn Munk, David T. Long, W. Berry Lyons

This session encourages presentations on basic and applied research on trace elements and organics in the environment. Topics include those that relate to understanding and modeling the sources, transport, and fate; human and ecosystem health; environmental assessment and remediation.

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CAMS	C	0.50
XCAMS	Be, C, Al	0.50
UAMS	Be, C, Al, Ca	1.00
IAMS	C, I	0.50
Actinide AMS	actinides	1.00

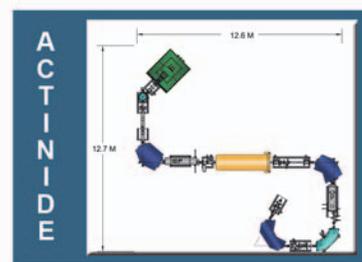
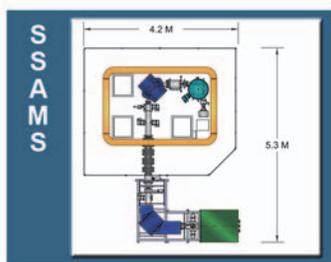
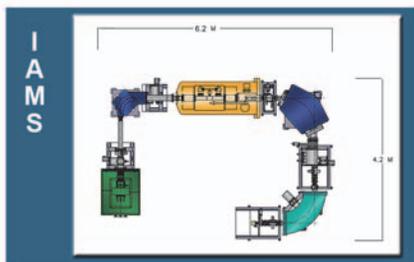
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## A CONFERENCE IN REVIEW: THE 25<sup>th</sup> V.M. GOLDSCHMIDT CONFERENCE

The 25<sup>th</sup> V.M. Goldschmidt Conference (2015) was held in the beautiful city of Prague, the capital of the Czech Republic. Prague has an amazing cultural heritage, a unique cuisine, large quantities of affordable accommodation, and world-class conference facilities. Building on our knowledge from 2011, we rearranged the conference layout for improved poster presentations and provided upgraded internet access. We wish to thank the Prague City Council for their financial support and for, once again, providing transit passes to allow all delegates free travel around the city. We also wish to recognize our sponsors, Nu Instruments and The Geochemist's Workbench.



The magnificent city of Prague (Czech Republic).

There were 3,660 abstracts submitted, 1,940 oral presentations, and 1,678 posters. The total number of registrants was 3719 (32% students), the 20 largest delegations were from the following countries:

- |                        |                    |
|------------------------|--------------------|
| ■ USA (717)            | ■ Korea (102)      |
| ■ Germany (527)        | ■ Russia (71)      |
| ■ United Kingdom (426) | ■ Belgium (58)     |
| ■ France (287)         | ■ Denmark (58)     |
| ■ Japan (212)          | ■ Spain (57)       |
| ■ China (205)          | ■ Sweden (56)      |
| ■ Australia (183)      | ■ Italy (42)       |
| ■ Czech Republic (152) | ■ Netherlands (42) |
| ■ Switzerland (149)    | ■ Austria (39)     |
| ■ Canada (131)         | ■ Brazil (36)      |

### Organizing the Conference

The Goldschmidt conference is organized in alternate years by the European Association of Geochemistry (EAG) and by the Geochemical Society (GS), with the Geochemical Society of Japan as principal co-sponsor. The EAG organized the 2015 Goldschmidt. However, the conference is truly a community wide effort: over 500 geochemists volunteered their time either as theme chair, session chair, session chair, blogger, mentor, or as a member of one of our committees. We are indebted to all for their efforts in having made the 2015 meeting a great success.



Eric Oelkers, the convener of the 2015 V.M. Goldschmidt Conference, welcoming the community to Prague.

The principal convenors were the organizing committee chairman, **Eric Oelkers**; EAG's current president, **Liane G. Benning**; and local convenor, **Martin Novak**. The administration of the conference was ably run by Cambridge Publications, led by **Jacquie Storey**, with the support of **Marie-Aude Hulshoff**, EAG Business Office Manager.

Our science committee of **Eric Oelkers**, **Liane G. Benning**, **Dan Frost**, **Catherine Jeandel**, **Wilhelm Heinrich**, **Kirsten Küsel** and **Hisayoshi Yurimoto** identified 24 science themes and theme chairs. Each science committee member then formed their own committee that then identified 4



Enjoying the banquet at the Art-Nouveau French Restaurant within the Prague Municipal House.



The banquet was followed by dancing until 1 a.m. in the Smetana Concert Hall at the Prague Municipal House.



Some of the student volunteers who helped run a wonderfully smooth conference.



Inside the Prague Conference Centre.

to 8 sessions within their themes and selected scientists to convene those sessions. Further sessions were solicited through an open call. In total, this led to a total of 177 sessions distributed over the 24 themes.

### Field Trips and Workshops

The conference was preceded by 12 workshops, 11 of which were hosted in Prague at Charles University. Total attendance at the workshops was 400. Seven field trips ran before and after the conference and had a total attendance of 123. The organizing committee wishes to thank once more Charles University and the Czech Geological Survey for



Liane G. Benning, EAG President (left) and Barbara Sherwood Lollar, GS President (right), presenting the Distinguished Lifetime Achievement Award to Paul Beattie of Cambridge Publications.

their hospitality, as well as all the field trip and workshop organizers for their enthusiasm and energy in bringing their diverse skills and knowledge to the Prague Goldschmidt.

### The Conference

After a well-attended icebreaker on Sunday afternoon, the conference began in earnest at 8:30 a.m. on Monday, 17 August. The plenary lectures and formal opening ceremony took place immediately before lunch. After welcoming remarks from the convenor, **Peter Sale** presented his plenary lecture, "Oceans in the Anthropocene: End of the High Seas; Need for Repair and Reasoned Management". The plenary lectures on succeeding days were presented by **Janne Blichert-Toft** (Neo-Plumbotectonics), President of the Geochemical Society **Barbara Sherwood Lollar** ("Dark Energy from the Deep Hydrosphere: Water-Rock Reactions Sustaining Deep Subsurface Microbiology"), **Andrew Revkin** ("Can Science Help Shape a 'Good' Anthropocene?") and Gast Lecturer **Ann Pearson** ("Organic Geochemical Proxies"). You can find videos of those lectures on the Goldschmidt Conference Archive at [goldschmidt.info](http://goldschmidt.info).

Oral sessions ran from 08.30–11.30 (with refreshments) and from 14.00–17.00. After the oral sessions, poster sessions ran from 17.00–19.00, with accompanying unlimited beer and wine. The posters occupied good locations within the main building of the conference centre.

Numerous social events were held during the week. In addition to the icebreaker, these included a classical concert at St. Ignatius church, dinner at the Brevnov Abbey, and the conference banquet, which was held at the magnificent Municipal House in central Prague. The banquet was attended by over 1000 delegates and included dancing until 01.00.

### Special 25<sup>th</sup> Anniversary Events

In celebration of the 25<sup>th</sup> anniversary of the Goldschmidt conferences, a number of special events were held. A special ceremony was held at the beginning of the first plenary session to honour Hu Barnes, who launched the first Goldschmidt conference in May 1988 in Baltimore (Maryland, USA), which was attended by 464 participants. The 2015 meeting featured 25 plenary talks that highlighted the 25 greatest advances in geochemistry over the past quarter century. These talks, given by the leaders of the various conference themes, were designed to introduce our community to the broad range of advances made throughout the field of geochemistry. Finally, there was the selection of 50 EAG–GS Student Ambassadors.

### Student Program and Support

**Heather Stoll**, Student & Mentoring Program Leader, put in a herculean effort to generate a diverse and greatly appreciated student program. Her efforts were clearly successful because 32% of the total delegates were students, a percentage far exceeding past conferences. The student program included a series of lunchtime events that offered advice and guidance on aspects of one's early

career, such as career planning and how to publish manuscripts. A new lunchtime 'Meet the Plenary' event was organized where the students could meet directly with the plenary speakers, after the speaker had given their talk, to discuss further the presentation. Perhaps most appreciated was the student mentor program. This program, started last year at the Sacramento conference, links students with senior mentors who volunteered their time to help the student navigate their way through the conference. A total of 120 mentors and 241 students participated in the 2015 program.

We wish to thank the organizations which supported these events: German Mineralogical Society (DMG); International Society for Environmental Biogeochemistry (ISEB); three groups from the Mineralogical Society of Great Britain and Ireland (MSGBI) that are the EMG (Environmental Mineralogy Group), GG (Geochemistry Group) and VMVG (Volcanic and Magmatic Studies Group); Italian Geological Society (SGI); Italian Society of Mineralogy and Petrology (SIMP); Isotope Society of France (SFIS); as well as Elsevier, Exxon Mobil and Nature Communications.

Through the generosity of the EAG, NASA, and the National Science Foundation (NSF) a total of 131 student delegates received a waived registration to the conference and several more received support to cover their travel and living costs while attending the conference.

### Media Coverage

Particular efforts were made to identify stories that would be of interest to the general public and that might receive wide media coverage. Following initial selection by the session chairs, Tom Parkhill, Goldschmidt Press Officer, wrote and distributed 5 press releases:

- The 'End of the high seas', or we watch the seas die
- Scientists and NASA astronauts developing near real-time osteoporosis and bone cancer test
- Possible test for liver cancer using technology for analysing rocks and minerals
- Research shows that comet impacts may have led to life on Earth — and perhaps elsewhere
- The unbearable lightness of helium may not be such a problem after all.

