

Elements

An International Magazine of Mineralogy, Geochemistry, and Petrology

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Kaolin

PAUL A. SCHROEDER and DAVID L. BISH, Guest Editors

From Ancient Porcelains to Nanocomposites

Kaolin-Group Minerals: Environmental Recorders

Mining and Processing Kaolin

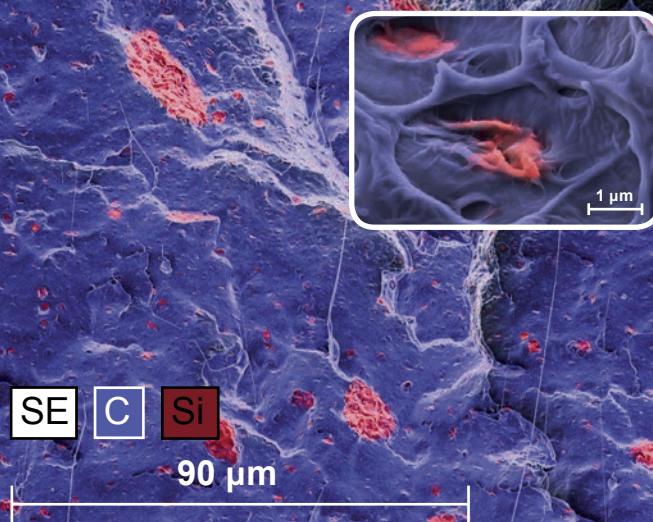
Interactions in the Environment

From Platy Kaolinite to Nanorolls

Kaolins and Health



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The micrographs show EDS maps of a polymer nanoclay composite. The polymer is represented by carbon (blue) and the clay by silicon (red). The sample consists of metallocene linear low density polyethylene and 2.5 wt.% organically modified montmorillonite. The composite was studied to improve its properties such as mechanical and thermal stability. The results show that the nanoclay particles have formed agglomerates.

The large element map (4076 x 3072 pixels, 110 nm pixel size) was acquired with an annular XFlash® silicon drift detector. The SDD is inserted between the pole piece and the sample, and ideally suited for the analysis of topographically complex samples. Shadowing effects are minimized by collecting X-rays using four separate detector segments. A low accelerating voltage of 3 kV and a low beam current of 220 pA was applied to examine the fine structure of the beam sensitive sample at the sub- μm scale. These conditions produced an input count rate of 27 kcps due to the large solid angle of 1.1 sr. Sample courtesy: D. P. S. Dalto, M. J. O. C. Guimarães, M. E. F. Garcia, UFRJ/Rio de Janeiro, Brazil.

More details can be found at: www.bruker.com/elements

Elements

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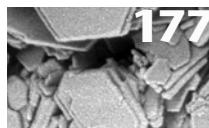
ABOUT THE COVER:

Kaolinite's first sophisticated use was in porcelains from Jingdezhen, China. Chinese plate (47.6 cm across) from the Yuan period (1271–1368); Jingdezhen ware; porcelain with underglaze, cobalt-blue decoration, from the collection of the Seattle Art Museum. PHOTO: PAUL MACAPIA, REPRODUCED WITH PERMISSION.

Background image: scanning electron microscope image (false color) of well-ordered kaolinite from sedimentary-hosted kaolin deposit in Georgia, USA; width of view is 4 µm. PHOTO: ROBERT J. PRUETT, IMERYS OILFIELD SOLUTIONS

Kaolin

Guest Editors: **Paul A. Schroeder** and **David L. Bish**



Kaolin: From Ancient Porcelains to Nanocomposites

Paul A. Schroeder and Gary Erickson



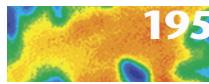
Kaolin-Group Minerals: From Hydrogen-Bonded Layers to Environmental Recorders

Etienne Balan, Georges Calas, and David L. Bish



Mining and Processing Kaolin

Jessica Elzea Kogel



Interactions of Kaolin Minerals in the Environment

Randall T. Cygan and Kazue Tazaki



From Platy Kaolinite to Nanorolls

Christian Detellier and Robert A. Schoonheydt



Kaolins and Health: From First Grade to First Aid

Lynda B. Williams and Stephen Hillier

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SOCIETY NEWS EDITOR: Andrea Kozioł (Andrea.Kozioł@notes.udayton.edu)

Mineralogical Society of America
3635 Concorde Pkwy Ste 500
Chantilly, VA 20151-1110, USA
Tel.: 703-652-9950; fax: 703-652-9951
business@minsocam.org
www.minsocam.org



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

SOCIETY NEWS EDITOR: Kevin Murphy (kevin@minersoc.org)

The Mineralogical Society
12 Baylis Mews, Amyand Park Road
Twickenham, Middlesex TW1 3HQ, UK
Tel.: +44 (0)20 8891 6600
Fax: +44 (0)20 8891 6599
info@minersoc.org
www.minersoc.org



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.

SOCIETY NEWS EDITOR: Pierrette Tremblay (ptremblay@mineralogicalassociation.ca)

Mineralogical Association of Canada
490, de la Couronne
Québec, QC G1K 9A9, Canada
Tel.: 418-653-0333; fax: 418-653-0777
office@mineralogicalassociation.ca
www.mineralogicalassociation.ca



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*.

SOCIETY NEWS EDITOR: Ian Bourg (icbourg@lbl.gov)

The Clay Minerals Society
3635 Concorde Pkwy Ste 500
Chantilly, VA 20151-1110, USA
Tel.: 703-652-9960; fax: 703-652-9951
cms@clays.org
www.clays.org



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SOCIETY NEWS EDITOR: Seth Davis (seth.davis@geochemsoc.org)

Geochemical Society
Washington University
Earth & Planetary Sciences
One Brookings Drive, Campus Box #1169
St. Louis, MO 63130-4899, USA
Tel.: 314-935-4131; fax: 314-935-4121
gsoffice@geochemsoc.org
Explore GS online at www.geochemsoc.org

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 2700 members that leads the biannual European Goldschmidt conference organization, publishes *Geochemical Perspectives*, recognizes scientific excellence through awards, sponsors workshops and conferences in Europe and organizes a Distinguished Lecture Program.