Some of the stories achieved considerable international coverage, which enhanced the impact of the Goldschmidt Conference and of our science to the general public.



My electronic equipment has been miniaturised of course, but unfortunately the adaptors and chargers haven't!

### Summing-Up

Prague 2015 proved to be a highly successful Goldschmidt Conference. This demonstrates, yet again, that attractive locations with reasonable accommodation costs are of major importance when organizing this conference. Making sure the conference centre itself ran smoothly was largely due to the magnificent efforts of **Martin Novak**, the head of the local committee. This huge meeting was effectively trouble-free and the feedback to date has been very positive: all of which makes Prague an attractive venue for a future Goldschmidt conference.

In conclusion, I wish to thank the members of the organizing and science committees, and the geochemical community as a whole, for all the hard work that they put into ensuring that the 2015 meeting was a great success.

**Eric H. Oelkers**

Chair of the Goldschmidt2015 Organizing and Science Committees

# 35<sup>TH</sup> INTERNATIONAL GEOLOGICAL CONGRESS

27 AUGUST - 4 SEPTEMBER 2016 | CAPE TOWN, SOUTH AFRICA



The Scientific Programme contains over 50 Themes in 3 Main Topics:

- *Geoscience for Society*
- *Geoscience in the Economy*
- *Fundamental Geoscience*

The Call for Abstracts will open on 1 July 2015.

The 1st and 2nd Circulars can be downloaded from the Website.

Details of the Scientific Program are available on the website.

Contact the Scientific Program Chair, Laurence Robb on [laurence.robb@earth.ox.ac.uk](mailto:laurence.robb@earth.ox.ac.uk)

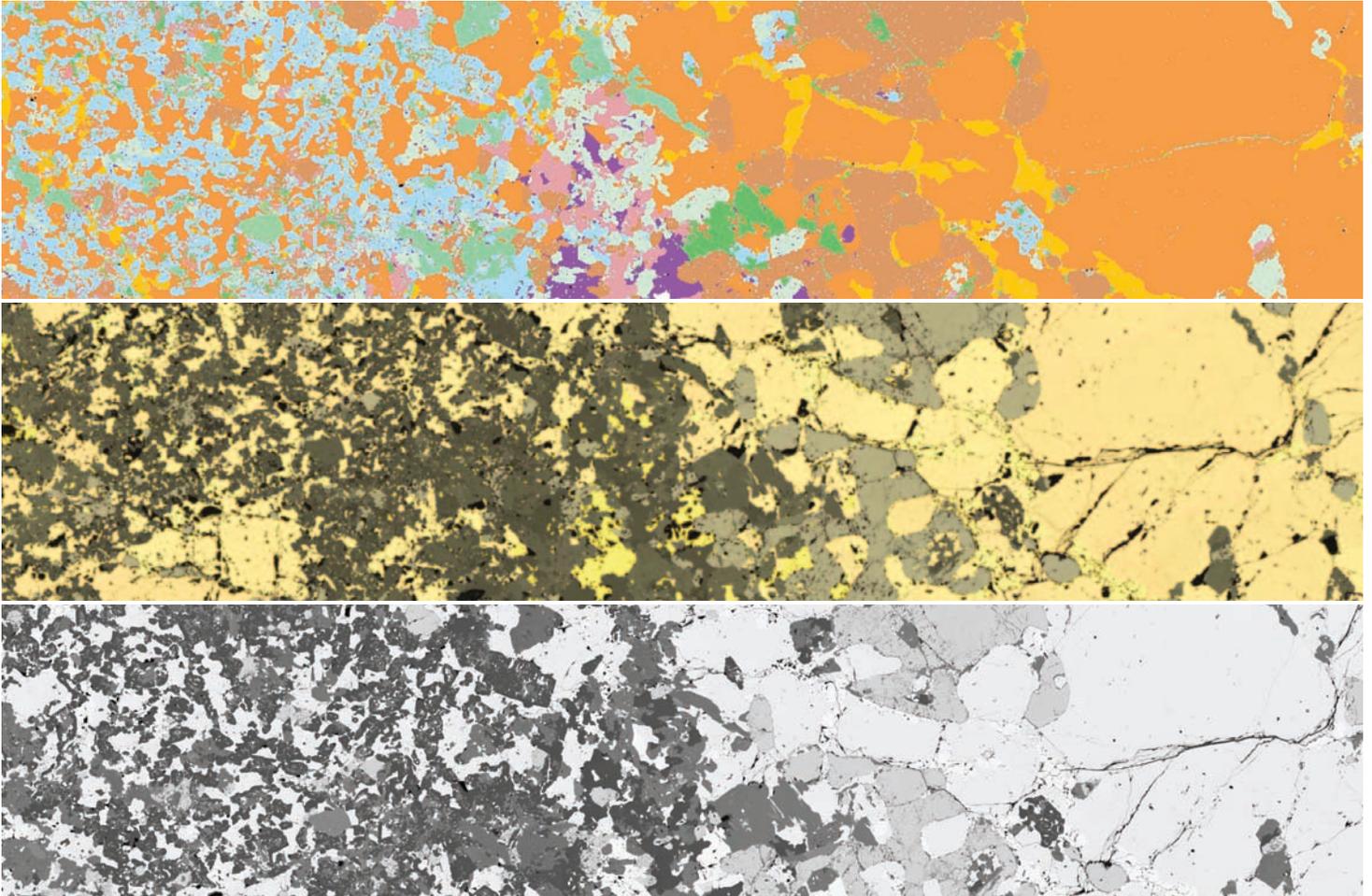
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Images of a nickel sulphide ore. Sample courtesy of Leicester University, UK.



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## MEET PLUTO AND CHARON ... AND NIX ANDHYDRA!

Kelsi Singer\*

In July 2015, eighty-five years after the discovery of Pluto, NASA's New Horizons spacecraft flew through the Pluto system and sent back the first high-resolution pictures of the planet and its five moons. The stunning images and spectroscopic data revealed that Pluto and its large moon Charon have diverse geological terrains and surface compositions. Pluto's atmosphere also held surprises: hazes more extensive than expected were illuminated by sunlight during departing observations (Fig. 1D). Thus far, only a tiny fraction of the New Horizons data has been returned thus far, but our understanding of the Pluto system is already being revolutionized.

New Horizons' encounter with Pluto and its moons began in January 2015, with the closest approach to Pluto occurring at 11:50 UTC on July 14. New Horizons dove through the Pluto system well inside the orbit of Charon. New Horizons is equipped with a visible imager, a four-color imager (blue at 400–550 nm, red at 540–700 nm, near-infrared at 780–975 nm, and a narrow methane absorption band at 860–910 nm); a high spectral resolution camera (1.25–2.5  $\mu\text{m}$  range), an ultraviolet instrument for atmospheric airglow and occultation observations; a radio science experiment for more atmospheric studies; and instruments for detecting energetic particles, plasma, and dust (Stern 2008 and references therein).

Before New Horizons arrived at Pluto, the best images of the planet had been taken by the Hubble Space Telescope and were only 11 pixels across. These images had been combined to produce the best maps of Pluto, which revealed a surface of featured highly contrasting dark and bright splotches (Buie et al. 2010). New Horizons imaged all of the illuminated parts of Pluto and Charon in the weeks and months

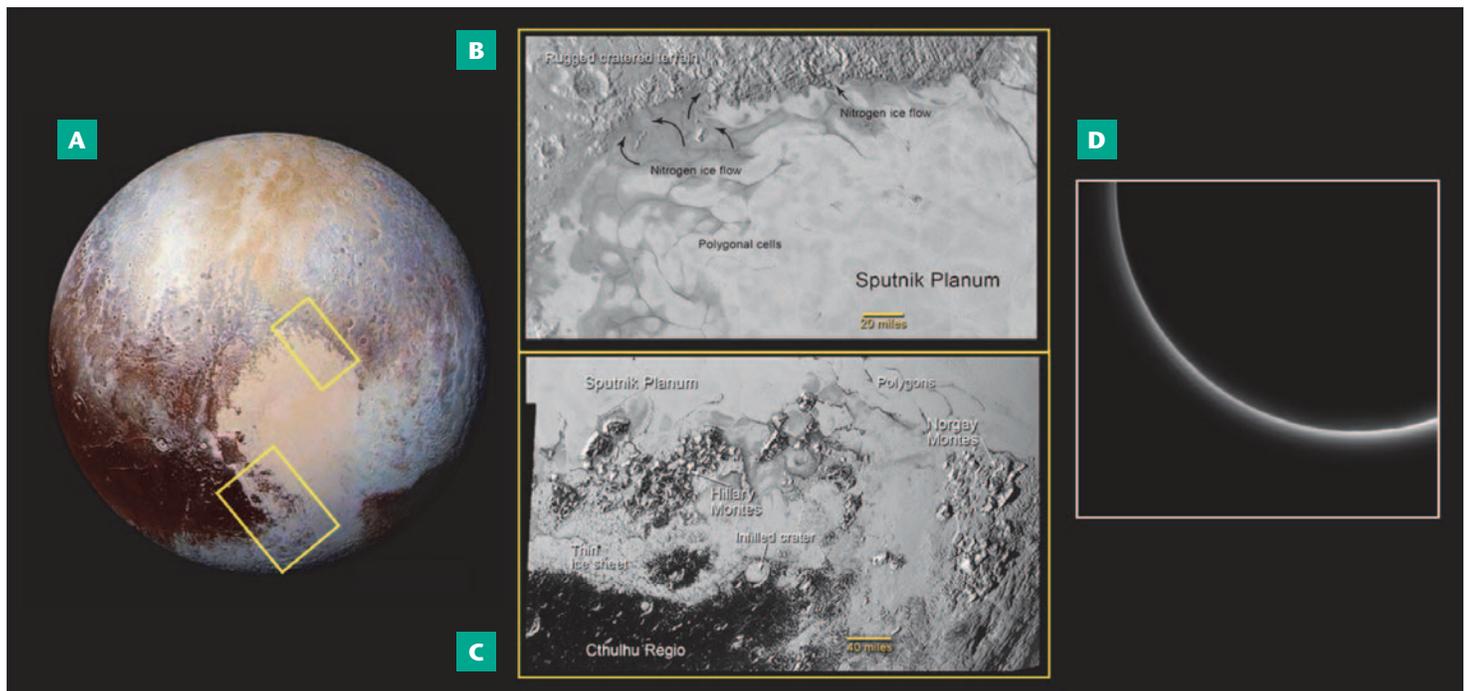
before closest approach. And, as it sped past, even better resolution was achieved for one hemisphere than for the other (shown in Figs. 1 AND 2). The highest resolution images ( $\sim 80$  m per pixel  $\{\text{px}^{-1}\}$  for Pluto;  $\sim 160$  m  $\text{px}^{-1}$  for Charon) were taken over a narrow strip and have not yet arrived back on Earth, but images already a thousand times better than those from the amazing Hubble have come back—at 400 m  $\text{px}^{-1}$ . New Horizons data has shed light on a number of unknowns but also raised some new, and very interesting, questions.

## PLUTO

The brightest spot ( $\sim 1,187$  km in radius) seen in the Hubble maps of Pluto turned out to be an expanse of nearly-flat ice the size of Texas (USA) (Fig. 1A) without any obvious craters visible at the available image resolution (Figs. 1B, 1C). This terrain displays polygonal subareas, often bounded by dark material or shallow troughs, and also shows signs of material flow. Water ice ( $\text{H}_2\text{O}$ ) would be completely rigid and stiff at Pluto's surface temperatures ( $\sim 35$  K), but  $\text{N}_2$  ice could exhibit glacier-like flow. Indeed, spectroscopic measurements from New Horizons detected carbon monoxide ( $\text{CO}$ ), methane ( $\text{CH}_4$ ), and molecular nitrogen ( $\text{N}_2$ ) in the region, all of which are volatile ices at Pluto's temperatures. From its density, we know  $\text{H}_2\text{O}$  makes up about one-third of Pluto, but this water-ice bedrock is overlain by at least a veneer of more volatile ices. New Horizons also discovered the more complex hydrocarbons of ethylene and acetylene in Pluto's atmosphere. As these, and other heavy hydrocarbons, settle to cooler parts of the atmosphere they condense into the icy haze seen in FIGURE 1D.

Pluto also has cratered terrains and terrains of intermediate and dark albedos. However, much of the surface seems to have been modified because we see few fresh-looking craters. It was predicted that surface modification could occur through atmospheric interaction over Pluto's complex seasonal cycles and, potentially, through relatively recent

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**FIGURE 1** (A) Base map of Pluto at 2.2 km per pixel ( $\text{px}^{-1}$ ) resolution, color-enhanced, showing the compositional diversity of Pluto's surface. (B) Close-up of the upper rectangular inset from 1A showing the contact of the bright, smooth region informally known as Sputnik Planum, with degraded cratered terrains to the north ( $400$  m  $\text{px}^{-1}$ ). (C) Close-up of the lower rectangular

inset from 1A showing the two sets of mountain ranges found near the southwestern edge of Sputnik Planum ( $400$  m  $\text{px}^{-1}$ ). (D) Pluto's hazes backlit by the sun in a departing image ( $1.8$  km  $\text{px}^{-1}$ ). These hazes extend up to 80 km above the surface, several times higher than predicted. IMAGE CREDITS: NASA/JHUAPL/SWRI.

geologic activity (Moore et al. 2015, and references therein). We see hints of both surface modification agents with the current data. As more data is returned from New Horizons, we will have better constraints on the atmospheric structure, the escape rate of molecules into space, and the style and timing of geologic activity.

### CHARON: PLUTO'S LARGEST MOON

At ~606 km in radius, Charon is Pluto's biggest moon. And as befits such a moon, it displays its own set of unique and varied terrains, including smooth expanses, a swath of subparallel cliffs stretching ~1,000 km, and various cratered landforms (FIG. 2). It has two unusually striking features: a dark polar region, and several sharp mountain peaks that appear to be jutting out of moats (FIG. 2 INSET). Large-scale topography can be seen on the limb of Charon, with the most prominent feature being a deep canyon (upper right in FIG. 2 MAIN IMAGE). The craters on Charon are more obvious than those on Pluto; nevertheless, the evidence of widespread tectonic activity and a number of younger-looking surfaces indicate that Charon has also seen a fair amount of internally driven geologic activity.

### NIX AND HYDRA: TWO OF PLUTO'S SMALL MOONS

In addition to the large round moon of Charon, Pluto also has four irregularly shaped moons: Nix, Hydra, Kerberos, and Styx. The larger two irregular moons are Nix and Hydra (~30–45 km in diameter) and were discovered from Hubble data in 2005 (Stern et al. 2006, Weaver et al. 2006, and references therein): this was shortly before New Horizons was launched in January 2006. The two smaller moons, Kerberos and Styx, were discovered in 2011 and 2012, respectively, from additional Hubble observations (Showalter et al. 2011, 2012). New Horizons imaged all four moons at variable resolutions, but only Nix and Hydra images have been returned to date (FIG. 3). These moons show their own interesting features, such as bright and dark surfaces and color splotches that might be associated with impact features.

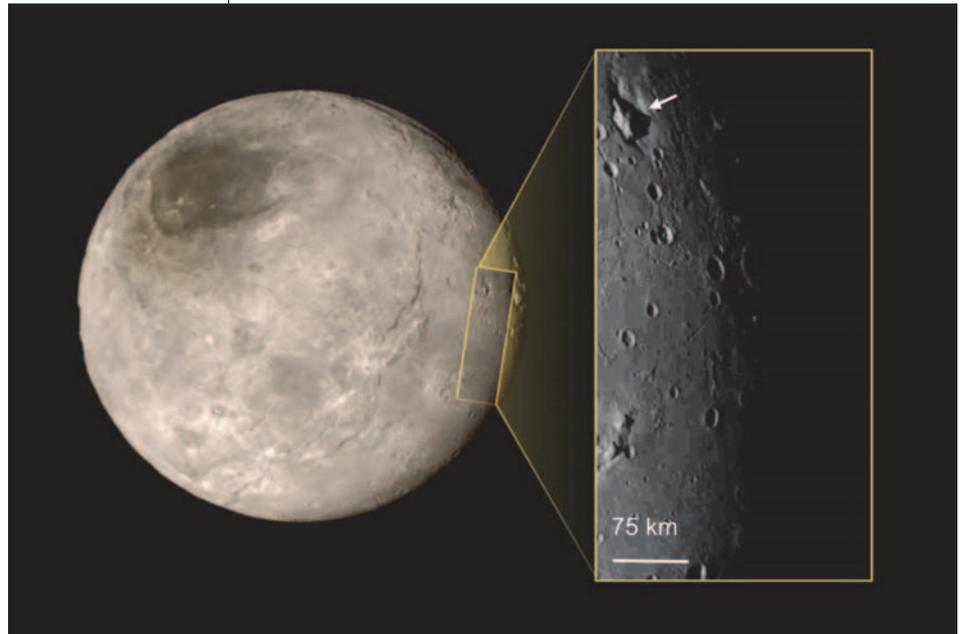
### SUMMARY

The unique features of Pluto and its five moons are expanding our knowledge of how the Solar System formed and how the Pluto system formed and evolved. The young-looking surfaces of Pluto and Charon are also forcing us to reconsider how mid-sized bodies retain or expend internal heat and so allow for geologic activity into relatively recent times. Stay tuned as New Horizons returns more data over the coming months. For all the latest news, videos, and updates from New Horizons, please visit [www.nasa.gov/newhorizons](http://www.nasa.gov/newhorizons) and [pluto.jhuapl.edu](http://pluto.jhuapl.edu).

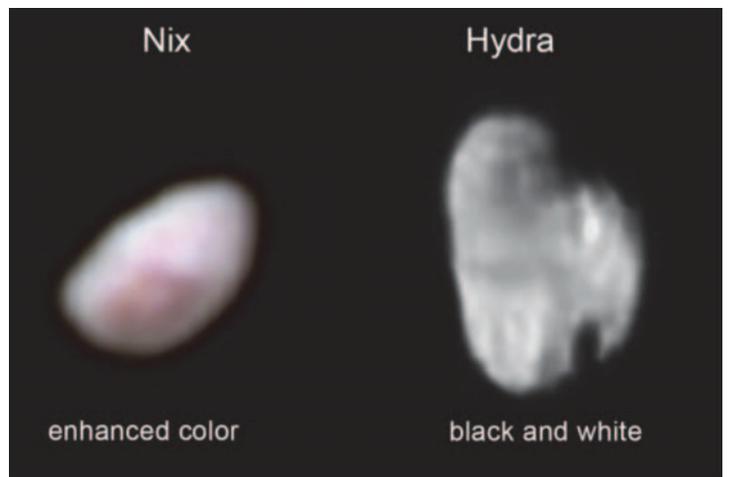
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**FIGURE 2** Charon ( $2.3 \text{ km px}^{-1}$ ) and higher resolution inset ( $\sim 400 \text{ m px}^{-1}$ ) illustrating a smooth area with superimposed impact craters and an unusual mountain in a moat (white arrow). IMAGE CREDIT: NASA/JHUAPL/SWRI.