SOCIETY NEWS EDITOR: Ruben Kretzschmar (ruben.kretzschmar@env.ethz.ch)

MEMBERSHIP INFORMATION:
www.eag.eu.com/membership



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SOCIETY NEWS EDITOR: Chris Gardner (lgeochemistry@gmail.com)

IAGC Business Office
275 Mendenhall Laboratory
125 South Oval Mall
Columbus, OH 43210, USA
Tel.: 614-688-7400; fax: 614-292-7688
www.iagc-society.org



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SOCIETY NEWS EDITOR: Anne-Marie Boullier (Anne-Marie.Boullier@obs.ujf-grenoble.fr)
SFMC
Case postale 115, 4 place Jussieu
75252 Paris cedex 05
sfmc@ccr.jussieu.fr
www.sfmc-fr.org



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 interests of exploration geochemists, facilitate the acquisition and distribution of scientific knowledge, promote the exchange of information, and encourage research and development. AAG membership includes

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SOCIETY NEWS EDITOR: Patrice de Caritat (Patrice.deCaritat@gc.gov.au)

Association of Applied Geochemists
P.O. Box 26099
Nepean, ON K2H 9R0, Canada
Tel.: 613-828-0199; fax: 613-828-9288
office@appliedgeochemists.org
www.appliedgeochemists.org



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 members, who include M. v. Laue, G. v. Tschermak, 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*, *Mit*, and *Elements*.

SOCIETY NEWS EDITOR: Klaus-Dieter Grevel (Klaus-Dieter.grevel@ruhr-uni-bochum.de)

Deutsche Mineralogische Gesellschaft
dmg@dmg-home.de
www.dmg-home.de



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.

SOCIETY NEWS EDITOR: Michele Lustrino (Michele.Lustrino@uniroma1.it)

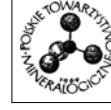
Società Italiana di Mineralogia e Petrologia
Dip. di Scienze della Terra
Università di Pisa, Via S. Maria 53
I-56126 Pisa, Italy
Tel.: +39 050 2215704
Fax: +39 050 2215830
segreteria@socminpet.it
www.socminpet.it



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*.

SOCIETY NEWS EDITOR: Michael Wiedenbeck (michawi@gfz-potsdam.de)

International Association of Geoanalysts
Ms. Jennifer Cook, Hon. Sec.
British Geological Survey
Keyworth, Nottingham, NG12 5GC, UK
<http://geanalyst.org>



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*.

SOCIETY NEWS EDITOR: Zbigniew Sawlowicz (zbigniew.sawlowicz@uj.edu.pl)

Mineralogical Society of Poland
Al. Mickiewicza 30,
30-059 Kraków, Poland



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* (J MPS), the *Ganseki-Koubutsukagaku* (GKK), and *Elements*.

SOCIETY NEWS EDITOR: Toru Inoue (inoue@sci.ehime-u.ac.jp)

Japan Association of Mineralogical Sciences
c/o Graduate School of Science, Tohoku University
Aoba, Sendai, 980-8578, Japan
Tel./fax: 81-22-224-3852
KYL04223@nifty.ne.jp
<http://jams.la.coocan.jp>

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Tel./fax: +48 12 6334330
ptmin@ptmin.pl
www.ptmin.agh.edu.pl

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 *Macía*, a new journal containing scientific news, abstracts, and reviews. Membership benefits include receiving the *European Journal of Mineralogy*, *Macía*, and *Elements*.

SOCIETY NEWS EDITOR: Juan Jimenez Millan (jmillan@ujaen.es)

Sociedad Española de Mineralogía
npvsem@lg.ehu.es
www.ehu.es/sem

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 organizes the annual Swiss Geoscience Meeting and publishes the *Swiss Journal of Geosciences* jointly with the national geological and paleontological societies.

SOCIETY NEWS EDITOR: Urs Schaltegger (urs.schaltegger@unige.ch)

Swiss Society of Mineralogy and Petrology
Université de Fribourg, Département des Géosciences
Chemin du Musée 6, Pélalles 1700 Fribourg, Switzerland
Tel.: +41 26 300 89 36
Fax: +41 26 300 97 65
<http://ssmp.scatweb.ch>

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SOCIETY NEWS EDITOR: Cari Corrigan (corrigan@si.edu)

MEMBERSHIP INFORMATION:
<http://meteoriticsociety.org>



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SOCIETY NEWS EDITOR: Toru Inoue (inoue@sci.ehime-u.ac.jp)

Japan Association of Mineralogical Sciences
c/o Graduate School of Science, Tohoku University
Aoba, Sendai, 980-8578, Japan
Tel./fax: 81-22-224-3852
KYL04223@nifty.ne.jp
<http://jams.la.coocan.jp>

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PRINCIPAL EDITORS

JOHN W. VALLEY, University of Wisconsin, USA
(valley@geology.wisc.edu)
PATRICIA M. DOVE, Virginia Tech, USA
(dove@vt.edu)
GORDON E. BROWN JR., Stanford University, USA
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MICHAEL WIEDENBECK, International Association of Geoanalysts

EXECUTIVE EDITOR

PIERRETTE TREMBLAY, tremblpi@ete.inrs.ca

EDITORIAL OFFICE

490, rue de la Couronne
Québec (Québec) G1K 9A9, Canada
Tel.: 418-654-2606 Fax: 418-653-0777
Layout: POULIOT GUAY GRAPHISTES
Copy editor: THOMAS CLARK
Proofreaders: THOMAS CLARK and DOLORES DURANT
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KAOLINS: NANOMINERALS WITH A PROUD HERITAGE

Gordon Brown

Imagine that you were one of the early *Homo sapiens* agriculturalists living during the Upper Paleolithic period near what is now called Kauling (or Gaoling) in Jiangxi province of China. Roughly 25,000 years later, Chinese geologists would discover that the local kaolin deposit was derived from the alteration

of a granite stock of Middle Jurassic age (Chen et al. 1997). Further imagine that your small band of agriculturalists had established a village near a stream. While playing along the stream's bank, your children noticed a soft, malleable material they could form when wet into small objects resembling some of the local wildlife. To their delight, these small objects hardened into a brittle material when exposed to sunlight, preserving the shapes of the model squirrels and foxes they made.

Stimulated by your children's discovery, you also gathered some of this soft plastic material and molded it into different shapes, including several small pots. During the day, your pots hardened in the sunlight, and on your next visit to the stream, you scooped up water in the pots, drank from one of them, and carried the pots filled with water back to your nearby campsite. When you checked on the pots early the next day, you discovered that the dried material had become wet again, the pots had slumped, and the water had leaked out. You crafted a new pot and later carelessly dropped it into a bed of red-hot coals in your campfire, where it baked overnight. The next time you filled this "fired," rock-hard pot with water, it did not dissolve, and you found that water could be stored in it for weeks with little or no damage to the pot.

This primitive technology was likely discovered in many other parts of Eurasia and Africa by other early *Homo sapiens* agriculturalists and was exported to Southeast Asia, Australia, and North and South America by early humans. The accidental discovery that this soft, plastic material, now known as kaolin and often containing fine-grained quartz, mica, and other minerals, could be formed and fired into useful objects, such as pots for storing water and grains, was an important one. However, these early *Homo sapiens* had no idea what changes the firing process caused to the clay pot. We now know that firing a kaolinite pot to ~1000°C causes the kaolinite to dehydrate and transform into a harder, less porous, waterproof form known as stoneware. Firing such a pot to ~1650°C causes the kaolinite to partially melt and form a glassy material, which when formed into thin pieces is known as porcelain or "fire china," after the country where this process originated (Hurlbut 1970).

Early potters learned how to glaze their pots with a paint or slip of watery clay before firing, which made them even more durable and impervious to water. The durability of fired clay objects is well known to archaeologists, who have traced

human activities throughout prehistory based in part on pieces of broken pottery, or potsherds, from different periods (see photo). Another early use of kaolin was consumption by humans and animals for gastrointestinal ailments—a practice known as geophagy (Laufer 1930). This practice is thought to date back 2 million years to *Homo habilis*, based on evidence found in what is now Zambia (Young 2011) and it continues today in many parts of the world.



A stoneware shard from one of the earliest pots, dated at 20,000 BP and discovered in the Xianren cave, Jiangxi province, China. FROM WU ET AL. (2012), REPRINTED WITH PERMISSION FROM AAAS

Since these early uses, kaolin-group minerals have found many modern technological uses in materials science (ceramics, papers, pigments, plastics, nanocomposites, and bionanocomposites), as well as in modern medicine (antibacterial applications, drug delivery in cancer treatments, and targeted gene therapy using tubular halloysites). In hindsight, clay minerals such as kaolinite have played a prominent role in the development of civilization, and pottery and art objects made from clay have helped modern humans understand these developments. In addition, Earth and soil scientists now understand the layered, atomic-level structure and unique properties of clay minerals, which are among the most abundant natural nanomaterials. They also understand the chemical weathering processes responsible for clay deposits such as the Kauling kaolin deposit in China, as well as the important role that fine-grained clay minerals play in a variety of geochemical and pedogenic processes, such as the sorption and release of contaminant and nutrient elements and molecules in aquatic systems and soils.

This issue of *Elements* focuses on kaolin-group minerals and emphasizes their special place in the early cultural history of China, which is well known for developing porcelain-making techniques. It also discusses the atomic-level structure and polytypism (different layer stacking sequences) of kaolin-group minerals, high-pressure kaolinite polytypes, the importance of defects and impurities in kaolinite, and the ability of kaolinite to reveal its environmental history through defects induced by radiation damage. Another important process discussed in this issue is the interaction of kaolin-group minerals with the environment, especially with ions in aqueous solutions and bacteria. Particularly fascinating are the articles on the history of mining and processing of

Cont'd on page 164

THIS ISSUE

This issue illustrates admirably how materials known and used since the dawn of humanity may still have many surprises in store for us in terms of new uses and applications. Guest Editors Paul Schroeder and David Bish chose to present the whole spectrum of uses of kaolin, from ancient porcelains to nanocomposites.

In her article about mining kaolin, Jessica Elzea Kogel provides an excellent snapshot of mining today, and I encourage all to read it. She stresses the importance of mining responsibly, with a plan for returning the land to a postmining use that will have value to the local community. Gaining acceptance by the local community ("social license") by involving all stakeholders is just as important as drilling to delimit the ore resources.

Why does mining get such bad press then? In a recent issue of *Canadian Geographic*, the possibility of mineral exploration, let alone exploitation, in an isolated area of Jordan was seen as a catastrophe. This is a paradox, because we consume greater and greater amounts of resources per capita. These resources need to be dug up from the ground somewhere—as long as it is not in our own back yard. Sadly none of the mining companies approached by the guest editors chose to advertise in this issue to let us know how they have embraced the challenge of gaining acceptance from local communities. And perhaps this is part of the mining industry's problem.

I am very fond of this issue's Parting Shot. The idea germinated at the last GSA meeting in Denver. Over a glass of wine, Rod Ewing was telling a few of us how he enjoyed reading Ian Parsons' Parting Shots. "He could write about a brick and make it interesting," said Rod. Ian rose to the challenge—read his Parting Shot about the Friendly Brick (by the way, the lovely little girl in the picture is my granddaughter, Ellie Rose). And kaolin was the perfect issue in which to publish this Parting Shot.

TRANSITION

I am thrilled that Jodi Rosso has been chosen to succeed me at the end of this year (see accompanying text). I did not know Jodi personally but thought she had the perfect profile for the job. So I was delighted that after an international search, the search committee came to the same conclusion. For the last month Jodi and I have conversed during weekly Skype calls, and it has been inspiring to share ideas and make plans. At the Goldschmidt Conference in Sacramento, we intend to map out the next few months to ensure that the transition is complete by the end of the year.

EDITORIAL *Cont'd from page 163*

kaolin-group minerals, the development of environmentally sensitive modern mining practices, and the many uses of kaolin-group minerals in modern technology and medicine. After reading these articles, it should be clear that kaolin-group minerals had a major impact on early humans and that they continue to impact modern humans through their many and varied uses.

Gordon E. Brown Jr.

Principal Editor in charge of this issue

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FROM A READER

"Thought you might like this... Served up while on a KLM flight, and I really was reading the latest issue!! Not that I would recommend the wine especially." — John Ludden

**FREE TO STUDENTS**

Students take note: In this issue, two of our regular advertisers are offering for the first time free student editions of their software.