**FIGURE 3** The small moons Nix ( $3.14 \text{ km px}^{-1}$ ) and Hydra ( $1.13 \text{ km px}^{-1}$ ) show compositional diversity and potential impact craters. This is the best image of Hydra, as taken by New Horizons. Nix images at  $\sim 300 \text{ m px}^{-1}$  are still onboard the spacecraft waiting to be sent back. IMAGE CREDIT: NASA/JHUAPL/SWRI.

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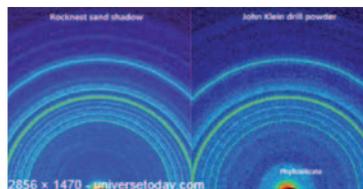
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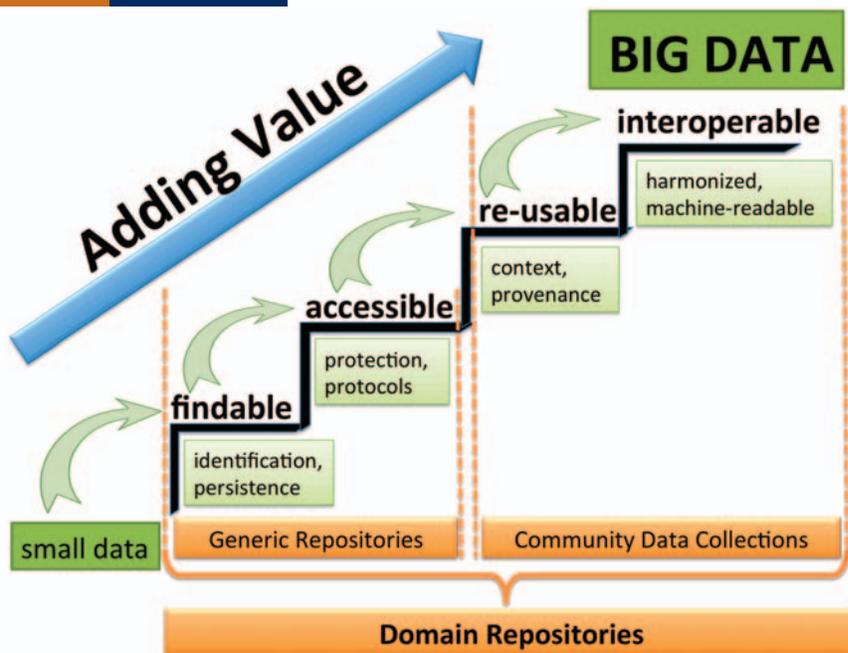
# THE NEW PARADIGM OF DATA PUBLICATION

Kerstin Lehnert and Leslie Hsu<sup>1</sup>

Open and persistent access to scientific data has become a popular topic. Accessing past, present, and future scientific data is fundamental to making scientific research transparent and reproducible, and it ensures that the products of past and current research can be re-used to empower future science and to benefit society. Governments, funders, academic institutions, professional societies, and publishers alike have issued new data policies, statements, and directives that endorse or demand open access to data. As a consequence, scientific workflows, research communication, and scholarly values are changing to recognize and encourage data sharing. And new ways for making data open and persistently accessible have emerged: Data Publication.

Scholarly publication has always been the preferred way of making data available, especially in disciplines such as mineralogy, petrology, and geochemistry where data volumes are small enough that they can be included in articles as data tables and/or electronic supplements. Unfortunately, data published in this way becomes highly dispersed across the literature; finding, accessing, and mining this data is difficult to impossible. The review process primarily focuses on the scientific relevance of the presented results and not on aspects of data re-usability; compliance with data standards is not enforced and critical metadata are often missing. And then there are all those data that did not give rise to a publication. What happens to them? They usually stay hidden on local hard drives and are eventually lost.

Data should be submitted to a domain repository where they will be properly curated and preserved, and where their value will grow as they become discoverable, citable, re-usable, and integrated with similar data into comprehensive, large-scale data collections (FIG. 1). Such data collections, or syntheses, are the foundation for the type of data-driven, abductive discovery that Hazen (2014) envisions for mineralogy. In igneous geochemistry and petrology there are the databases of PetDB, GEOROC, and NAVDAT, which have already made this type of data-driven science a reality. These databases integrate thousands of statistically significant and dense sampling measurements into large-scale searchable syntheses that have, for more than a decade, driven important global scientific discoveries (Lehnert and Langmuir 2007) and changed



**FIGURE 1** A summary of how data repositories augment the value of small data to eventually grow into BIG data resources for advanced data-driven research. The figure illustrates the difference between generic and domain-specific repositories and what community data collections can offer. Community data collections are smaller, thematically focused, well-curated, and offer data systems that are highly valuable resources for specific science communities, but they lack the sustainability, infrastructure, and data curation practices that constitute a domain repository

the way “geochemists do geochemistry” (Hofmann 2008). Examples of the impact of these databases include studies on the diversity in mid-ocean ridge basalt (MORB) composition (Gale et al. 2013), on the global distribution of elements in Earth’s outermost layers (Rauch 2011), and on global patterns of intraplate volcanism (Conrad et al. 2011). Developing and maintaining these databases isn’t easy. Significant effort is required to compile data from individual articles and there are struggles with incomplete, inconsistent, and ambiguous metadata. That sort of effort is neither scalable nor sustainable, but it could be if all the relevant original data were saved directly to a domain repository.

Publishers now acknowledge that domain data repositories are best poised to ensure access and maximize impact of data. In October 2014, publishers and Earth science data facilities formed a new partnership: the Coalition for Publishing Data in the Earth and Space Sciences (COPDESS, <http://www.copdess.org>; Hanson et al. 2015) (FIG. 2). They signed a joint Statement of Commitment that, among other recommendations, advocates that “Earth and space science data should, to the greatest extent possible, be stored in appropriate domain repositories that are widely recognized and used by the community, follow leading practices, and can provide additional data services.”



**FIGURE 2** Publishers, leaders of Earth science data facilities, and funders met at the AGU Headquarters in Washington, DC, in October 2014 and established the Coalition for Publishing Data in the Earth and Space Sciences (COPDESS, <http://www.copdess.org>).

<sup>1</sup> Lamont-Doherty Earth Observatory  
Columbia University, Palisades, NY, USA



This recommendation applies to traditional journals as well as to the new type of data journals, e.g. *Geoscience Data Journal* (Wiley), *Scientific Data* (Nature Publishing Group), *Earth System Science Data* (Copernicus), and *Earth & Space Science* (AGU/Wiley). Data journals offer a way to publish (and get credit for!) data without the requirement to present novel discoveries or groundbreaking insights. Articles in data journals describe the data and methods of collecting and processing them. The actual data are submitted to a digital repository. As an example, see the article “RU\_CAGeochem, a database and sample repository for Central American volcanic rocks at Rutgers University,” which was published in the *Geoscience Data Journal* by Carr et al. (2014; doi: 10.1002/gdj3.10) with the data deposited in the EarthChem Library (Carr et al. 2015; doi: 10.1594/IEDA/100534). This type of data publication offers a great opportunity for late-career scientists, in particular, to share and preserve any unpublished data that are in danger of being lost when they retire. The IEDA Data Rescue initiative (Hsu et al. 2015) helped several investigators to compile and publish valuable geochemical data of Apollo samples that had not been in digital form or accessible in any publication (Delano 2014).

So, what constitutes an “appropriate” domain repository, and how do you find the right one for your data? A repository needs to have the expertise, operational infrastructure, and sustainability to comply with leading practices for data stewardship; an editorial process to assess the quality of submitted data and metadata; use of persistent and globally unique identifiers such as the Digital Object Identifier (DOI) and international Geo Sample Number (IGSN) so data can be properly cited and linked; provisions for the data’s secure and long-term preservation; protection of deposited data until released for public access; and clear policies for the use and citation of data holdings. Domain repositories must maintain standards for relevant context and provenance information, which is usually very specific for a given data type (e.g. fractionation correction for isotope ratio measurements) (Deines et al. 2003; Goldstein et al. 2014). Appropriate repositories enrich and organize data to facilitate new discoveries. Generic data repositories, such as FigShare, Dryad, or institutional repositories, simply lack the expertise to do this. Databases such as the Library of Experimental Phase Relations (LEPR; <http://lepr.ofm-research.org/>; Hirschmann et al. 2008), MetPetDB (database for metamorphic petrology data, <http://metpetdb.rpi.edu/>; Spear et al. 2009),

and RRUFF (database of Raman spectra, X-ray diffraction, and chemical data for minerals; <http://rruff.info>) offer important domain-specific features, but currently lack the ability to guarantee long-term preservation of data or citability of contributed data. Trusted domain repositories use widely accessible open formats and work with institutions to guarantee access for decades into the future, migrating data to new formats and media as they evolve.