The Geochemist Workbench student edition is offered to students currently registered as full-time undergraduates or graduates at an accredited university offering degrees in geoscience. Students can apply on the website <http://student.gwb.com>.

As part of its 20th-birthday celebrations, CrystalMaker has launched a free "CrystalViewer" program. This is designed for use by individual students, to empower and inspire them to explore our microscopic world. CrystalViewer includes a library of over 120 structures, including a range of minerals, advanced materials (many derived from mineral prototypes), plus a teaching library of crystal chemical compounds.

Pierrette Tremblay, Executive Editor

DR. JODI ROSSO APPOINTED NEW EXECUTIVE EDITOR OF *ELEMENTS* STARTING JANUARY 1, 2015

After an extensive international search over the past year and with 35 applicants from 10 countries, Jodi Rosso was selected as the next Executive Editor for *Elements*. She will replace current Executive Editor Pierrette Tremblay, who will step down at the end of 2014 after 10 years.

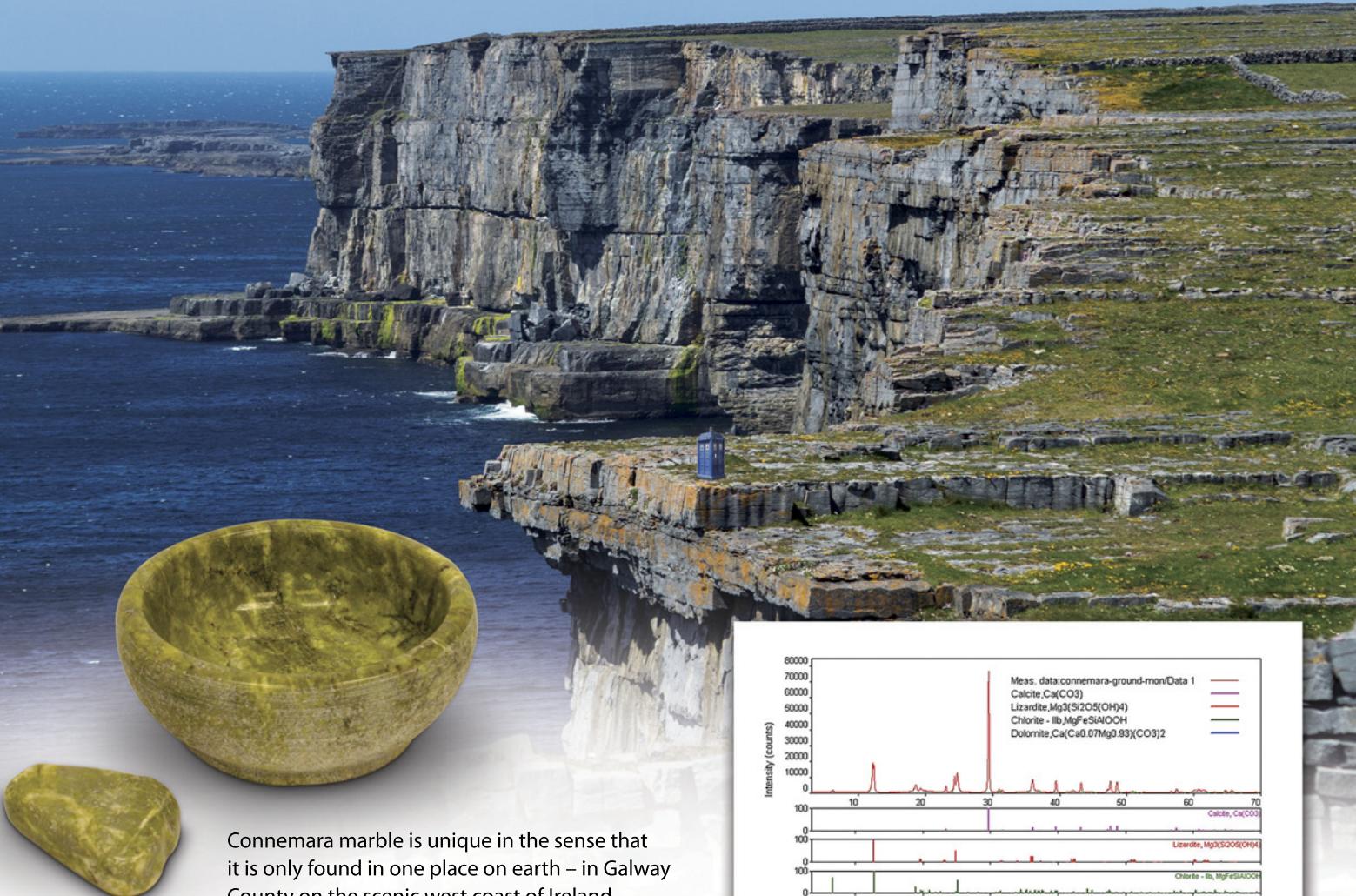
Jodi brings her extensive and diverse experience in mineralogy, petrology, and geochemistry (MPG) to *Elements*. She received her PhD from Stanford University (USA) with an emphasis in geochemistry. Since 2000, she has been the series editor of *Reviews in Mineralogy and Geochemistry*, a joint publication of the Mineralogical Society of America (MSA) and the Geochemical Society, overseeing the publication of 29 volumes on a wide range of MPG subjects. She also serves as editor of the Monographs series, published by MSA.

Jodi is a devoted reader of *Elements* and, being particularly fond of Parting Shots, she likes to start reading each issue from its last page. Her considerable publication experience with RIMG volumes, her research training in MGP, and her enthusiasm and creativity were compelling qualities for her being selected for the position.

She and the retiring executive editor will work closely over the next several months to ensure a smooth transition of leadership at the magazine. Please welcome Jodi Rosso to the *Elements* family.

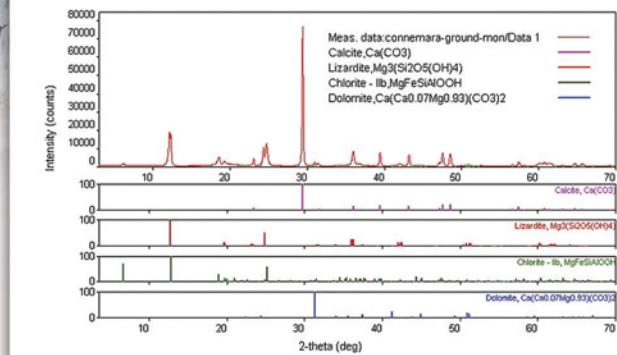
Executive Editor Search Committee (appointed by *Elements*' Executive Committee): Barb Dutrow, chair; Liane G. Benning, Bernardo Cesare, Rod Ewing, John Valley, J. Alex Speer (ex officio)

Phase identification and Rietveld refinement of Connemara marble with a benchtop X-ray diffractometer



Connemara marble is unique in the sense that it is only found in one place on earth – in Galway County on the scenic west coast of Ireland.

In addition to containing a limestone mineral (calcite), three other phases belonging to the serpentine mineral family are found in Connemara Marble. The main polymorphic forms are chrysotile, antigorite, and lizardite. X-ray diffraction is a viable technique to identify and pinpoint the exact phase of the serpentine family.



Mineral	Chemical Formula	Wt %
Lizardite	Mg ₃ (Si ₂ O ₅ (OH) ₄)	38.2
Calcite	CaCO ₃	44.5
Chlorite - IIb	MgFeSiAlOOH	15.1
Dolomite	CaMg(CO ₃) ₂	2.2

Specimens of Connemara marble were pulverized and analyzed with the Rigaku MiniFlex benchtop XRD. A Rietveld analysis was performed using the model obtained from these phases.



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KIM TAIT APPOINTED THE INAUGURAL TECK CHAIR IN MINERALOGY



The Royal Ontario Museum has appointed Dr. Kim Tait as the inaugural Teck Chair in Mineralogy. Dr. Tait, a ROM curator of natural history and associate professor of geology at the University of Toronto, joined the Museum in 2007. She holds a bachelor of science in geology from the University of Manitoba and a PhD in geosciences from the University of Arizona, and is a fellow of the Canadian Gemmological Association.

The Teck Chair is a new position at the Museum, endowed by Vancouver-based diversified resource company Teck as part of its commitment to support leading-edge research in Earth sciences at the ROM. In her new role, Kim will lead scholarly research, publications, and strategic acquisitions. She will contribute to ROM Earth & Space by developing permanent galleries, major exhibitions, public programming, and education. Kim has been a councilor of the Mineralogical Society of America and the Mineralogical Association of Canada.

HUMBOLDT FOUNDATION AWARDS

Friedrich Wilhelm Bessel Research Award



David Peter Dobson of the Department of Earth sciences, University College London, is the recipient of a Friedrich Wilhelm Bessel Research Award, granted by the Alexander von Humboldt Foundation in recognition of lifetime achievements in high-pressure research. David Dobson graduated in geology from Bristol University in 1991 and received his PhD from the University of London in 1996. He performs high-pressure measurements of the physical properties of minerals using *in situ* multi-anvil press techniques. His areas of interest include the transport properties and rheology of mantle minerals, the origin of deep seismicity, iron–nickel–light-element alloy systems, and studies of post-perovskite analogue phases. Press work extends into David's personal life, where he is an accomplished relief printmaker with his own antique Columbian press.

Humboldt Research Awards

The Humboldt Foundation grants up to 100 Humboldt Research Awards annually. The awards are granted to academics whose fundamental discoveries, new theories, or insights have had a significant impact on their own discipline and who are expected to continue making cutting-edge achievements in the future. Academics from abroad, regardless of their discipline or nationality, may be nominated by established academics in Germany. Award winners are invited to spend a period of up to one year cooperating on a long-term research project with specialist colleagues at a research institution in Germany. The award is valued at 60,000 euros. Three members of our community received such an award in 2014.



Björn Jamtveit is internationally known for his outstanding achievements in the application of physical principles to pattern formation in the Earth. He has investigated patterns over a range of spatial scales, from micron-scale compositional periodicities in individual minerals to travertine terrace periodicities in hot springs and fracture patterns associated with mineral reactions. In Germany he intends to work at the University of Münster on a combination of modeling and laboratory experiments on nanoscale fracturing during fluid–mineral reactions.



Simon P. Turner is a leading geochemist and geochronologist at Macquarie University in Australia. He has worked on a broad range of topics related to igneous petrology and geochemistry, including granite genesis, sediment provenance, crustal growth, and the origin of continental flood basalt and mid-ocean ridge, ocean island, and island arc lavas. He is an international authority on the application of short-lived, uranium-series isotopes to constrain the timescales of magma forma-

tion, transport, and differentiation, as well as soil production and erosion rates. During his stay in Germany, he will use uranium-series data and other geochemical tools to solve a wide variety of problems related to the timing of magmatic processes and the origin of volcanism at the South Atlantic mid-ocean ridge, the Kamchatka subduction zone, and intraplate volcanic regions, such as the Canary Islands.



Howard J. Spero is a leading geobiologist and geochemist at the University of California at Davis. His pioneering contributions have been influential in advancing the field of paleoceanography. Through laboratory experiments with living planktonic foraminifera, he has groundtruthed relationships between environmental properties, such as temperature, salinity, and pH, and foraminifera shell geochemistry to reconstruct past environmental conditions and ocean chemistry from

the fossil record. His research has produced an array of new tools that have allowed scientists to resolve major changes in Earth's climate system over the last 50 million years. In Germany, he will continue his research at the Alfred-Wegener-Institut Helmholtz-Zentrum für Polar- und Meeresforschung, especially with regard to reconstructing the ocean's carbonate system and carbon cycle, in order to more fully link paleoclimatology with predictions of future climate scenarios in a high-CO₂ world. He was chosen as the Faculty Research Lecturer for 2014 at the University of California at Davis. The Faculty Research Lecture Award is the highest honor the Davis Division of the Academic Senate accords its members.