Recognized domain repositories for the mineralogy/petrology/geochemistry community are sparse. EarthChem ([www.earthchem.org](http://www.earthchem.org)) provides services for long-term accessibility, persistent identification, and quality assurance of geochemical and petrological data following community-vetted guidelines and using the data curation infrastructure of the Interdisciplinary Earth Data Alliance (IEDA, [www.iedadata.org](http://www.iedadata.org)), an accredited member of the World Data System. EarthChem provides data templates to help investigators organize and format different types of data and the appropriate metadata. EarthChem data managers assist users and perform quality assessment. Users have control over the date that their data become available for public download.

Interdisciplinary Earth Data Alliance’s data curation services are currently serving EarthChem and the Marine Geoscience Data System, and it is expanding. Interdisciplinary Earth Data Alliance is now also partnering with LEPR and MetPetDB to allow these latter data collections to use its services and so make these latter data collections function as proper repositories for their specific communities. By becoming partners in the Interdisciplinary Earth Data Alliance, LEPR and MetPetDB will be able to provide long-term preservation of data and DOI registration of submitted datasets while maintaining control over their systems and user communications. This scalable approach will allow far more researchers within the Earth sciences community access to the data and should facilitate greater publication options.

By promoting and applying best practices of data publication and citation, investigators can help sustain the cyberinfrastructure resources that enable data to be accessed by the wider research community and thereby create a positive feedback to more accessible data.

We encourage you to take part by publishing your data in the EarthChem Library. If you cannot find a template for your specific data type, we invite you to contact EarthChem

at [info@earthchem.org](mailto:info@earthchem.org) and help us develop it. The EarthChem Library files are linked to published manuscripts, contributing to the causes of reproducible science and reusable data.

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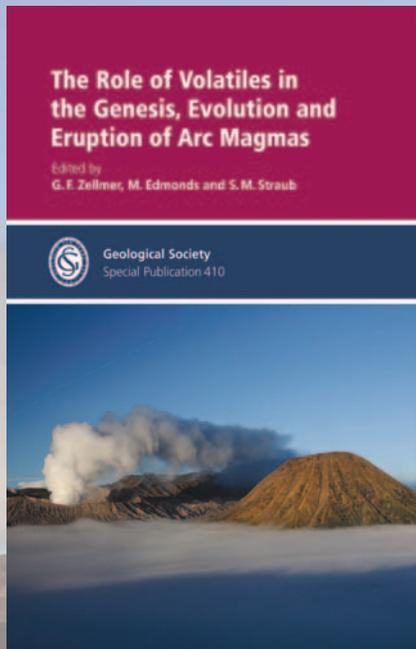
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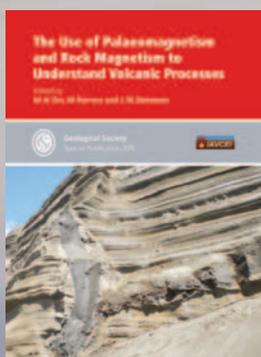
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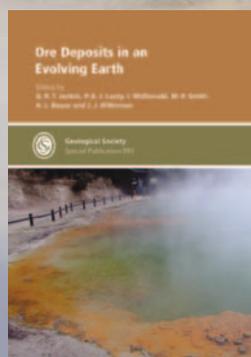
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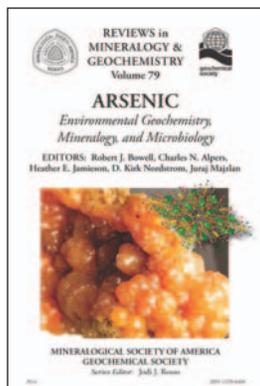
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## ARSENIC ENVIRONMENTAL GEOCHEMISTRY, MINERALOGY, AND MICROBIOLOGY<sup>1</sup>

Arsenic is an element with a fascinating and, in many ways, frightening history. Long before its isolation as an element in 1250, it was known (probably in the form of the naturally occurring oxide) to ancient civilisations, such as the Romans, for its poisonous properties. Indeed, it was almost certainly a favourite 'weapon' of assassins in those distant times. Interest in arsenic in the modern era still centres on its poisonous character, but now it is the inadvertent release of arsenic into sediments, soils and waters that is the focus. In particular, anthropogenic arsenic associated with the mining and processing of arsenical ores, or associated with the industrial uses of arsenic, have been of major concern. Of even more concern has been the natural contamination of aquifers in countries such as Bangladesh and Bengal. The impact of aquifer contamination on the health of millions of people has led to this being described by epidemiologists as 'the greatest poisoning of a population in history'.



Given these concerns, it is not surprising that the literature on arsenic, including its mineralogy and geochemistry, has grown very rapidly in recent years. Contributions have ranged from popular texts, such as the excellent book *Venomous Earth* by Andrew

A. Meharg (2006, Macmillan Publishers Ltd.), to articles in all of the leading specialist journals in the field. *Elements* magazine devoted one of its early issues, which I had the privilege of editing, to arsenic (*Elements* 2006, v2n2; see also the update by Vaughan and Polya in *Elements* 2013, v9n4, p315-316). In rapidly developing areas of science, it is essential to have good review papers and books which provide pathways into the subject matter for teachers and researchers. The *Reviews in Mineralogy and Geochemistry* (RiMG) series published by the Mineralogical Society of America and the Geochemical Society fulfil precisely this role, and many in this series have become 'classics'. Volume 79 of the RiMG Series, entitled *Arsenic: Environmental Geochemistry, Mineralogy and Microbiology*, is a timely and welcome addition to this list of publications. As with the majority of RiMG books, its publication has been linked to a short course that brought together the authors of the fourteen chapters with attendees, who ranged from beginning students to established researchers.

The book begins with a sixteen-page introductory overview of the environmental geochemistry of arsenic written by the editors of this volume (Bowell, Alpers, Jamieson, Nordstrom and Majzlan). The second chapter, entitled 'Parageneses and Crystal Chemistry of Arsenic Minerals', is a comprehensive review of what the authors (Majzlan, Drahota and Filippi) rightly call the 'labyrinthine world of arsenic minerals' – there are more than 560 minerals containing arsenic as an essential constituent. This chapter makes up more than a quarter of the book, is very well illustrated with 68 figures, and lists almost 700 references to the original sources. The majority of the illustrations are beautifully clear representations of the crystal structures of the important arsenic-containing minerals and mineral families. The 'parageneses' referred to in the title of Chapter 2 are the subject matter of the first third of this chapter. Here the term 'paragenesis' is used in the sense of characteristic assemblages (such as magmatic–hydrothermal arsenic minerals, arsenic minerals in coal, in mine wastes, or in soil and fluvial systems). As is appropriate, this part of the book is illustrated photomicrographs, field photographs and hand-specimen

photographs. It is a pity that these could only be reproduced in black and white. Cost is generally a concern when using full-colour images, although an insert with 22 colour plates tied to a number of the other chapters is a welcome addition mid-way through this volume.

The information provided in Chapter 2 comes mainly from data obtained using the long-established techniques of mineralogy, ranging from field observations to optical and electron microscopy to X-ray crystallography. Another fundamental area essential to understanding the structure and stability of arsenic minerals, and also of arsenic species in aqueous solution, is concerned with their thermodynamic properties, which are reviewed in Chapter 4 by Nordstrom, Majzlan and Konigsberger. As these authors point out, quantitative geochemical calculations that enable one to predict the behaviour of arsenic in the environment are not possible without reliable thermodynamic databases. The authors review existing thermodynamic data 'with a focus on internal consistency, and the quality of the original measurements' and where possible 'update with new data' and point out discrepancies. This chapter, like others in this volume, is packed with detailed data, much of it in the form of tables.

The dramatic increase in the amount of published data on arsenic mineralogy and geochemistry in recent years has been partly due to technique development. In particular, synchrotron radiation has provided (and is providing) new insights into the occurrence and speciation of arsenic, including at low concentrations in solids or fluids and at surfaces. Chapter 5 by Foster and Kim on X-ray absorption spectroscopy as applied to arsenic speciation in solids provides an excellent review of one aspect of such studies. In understanding the behaviour of arsenic in the environment, speciation is a crucial factor. Speciation is a topic directly addressed in two other chapters. Leybourne, Johannesson and Asfaw (Chapter 6) offer practical guidance for measuring arsenic speciation in environmental media, ranging from the problems of sampling and preservation of samples to discussions on the wide variety of measurement techniques. Campbell and Nordstrom (Chapter 3) focus on aqueous speciation and the processes of adsorption of arsenic on mineral surfaces. They also review redox reactions of arsenic and provide speciation calculations for sets of reported water compositions (i.e. acid mine, geothermal and ground waters) to show the behaviour of arsenic speciation over a wide range of natural conditions.