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BLACK BEAUTY: A UNIQUE 4.4 GA, WATER-RICH METEORITE FROM MARS

Carl Agee*

Northwest Africa (NWA) 7034, and its pairings, is a new type of Martian meteorite discovered recently in Western Sahara. NWA 7034, also known as "Black Beauty" because of its dark, shiny appearance (Fig. 1), contains ten times more water than other Martian meteorites. This, combined with its anomalous oxygen isotope values and ancient zircons, makes it an extraordinarily valuable specimen for understanding surface processes, aqueous alteration, and atmosphere-lithosphere exchange reactions that existed on Mars as far back as 4.4 billion years ago. Black Beauty appears to be the first Martian meteorite to match the surface geochemistry of Mars, as seen by landers and orbiters, and as such, it has particular relevance to the current Mars Science Laboratory mission at Gale Crater.



FIGURE 1 Three hand samples of NWA 7034, the Martian meteorite known as Black Beauty due to its shiny black appearance. PHOTO CREDIT: UNIVERSITY OF NEW MEXICO

Reported last year by a consortium of over a dozen workers (Agee et al. 2013), NWA 7034 is the first and only Martian meteorite breccia (Fig. 2). The original 320 g mass of NWA 7034 was found by an anonymous nomad meteorite hunter in 2011 in Western Sahara (considered by Morocco to be part of its country). The meteorite changed hands between the nomads and meteorite dealers, who sent it to the University of New Mexico for classification. A Martian origin was suspected based on Fe/Mn ratios, which are often used to distinguish planetary basalts (Agee et al. 2013), and was confirmed by the presence of noble gases matching those of the Martian atmosphere (Cartwright et al. 2013; Grady et al. 2014). This technique has been the practice since Bogard and Johnson (1983) confirmed EETA 79001 as being Martian by comparing noble gases trapped in pockets of impact melt glass with measurements of the composition of the Martian atmosphere as measured directly by Viking landers. Black Beauty has a basaltic bulk composition but is made up of numerous clasts of various lithologies set in a fine-grained matrix (Figs. 3, 4).

* University of New Mexico, Institute of Meteoritics, Albuquerque, New Mexico, USA
E-mail: agee@unm.edu

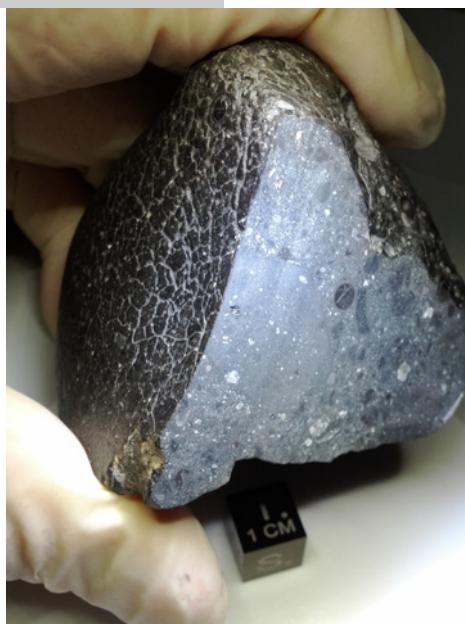


FIGURE 2 The main mass of NWA 7034. Both the fusion-crusted exterior and a sawn face showing the interior breccia are visible. PHOTO CREDIT: UNIVERSITY OF NEW MEXICO

At present, at least six different igneous rock types have been found in the 1–2 kg of the breccia now identified as NWA 7034 (owing to new finds). These include basalt, trachyte, and andesite. These compositions are remarkably similar to the rocks analyzed by APXS on the Spirit Rover at Gusev Crater and more recently with ChemCam on the Mars Science Lab at Gale Crater. Thus Black Beauty is the first tangible sample of the surface of Mars as determined by NASA missions. Secondary alteration products in clasts, spheres, and pebbles of Martian origin are abundant in Black Beauty, and the water-bearing phases include maghemite, ferrihydrite, phyllosilicates, and apatite, which sum to approximately 6000 ppm bulk water—10 to 30 times higher than in other Martian meteorites.

Age determinations on Black Beauty reveal the breccia's diversity and its complex origin, which likely reflect surface processes operating during a span of a few billion years of Martian history. Rb/Sr dating of the bulk sample done at the University of New Mexico gave an age of ~2.1 Ga; however, bulk Sm/Nd dating done at NASA Johnson Space Center gave an age of ~4.4 Ga. Humayun et al. (2013) reported ancient zircon U-Pb ages of ~4.4 Ga, but they also found a younger population of zircon with ages of ~1.7 Ga, and subsequent studies have found many apatite, zircon, and baddeleyite grains with ages of ~1.4 Ga. Luckily for the chronologists, Black Beauty has populations of apatite and zircon throughout the matrix and in most clasts, which is offering the opportunity to date individual lithic domains, thus



FIGURE 3 A polished surface of the interior of NWA 7034 clearly exhibiting clasts of various lithologies set in a fine grained matrix.
PHOTO CREDIT: UNIVERSITY OF NEW MEXICO

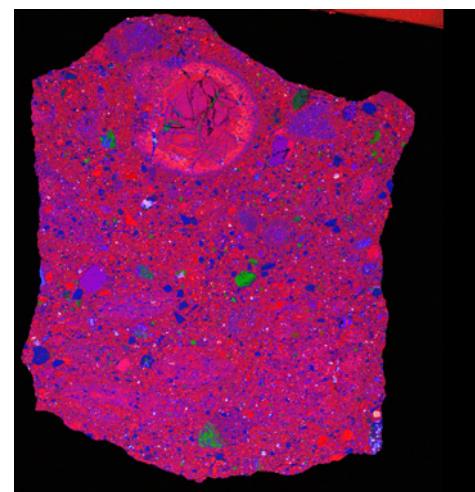
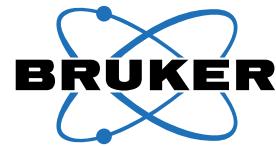


FIGURE 4 Elemental SEM map of a thin section of NWA 7034 showing clasts with clear compositional differences. Red = Mg, green = K, blue = Ca. IMAGE COURTESY OF ROMAIN TARTÈSE, OPEN UNIVERSITY

revealing the sequence of events that brought this breccia together, prior to its being blasted off Mars around 11 million years ago. Indeed, NWA 7034 is not simply a single meteorite sample; it is more like a Martian geologic field area all contained within one rock—and there is still much to explore!

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SETTING UP OR RENOVATING A LABORATORY

Penny King* and Vickie Bennett*

Receiving money to set up or renovate a lab is a wonderful experience! Many researchers have a euphoric moment, imagining the possibilities for a new, slick, streamlined workflow that will result in hundreds of papers! That is ... until reality sets in and it becomes apparent that a lot of work is involved. Setting up a lab does not need to be stressful though (e.g. Wiedenbeck 2013); it just involves a lot of planning, communication and adjustments to timetables and scope – similar to renovating a home. Laboratories in the Earth sciences today cover a wide spectrum, from specialised facilities for instrumentation (Fig. 1) to clean labs for organic or trace element geochemistry (Fig. 2) and to rock-crushing and computer labs. Books could be written on the experience of lab renovations, and every researcher will have distinctive needs. In this article, we provide a ‘checklist’ of sorts for the process of setting up the types of laboratories used by most *Elements* readers.

For graduate students and postdocs: our advice is to start thinking about your own lab now. Figure out what works well in the beautiful lab that you currently work in and what you think could be improved given the opportunity? Why is the layout the way it is? When maintenance or repairs are needed in the lab, pay attention to what is going on and talk to your supervisor or the lab manager about operational details (most of us really like talking about our labs and their special design). If there are particular types of equipment that you like or dislike, make a note of them.

FIRST THINGS FIRST: COMMUNICATION

Setting up a lab is a time when communication skills are at a premium. This is the time to talk to former supervisors and colleagues who have installed similar laboratories. Or better still, visit them – to get their tips on processes and supplies. Knowing what doesn’t work or where they have had problems is as important as knowing what does work. If you plan to use specialized instruments, the instrument salesperson may have important tips on the renovation and installation process, as well as room specifications for the particular instrument that will need to be met before installation. Expect to be in contact with building contractors like plumbers, electricians and carpenters, and for a new lab or major refurbishment even architects. Your building manager (or equivalent) will likely supply a lot of advice and may help with budgets and contacts. Finally, you will need to coordinate carefully with occupational safety advisors in your workplace to

FIGURE 1 The sensitive high-resolution ion microprobe (SHRIMP) lab at the Australian National University houses three different ion microprobes, with plenty of surrounding space for modifications and installation. Prof. Trevor Ireland for scale.



ensure that the lab design meets the current safety requirements of your institution. The requirements may include safety showers and eye-wash stations and possibly wheelchair accessibility. This is something that needs to be done early in the planning process and included in the budget to avoid unpleasant surprises.

PLANNING A LAB THAT WORKS FOR YOU

You might wish to first start with a list of the processes to be used in your lab to ensure that you have a good workflow in the room. For instance, if you need to access the sink for several different tasks, then a central position (for example, at the end of a peninsular bench) may work well. For clean labs you might design the workflow from the entrance to sequentially cleaner areas in the interior, perhaps with rooms within rooms. For instrument labs it is important to design easy accessibility for when instrument servicing is required. By clarifying how you will use the room, hopefully you can better communicate to your senior colleagues the need behind your requests – this process often results in changes to your floor plan!

BUDGETS AND TIMELINES

In almost all cases, despite how generous your start-up package, the budget probably will not allow you to have everything on your wish list. Prioritise the requirements of the lab necessary to achieve the best possible results, and distinguish functionality from the cosmetic. Yes, you might really need the highest-performance, most expensive fume hoods, but do you really need the most expensive furniture? The quality of data produced does not correlate with the total cost of the lab. Plan for the



FIGURE 2 Magda Huyskens checks a still in the isotope geochemistry clean lab at the Australian National University. Clean labs require particular attention to detail during renovations.

future – you want your lab to be functional and attractive now and several years from now. For example, in a chemistry lab the floors and bench tops may be rated acid resistant, but do dilute-acid spills cause stains? Typically, you will be given a choice of materials for floors and bench tops – try out some samples. Think also about what standard maintenance will be required, in terms of both budgets and lab access. Is it easy to access fume hood scrubbers or air filters for routine service or will the lab have to be shut down, and what will be the replacement costs? Consider energy efficiency in the design of the lab. For example, if you need cooling water find out if there is a building recirculating system that you can tap into or if you should install one in the lab rather than putting water down the drain.

During the planning process, the project coordinator at your institution will work with you to put together a timeline for completion of the lab. A usual first reaction is, “Will it really

* Research School of Earth Sciences
Australian National University
Canberra ACT 0200, Australia

take that long? I need to get data now!" Yes, it will take a long time and probably longer than forecast. Here is where you need to develop a good working relationship with the project coordinator: try to make him understand your particular requirements and listen as he explains his constraints. This is best done by regular, calm meetings. Particularly when renovating in older buildings, there will be surprises. The building plans may not be up to date, or there are problems with ducting, wiring or asbestos that will need to be addressed. This is where you and your construction team will need to be creative and flexible. It is extremely important to be clear in your own mind about the requirements for the lab. Some things you can compromise on and some things you cannot – for the latter you will need to provide reasonable justifications. Your lab will be unique, and although you are working with professional contractors they will likely not have come across your set of special requirements before. It may be puzzling to them why certain, more difficult materials have to be used or why a layout has to be a certain way. Be patient and stay on top of, but not in the way of, construction progress. Ask for regular walk-throughs and updates to catch mistakes (yours and theirs) as soon as possible. It is a long process, but the lab will get finished and it will all have been worth it. ■

REFERENCE

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FIGURE 3 These three drawers have different styles of inserts that provide storage for a range of items.

LAB CHECKLIST

Room requirements

- What size is required? How many people need to work in the lab? How many different processes will go on at once? How much and what type of storage (for tools, chemicals, etc.) is required? (Fig. 1)
- Will you need separate rooms or spaces for different processes or tasks?
- Are there any special requirements regarding vibrations, magnetism, temperature control, sunlight, drafts, dust-filtering, humidity control or sound damping?
- Can equipment be delivered to the lab easily (for example, through doors, corridors and elevators)?
- Are there benefits to having the lab close to other facilities, teaching classrooms, etc.?
- Will the room need particular paint, flooring or window coverings (Fig. 1)?
- Will the room need a pass-through airlock chamber for environmental control, or is a change area needed for coats, bags and outside shoes?
- Does the room require particular security (for example, motion sensors, locks, safes, doors with tempered-glass windows, phones)?