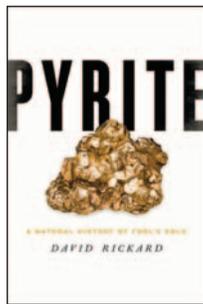
Another area of research on arsenic which has been growing very rapidly is the area I would describe as the 'geo–bio interface'. The recognition that interactions between microbes and minerals occur in environments at or near the Earth's surface is now well established, and related to this are the subjects discussed by Amend, Saltikov, Lu and Hernandez (Chapter 7) under the title 'Microbial Arsenic Metabolism and Reaction Energetics'. As these authors point out, there are over 240 strains of bacteria and archaea that can oxidize As(III) or reduce As(V) for energy gain or detoxification. The geo–bio interface of most significance, and which takes us to the heart of our concerns regarding the toxicity of arsenic, is, of course, the interface with humans. A brief, but useful, summary of the health risks of exposure to arsenic is given in Chapter 8 (Mitchell), which covers the various environmental sources, the nature of arsenic toxicity, the regions of the world affected by high arsenic levels, and the regulations governing maximum permissible levels with the example of the standards set in the USA. Chapter 9 is an interesting, but more specialised, contribution from Basta and Juhasz, who discuss the methods that can be used to test for the bioavailability of arsenic derived from soil ingestion by humans.

The remaining five chapters, a quarter of this book, return to material that will be much more familiar to most readers of RiMG volumes. Craw and Bowell (Chapter 10) provide an overview of arsenic minerals in mine waste, and these authors follow this up by an account of methods for the management of arsenic by the mining industry (Chapter 11).

<sup>1</sup> Bowell RJ, Alpers CN, Jamieson HE, Nordstrom DK, Majzlan J (eds) *Arsenic: Environmental Geochemistry, Mineralogy, and Microbiology*. Reviews in Mineralogy and Geochemistry 79, Mineralogical Society of America, i-xv + 635 pages, ISBN 978-0-939950-94-2, US\$40

PYRITE: A NATURAL HISTORY OF FOOL'S GOLD<sup>2</sup>

David Rickard has pulled off a remarkable trick by writing a book on mineralogy and geochemistry that will entertain and interest an unusually wide range of readers. The Preface indicates that the target audience is a popular readership. Indeed, the book is accessible to beginners of science and to amateur mineral enthusiasts. Yet it also provides a wealth of new knowledge for most professionals. Even though I thought I was fairly well informed about sulfides, I found the book full of surprises and very enlightening.



The title is simply *Pyrite*, the word stretching across the front cover in large capital letters, presumably stressing the importance of the mineral even before the book is opened. When reading the Prologue, I felt slightly skeptical by the phrase, repeated several times, that “pyrite is the mineral that made the modern world.” Is pyrite so very special? Does this mineral deserve a book to itself? The answer is an emphatic “Yes!” The first few chapters remove any doubts that a reader may have about the great importance and special role that pyrite has played in the history of our civilization.

Pyrite is one of the few minerals with which the general public is familiar, probably because of its fame as “fool’s gold.” It is appropriate, then, that the first chapter takes us on a dizzying journey through time and cultures, from ancient Greece via the medieval realms of England, Germany, and China, to modern Europe and North America, in search of the origins and uses of the concept of “fool’s gold,” and the association of this term with pyrite. It will probably astonish many readers to learn that pyrite played a major role in the colonization of both Canada and the United States by Europeans. The motivation was finding real gold, which usually turned out to be either inadvertently or fraudulently misidentified pyrite. An analysis of what “pyrite” meant

<sup>2</sup> David Rickard (2015) *Pyrite: A Natural History of Fool's Gold*. Oxford University Press, Oxford, UK, 320 pp, ISBN 978-0-19-020367-2, £20.49

## Arsenic... Cont'd from page 371

The last three chapters are essentially case studies of particular deposits: Chapter 12 on the Giant Mine (Yellowknife, Canada; by Jamieson), Chapter 13 on the Empire Mine (California, USA; by Alpers, Myers, Millsap and Regnier) and Chapter 14 on the Tsumeb Deposit (Namibia; by Bowell). These three chapters emphasise the importance of hydro-geochemistry and its influence on arsenate mineral stability. Unusually, the chapter on the Empire Mine also served as a field-trip guide for a visit by the short course participants. Another unusual feature coming at the end of this volume is a mineral-name index that lists the pages where particular minerals are mentioned. This index complements the appendices of Chapter 2, which list most of the arsenate, arsenite and common arsenic sulphide and arsenide minerals. Such editorial touches further enhance the usefulness of these tabulations.

Overall, this is a very welcome addition to the prestigious RiMG series and maintains the high standards that have been set in terms of authoritative content and excellent presentation. It is almost certain to become a ‘best seller’.

**David J Vaughan**  
University of Manchester, UK

during Classical, Arab, and Medieval times reveals that it was often called “marcasite”, whereas at other times the term “pyrite” referred to several different sulfide minerals. I was delighted to receive an explanation for how and why the widespread, and to me annoying, term “iron pyrites” got into the literature.

We also learn that the origins of our civilization are closely connected to pyrite. The use of fire was vital to the evolution of humans, and pyrite was key to making fire portable: the mineral was used in fire-lighting kits up to the Iron Age. In addition, because it was a source of sulfur and sulfuric acid, pyrite was the foundation for the development of the earliest chemical industry, pharmaceutical industry, the modern arms industry, and the production of fertilizers. I, like many mineralogists, had been vaguely familiar with the technological uses of pyrite. Yet, the text is rich in historical details and facts that I had never come across before. The insights of Rickard ensure a compelling read for all.

The first half of the book provides a fascinating account of the cultural history and practical importance of pyrite; the second half emphasizes more contemporary science. A chapter on the structure of pyrite introduces the reader to the history of crystallography and explains how pyrite played a pivotal role in science by being one of the first structures to be determined by W. H. Bragg and W. L. Bragg. The eye-catching pyrite cubes, dodecahedra, and framboids are a delight, and the formation pathways of distinct crystal morphologies are described in detail, again providing many surprising new facts. We are then drawn into the depth of the ocean: hydrothermal vents and the origins of massive sulfide deposits, then on to bacterial sulfate reduction and the formation of sedimentary pyrite, which is described in an engaging style and with great insight. We are then introduced to inorganic and bacterial oxidation of pyrite and their resulting acid environments, as well as the roles of sulfur compounds in atmospheric pollution. In places, the author uses pyrite as an excuse to wade into his favorite topics and educate his readership about important environmental issues.

All pieces of the pyrite geochemical puzzle fall into place in the chapter entitled “Pyrite and the Global Environment,” in which we receive the big picture of the role of pyrite in the global cycles of sulfur, oxygen, and carbon dioxide, and how sulfur isotopes in pyrite hold the key to understanding the history of our planet. Pyrite has been implicated in several origin-of-life hypotheses, which are summarized and made digestible for the nonexpert reader. The book concludes with a chapter that discusses current industrial uses of pyrite as a source of various metals (including gold), and we even get a glimpse into the possible future in which pyrite could be used as a material for solar cells.

This book convinces the reader that pyrite deserves its special distinction among minerals, both because of its historical and cultural importance and because of the major roles it has played in important areas of science and technology. In fact, halfway through the book I started wondering what other minerals could belong to the same exclusive club. It is hard to find more than a handful: quartz, calcite, magnetite, apatite, and halite are the ones that are on my list.

A strength of the book is its historical perspective in which every facet of science that is related to pyrite is viewed and narrated. The depth and breadth of the author’s knowledge, as well as his humor, makes the book a delightful read. My only critical comment concerns the figures: there are a number that are in greyscale that really should have been printed in color.

David Rickard’s several decades’ worth of original research experience and the associated knowledge he has accumulated are condensed in this highly entertaining and very informative book. I recommend it to anyone interested in geochemistry, in mineralogy, and in science generally.

**Mihály Pósfai**  
University of Pannonia, Hungary

2015

**October 4–7** GeoBerlin: Annual Meeting DGG–DMG–GV, Berlin, Germany. Web page: www.geoberlin2015.de

**October 4–8** MS&T'15: Materials Science & Technology Conference and Exhibition, combined with ACerS 117th Annual Meeting, Columbus, OH, USA. Web page: ceramics.org/meetings/acers-meetings

**October 8–11** Conference of the Mineralogical Society of Poland, Sandomierz, PL. Web page: www.konferencja-ptmin.us.edu.pl/?lang=en

**October 16–18** Gemmology Conference 2015, Vancouver, BC Canada. E-mail: dhawrelko@vcc.ca; Web page: www.gemconference2015.com

**October 24–31** Short Course "Geochemistry of Hydrothermal Ore Deposits", Ottawa, ON Canada. Web page: science.uottawa.ca/earth/short\_course

**November 1–5** Geological Society of America Annual Meeting, Baltimore, MD, USA. E-mail: meetings@geosociety.org; Web page: www.geosociety.org/meetings/

**November 4–5** The Earth's Mantle and Core: Structure, Composition, Evolution, Matsuyama, Ehime, Japan. Web page: www.elsi.jp/en/research/activities/workshops/2015/11/1104workshop.html

**November 9–13** Short Course "Introduction to Secondary Ion Mass Spectrometry in the Earth Sciences," Potsdam, Germany. Web page: www.gfz-potsdam.de/SIMS/short-course

**November 29–December 4** 2015 MRS Fall Meeting & Exhibit, Boston, MA, USA. Web page: www.mrs.org/fall-meetings/

**December 14–18** American Geophysical Union Fall Meeting, San Francisco, CA USA. Web page: fallmeeting.agu.org/2015/

2016

**January 18–22** 10<sup>th</sup> International Symposium on Environmental Geochemistry (ISEG10), Perth, Western Australia. Web page: www.iseg10.com/

**January 24–29** 40<sup>th</sup> International Conference and Expo on Advanced Ceramics and Composites–ICACC'16, Daytona Beach, FL, USA. Web page: ceramics.org/meetings/40th-international-conference-and-expo-on-advanced-ceramics-and-composites

**February 14–18** TMS Annual Meeting & Exhibition, Nashville, TN, USA. Web page: www.tms.org/meetings/annual-16/AM16home.aspx

**March 13–17** 251<sup>st</sup> ACS National Meeting & Exposition, San Diego, CA, USA. Web page: www.acs.org

**March 21–25** 47<sup>th</sup> Lunar and Planetary Science Conference, The Woodlands, TX, USA. Web page: www.hou.usra.edu/meetings/lpsc2016/

**May 16–18** 7<sup>th</sup> Geochemistry Symposium with International Participation, Antalya, Turkey. Web page: jeokimya.ankara.edu.tr/en/

**May 17–19** 8<sup>th</sup> International Conference on Mineralogy and Museums, Changsha, China. Web page: www.agiWeb.org/smmp/M&M8%20First%20Circular.pdf

**May 22–25** 10<sup>th</sup> South American Symposium on Isotope Geology (SSAGI), Puerto Vallarta, Mexico. Web page: www.ssagi10.geofisica.unam.mx/

**May 24–26** Pan-American Current Research on Fluid Inclusions Conference (PACROFI XIII), Columbia, MO, USA. Web Page: muconf.missouri.edu/Pacrofi/

**May 29–June 24** Vatican Observatory 2016 Summer School in Astrophysics: Water in the Solar System and Beyond, The Vatican. Web page: www.vaticanobservatory.va/content/specolavaticana/en/summer-schools-voss-/voss2016.html

**June 1–3** Geological Association of Canada–Mineralogical Association of Canada (GAC–MAC) Meeting, Whitehorse, Yukon, CA, USA. Web page: whitehorse2016.ca/

**June 5–8** 53<sup>rd</sup> Annual Meeting of the Clay Minerals Society, Atlanta, GA, USA. Web page: conferences.illinois.edu/CMS2016/index.html

**June 6–10** Inter/Micro: 68<sup>th</sup> Annual Applied Microscopy Conference, Chicago, IL, USA. E-mail: intermicro@mcri.org. Web page: www.mcri.org

**June 12–17** DUST2016: 2<sup>nd</sup> International Conference on Atmospheric Particles, Castellaneta Marina, Italy. Web page: www.dust2016.org

**June 19–22** AAPG 2016 Annual Convention & Exhibition, Alberta, Canada. Web page: www.aapg.org/events/conferences/ace

**June 26–July 1** Goldschmidt 2016, Yokohama, Japan. Web page: goldschmidt.info/2016/

**July 4–8** MECC2016: 8<sup>th</sup> Mid-European Clay Conference, Košice, SK. Web page: www.mecc2016.sav.sk/

**July 22–26** American Crystallographic Association Annual Meeting, Denver, CO, USA. Web page: www.amerystalasn.org/content/pages/main-annual-meetings

**July 24–28** Microscopy & Microanalysis 2016, Columbus, OH, USA. Web page: www.microprobe.org

**August 7–12** Annual Meeting of the Meteoritical Society, Berlin, Germany. Web page: www.meteoriticalsociety.org

**August 18–20** Seventh International Dyke Conference (IDC7), Beijing, China. Web page: idc7.csp.escience.cn/dct/page/1

**August 21–25** 252<sup>nd</sup> ACS National Meeting & Exposition, Philadelphia, PA, USA. Web page: www.acs.org

**August 21–26** International Congress on Ceramics–ICC6, Dresden, Germany. Web page: www.icc-6.com/

**August 27–September 4** 35<sup>th</sup> International Geological Congress, Capetown, South Africa. Web page: www.35igc.org

**August 28–September 2** 16<sup>th</sup> European Microscopy Congress – EMC2016, Lyon, France. Web page: emc2016.fr/en

**September 5–9** 6<sup>th</sup> International Workshop on Layered Materials, Kutná Hora, CZ. Web page: www.jh-inst.cas.cz/workshop2016

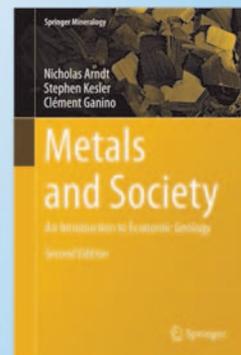
**September 9–13** AIPG 2016 National Conference, Santa Fe, NM USA. Web page: aipg.org/events/index.htm

**September 11–15** EMC2016 – 2<sup>nd</sup> European Mineralogical Conference, Rimini, Italy. Web page: emc2016.socminpet.it

**September 25–28** Geological Society of America Annual Meeting, Denver, CO, USA. E-mail: meetings@geosociety.org; Web page: www.geosociety.org/meetings/

**October 16–21** Water Rock Interaction 15 (WRI-15), Évora, Portugal. Web page: www.iagc-society.org/resources/WRI-15\_2016\_1st%20Announcement.pdf

The meetings convened by the societies participating in *Elements* are highlighted in yellow. This meetings calendar was compiled by Andrea Koziol (more meetings are listed on the calendar she maintains at [homepages.uydayton.edu/~akoziol1/meetings.html](http://homepages.uydayton.edu/~akoziol1/meetings.html)). To get meeting information listed, please contact her at [akoziol1@uaydayton.edu](mailto:akoziol1@uaydayton.edu)



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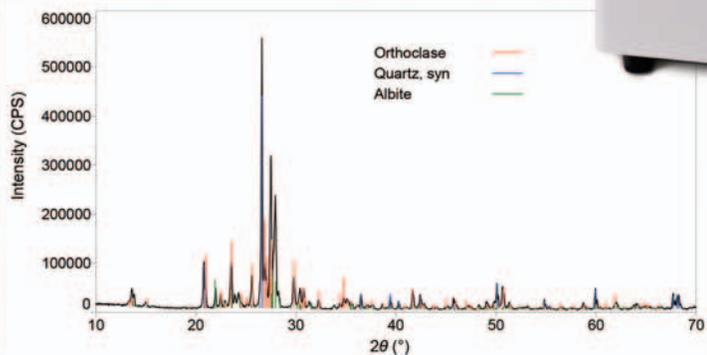
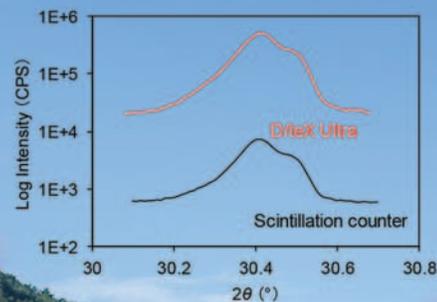
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Australian Scientific Instruments (ASI)	330
Bruker Nano	Inside front cover
Cameca	303
Carleton University	376
Excalibur	336
Geochemist's Workbench	Back cover
Geol Soc London	370
ICDD	367
IGC	363
IsotopX	360
JEOL	304
National Electrostatics Corporation (NEC)	359
Rigaku	374
SavilleX	343
SEG	310
Selfrag	301
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Stanford University	376
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Zeiss	364

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Mineral sample measurement conditions: Scan range:  $2\theta = 10 \sim 70^\circ$ , Step width:  $0.02^\circ$ , Scan speed:  $80^\circ / \text{min.}$  (about 1 min.)



## WILD AND WONDERFUL

The Skaergaard layered gabbro is probably the most studied of all igneous intrusions and has greatly influenced thinking on many aspects of igneous processes. The intrusion is on the East coast of Greenland, a little North of the Arctic circle at 68°10' N, to the east of the entrance to the large fjord of Kangerdlugssuaq. It came to prominence with a 1939 memoir by Lawrence Wager and Alex Deer, which caused something of a sensation at the time. At Skaergaard, igneous layering is spectacularly developed, with features that Wager and Deer interpreted as due to vigorous convection currents in a magma chamber that had been allowed to cool without disturbance and in which something akin to recognised sedimentary processes operated (Fig. 1). Wager later became a professor at Oxford University. Alex Deer became a professor at the University of Manchester and then the University of Cambridge, where he was Vice-Chancellor from 1971 to 1973. He is the 'D' in the 'DHZ'<sup>1</sup> (along with Howie and Zussman) that so many of us use.



**FIGURE 1** A photograph of layering similar to that described by Wager and Deer (1939, Plate 8, Fig. 1, which had the caption "Gravity differentiated layers separated by layers of average rock..."). The dark parts of layers are concentrations of olivine and clinopyroxene, the pale parts are mainly plagioclase. PHOTO: IAN PARSONS (1990)

FIGURE 2 was taken at the 'base house' on Skaergaard in 1953 and shows Lawrence Wager leaning against the window, Alex Deer smoking his pipe and Malcolm Brown sitting in the foreground. Malcolm went on to become a professor at Durham University and later Director of the British Geological Survey. Other members of the party were Dougie Weedon, sitting further back in the photo, Geoff Nichols, Charlie Hughes and myself. My boots appear at the far left. This was the return of Wager and Deer to East Greenland to continue their work on the now-famous intrusion, work that had begun in 1930 when Wager was a member of the British Arctic Air-Route Expedition that explored this then largely unknown coastline (see *Elements* 2007, v3n4, p295). The base house, erected in 1935, was in remarkably good condition in 1953, having been temporarily used as a radio station towards the end of World War II. It provided very comfortable accommodation while working nearby and a welcome refuge on return from the more frequent distant journeys. Unfortunately, it was later burnt down while being used by Greenlanders. The 1953 party was a combination of Oxford and Manchester university personnel and had the objective of deciphering Skaergaard. The Oxford group also studied the Kangerdlugssuaq syenite, while the Manchester group examined the Kap Edward Holm intrusion, both intrusions being on the far side of Kangerdlugssuaq.



**FIGURE 2** Left to right: Alex Deer, Dougie Weedon, Malcolm Brown and Lawrence Wager at the Skaergaard base house in 1953. PHOTO: PETER BROWN (1953)

Wager's ideas on organising an expedition were essentially to make it as simple as possible. He had a deep distrust of anything mechanical. When asked if a radio would be taken to communicate with the outside world during our months of isolation (the whole trip took three months) his reply was that if we took one it would break, and then when people did not hear from us they would want to rescue us and we would NOT want to be rescued (health and safety take note!). He also believed that you ought to be able to survive for a week on what you happened to find at the bottom of your rucksack. This philosophy was evident in the composition of the expedition food boxes: the ration per day, per man, was, in ounces (an ounce veing 28.35 g): pemmican 5.5, margarine 4.5, ships biscuits 4.5, porridge oats 2.5, milk powder 2.0, sugar 3.5, chocolate 3.0, potato flour 1.5, dehydrated vegetables 0.5, tea 0.25 (total 27.75 ounces of food). I remember being hungry and a lot thinner by the time I arrived back home. This is in great contrast to present-day lightweight ration boxes. On later trips to Greenland we always managed to eat with more sophistication, if not more effect. Some of the pemmican taken in 1953 was left over from 1935, though it did not come, I believe, from the bottom of Wagers' rucksack! The '35 brand proved to be much more appetising (if that is the right word to use about pemmican) than the later version. Being young and with a sweet tooth, I always ate my daily chocolate bar after the breakfast porridge and then had the evening torment of lying in my sleeping bag while listening to Deer laboriously sucking his. Deer also had a supply of dried onions that he liked to mix with his pemmican, to the distress of the rest of the party. At the end of the trip we were on our last ration box and the fjord was freezing over.

Being introduced to marvellous exposures of spectacular Skaergaard layering by the men themselves is a special memory. I could see those currents descending to sweep across the intrusion floor while depositing their gravity-stratified layers (Fig. 1). Years later, I accompanied Alexander R. McBirney on his first visit to Skaergaard, where he did so much to stimulate ideas on igneous processes. Standing on some particularly fine examples of the layering featured by Wager, I was rather thrown by Mac's comment of "You don't believe that do you?" Of course I believed it! When, as an ignorant postgraduate student, Wager was good enough to explain it to you, then you did not presume to think otherwise. It was not allowed. There may be many differing origins for igneous layering, like Parsons' upside-down Klokken peculiarity, but, for those Skaergaard layers, Wager was right – wasn't he?

For work on the Kap Edward Holm intrusion, Deer, Nichols and myself made the 20-mile crossing of Kangerdlugssuaq fjord in a 15 ft boat with a dubious engine which was said to be capable of operating off a variety of fuels, but which was something of an unknown item on any of them. I count those ice-bound (Fig. 3) hazardous journeys as the most perilous adventures I have ever been involved in. To this day, I am unable to

1 Deer WA, Howie RA, Zussman J (2013) *An Introduction to the Rock-Forming Minerals*, 3<sup>rd</sup> edition. Mineralogical Society, UK



**FIGURE 3** Looking towards the open sea from near the base house. The vertical cliff behind the mist is Kap Hammer, and the jagged skyline is entirely Palaeocene basalt flows. PHOTO: IAN PARSONS (1990)

decide whether Deer was an immaculate boatman or just unconcerned, or both. For some of our glacier travel we used a man-hauled sledge for moving gear. This was, in retrospect, a ridiculously heavy contraption but was used to get to camps high on the huge glaciers that we needed to traverse. The prospect of the heavy-weight sledge with its three attendants disappearing down one of the numerous very large crevasses was a constant source of enlivenment.

One memorable day saw Deer and myself leave camp to cross a large snowfield in order to reach rocks that he had seen on a 1935 winter dog-sledge journey. It was late in the day when we finally got to our objective, only to find that it was guarded by a very large bergschrund. Fortunately, a short descent enabled a bridge to be reached, but, having got there, our only collecting hammer was dropped and could be dimly seen stuck on an icy knob about fifty feet down. Later, there was some discussion about who had dropped the hammer, but I know who it was! With the hammer recovered, we collected our hard-won samples and the long return was made back to a very welcome camp. Deer's experience and determination were essential to achieving our objectives on these, at times, arduous days on Kap Edward Holm.

Despite his mountaineering background and his experience on Everest – without oxygen he reached 28,200 feet (8595 m) in 1933 – Wager strongly discouraged any activity not directly relevant to the geological program. He regarded any suggestion of taking in the odd summit, just because it was there, as highly frivolous. Not an unreasonable point of view, considering the time, effort and expense involved in getting to East Greenland in 1953. That was a time, not long after the war, when the area was hardly visited. Now the Blosseville coast is much frequented, and adverts for adventure trips can be found in glossy magazines. There is gold in some of the rocks on Gabbro Mountain, and the region has been overrun by helicoptering geologists of all nationalities. In 1953, wild-life around Kangerdlugssuaq was completely undisturbed. Nothing, apart from sealing activity in offshore waters, had significantly disturbed the area for many years. Bird life in the fjord was prolific, seals were abundant and other rare animals, such as the narwhal, were present. Now, however, bears, which travel south in the winter months, have become targets for hunters as they make their way back north and have to cross fjords such as Kangerdlugssuaq. Visits in later years have shown a scene greatly changed by human activities and hunting. Wager would not recognise his 1930s exploration paradise.

**Peter Brown**, University of St. Andrews  
petbrown@btinternet.com

Wager LR, Deer WA (1939) Geological investigations in East Greenland. Part III: The petrology of the Skaergaard intrusion, Kangerdlugssuaq, East Greenland. Meddelelser om Grønland 105: 1-323

## TENURE-TRACK FACULTY POSITION IN MANTLE PROCESSES

The Department of Geological Sciences seeks an outstanding scientist to lead a vibrant research program in the broadly defined area of Mantle Processes. Specific areas of interest include (but are not limited to) the composition, structure, and evolution of our planet over varying length and time scales. We are particularly interested in those who seek to make connections between deep and shallow processes (examples include how the dynamically flowing and recirculating mantle interacts with its crust, hydrosphere, and atmosphere). Research approaches should encompass some combination of field, laboratory, and modeling. The appointment will preferably be at the junior level (Assistant or untenured Associate Professor), but applications from scientists at all career levels will be considered. The successful applicant will be expected to develop a world-class independent program of research, interface where appropriate with existing programs in the Geological Sciences and in the School of Earth, Energy, and Environmental Sciences, and teach at the undergraduate and graduate level.

Applications should include a cover letter, curriculum vita, a statement of research and teaching interests, three recently-published representative papers, and the names and email addresses of three individuals from whom the search committee can request letters of reference. Please apply at: <https://academicjobsonline.org/ajo/jobs/6199>

Review of applications will commence October 31, 2015. The position will remain open until filled. Questions can be directed to: Lauren Nelson at [lnelson@stanford.edu](mailto:lnelson@stanford.edu)

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## DEPARTMENT OF EARTH SCIENCES (Geochemistry)

### ASSISTANT OR ASSOCIATE PROFESSOR

(Application Closing Date: November 30, 2015 or until the position is filled)

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Applicants must have a Ph.D. in Earth Sciences, have demonstrated excellence in teaching, and possess a strong commitment to research and scholarship, as reflected in publications. The successful candidate will have the ability to develop an externally-funded, high quality research program; will be committed to effective teaching at the undergraduate and graduate level; and will contribute effectively to the academic life of the Department. Proficiency in English is a requirement.

The Department is particularly interested in candidates with demonstrated expertise, experience and research interests in the field of isotope and/or elemental geochemistry, who are able to teach core courses in geochemistry. Preference will be given to candidates who have expertise with instruments such as a thermal ionization mass spectrometer (TIMS) and/or laser ablation inductively coupled plasma mass spectrometer (LA-ICPMS), and who also are engaged in the development of new techniques and innovative application of isotopic systems.

Information about the undergraduate programs of the Department of Earth Sciences and the link to the extended job advertisement may be found at [www.earthsci.carleton.ca](http://www.earthsci.carleton.ca). The Departments of Earth Sciences and Geography, at both Carleton University and the University of Ottawa, form the Ottawa-Carleton Geoscience Centre, a collaborative research and graduate institution with a wide range of research facilities.

Please send your application by email in one single PDF document to the attention of: Chair, Department of Earth Sciences, Carleton University, 1125 Colonel By Drive, Ottawa, Ontario, K1S 5B6 c/o Mrs. Sheila Thayer ([Sheila.Thayer@carleton.ca](mailto:Sheila.Thayer@carleton.ca)). Applications should include curriculum vitae, a cover letter, a teaching dossier including teaching experience, a statement outlining current and future research interests, and the names and addresses (including e-mail addresses) of three referees. The deadline for applications November 30, 2015. Applications will be accepted until the position is filled.

Please indicate in your application if you are a Canadian citizen or permanent resident of Canada.

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