Services

Are particular services needed, such as:

- a vacuum line
- exhausting fume hoods or clean-air boxes (or access to one)
- venting or delivery of gases / dry air
- a high-pressure, dry-air line
- chilled water
- tap or deionized water systems
- specific power requirements, including backup power
- safety shower, eye-wash station, fire extinguisher
- sinks with special traps
- wireless/Internet/phone connections

Cabinetry and furniture

- Should benches be of standing or sitting height? Will there be knee space or cupboards/drawers underneath? Will benches form a peninsula and/or rim the room? Will these need special surfaces (metal-free, acid- or scratch-resistant)?
- Are cupboards required above the benches? Do cupboards need glass fronts? Do drawers need to be made from special material or have storage inserts? (Fig. 3)

- Do you need a sink and draining rack or a dishwasher?
- Are chairs and/or stools required?
- Are tools best stored in cabinets or in specialized storage boxes or hanging systems?
- Is a flammable-solvents cabinet or chemical-storage cabinet required?
- Is easy access provided for safety equipment, like lab coats, gloves and safety glasses?
- Should gas-bottle harnesses be installed?
- Is the lab in a seismically active area requiring special shelving units?
- Is a specific area for heavy-tool work required?

Other items

- It is always easier to maintain equipment if the appropriate parts are nearby. Don't forget to plan some space for these items.
- A filing cabinet or bookshelf is not a luxury in labs where log books, instruction manuals, chemical safety sheets and reference books need to be stored.
- Space for a computer, data-backup hardware or a server, and a printer may be needed.
- Is there space for expansion? ■

AN ARTIST'S LIFE IN JINGDEZHEN, CHINA

Gary Erickson*

For the past nine years, I have been traveling to China to spend my summers in Jingdezhen, known as the “porcelain city of China.” This historic city has been producing ceramics for seventeen hundred years, with the first porcelains invented over one thousand years ago. Living and creating abroad has both challenged and rewarded me as an artist. The translation from low-temperature earthenware sculpture created in my Minnesota studio to pure white high-temperature porcelain in Jingdezhen has been a fascinating journey and almost as daunting as trying to learn the Chinese language.

For years I had been taught about kaolin in materials classes and used it in slips and glazes. When I hiked over a portion of Mount Gaoling for the first time, I visualized workers bringing kaolin out of the cave mines and down the well-worn path to the river for processing. The one thousand years of effort by miners, clay makers, throwers, mold makers, painters, and kiln firers flooded my mind. In my Jingdezhen studio I use the porcelain for the same properties that artists have appreciated for centuries. I am amused by the fact that someone like me—a six-foot-five-inch-tall, English-speaking Midwesterner—is now connected to the history of Chinese porcelain and part of the harmonious fabric of the porcelain industry.



Men and women transport porcelain throughout the town on wooden carts. They are vital to moving the work between the studios that make the porcelain, those that decorate the objects, and the kilns for firing them.

The designs found in growth processes in nature are commonalities of my earthenware and porcelain work. The concept of yin-yang (阴阳), the interaction of two energies that cause everything to happen, is the foundation for my Jingdezhen slip-cast porcelain forms, which embody a unique natural elegance, simplicity, and purity. Each form incorporates the spiral as a metaphor for the continuity of life. In Taoist thought, the spiral can be at once the beginning of all things and the way in which all things pursue their course. In an abstract way I strive to capture a spontaneous flow of energy that is not specific to any one object existing in the world but rather addresses something common to all.



The author standing next to a giant teapot created in one of the “bigware” factories. This piece was not made for a customer but as testament to the scale at which this studio can work.



Prof. Gary Erickson was helped during his 2013 summer in Jingdezhen by Chinese students from Macalester College where he teaches and students from the Jingdezhen Ceramic Art Institute. They volunteer to assist him in his studio with his artwork, while he gives them experience creating and teaches them about Jingdezhen and Western aesthetics towards ceramics.

My first experience working with Jingdezhen porcelain was humbling to say the least! I used my familiar Western technique of coil-building. When the pieces were fired to 2300 degrees Fahrenheit, they cracked and slumped—leaving nothing to show for my efforts. The second year, I left my ego at home and wisely decided to learn from the one thousand years of porcelain history in Jingdezhen. I began using molds and slip-casting, allowing the porcelain clay platelets to align, giving strength to my forms. Each cast, though nearly identical at first, was altered in ways to create one-of-a-kind pieces. The next challenge was the kiln firing. I knew that if fired in their final orientation, such as a

* Art & History, Macalester College
1600 Grand Avenue, St. Paul, MN 55105, USA
E-mail: ericksong@macalester.edu



Multiple throwers from a “bigware” factory throwing over four hundred pounds (180 kg) of clay for a single section of a vase that could be up to fifteen feet (4.6 m) tall. A master thrower utilizes up to four workers to support his hand through the throwing process.

horizontal form, the thin walls would slump at such high temperatures. Each piece needed to be somewhat precariously supported and fired on end to allow the spiral design to maintain its structural integrity. Convincing a kiln master to allow me to load my own work in this position was a challenge since they thought it would not work. It did work! Their perspective was, “Our traditions have been proven to work for centuries —so why change?” My Western-artist perspective was, “Let’s challenge the norm and try something new and unique.”

Division of labor was practiced in China centuries before the industrial revolution in Europe. The Jingdezhen porcelain industry was built on these practices and continues to use them today. Most foreign artists make their own clay, glazes, and molds and fire their own kilns. It took me a while to understand the flow of the city’s porcelain industry and how to utilize it. Once I let go of the self-imposed need to do it all myself, I found that my summers became very productive. Now I make my positive forms and bring them to a master mold maker who calculates the best approach with the fewest pieces needed for the mold and provides a finished mold in one day. After I purchase casting slip and when my forms are ready to fire, I call one of the several cart people who transport work between studios and other places. They bring my work to one of four public kilns used by artists and workshops in the Sculpture Factory Area. Whether you want to test a single piece or fire a body of work, it will be in and out of the kiln in less than twenty-four hours—very convenient, with quick results!

Over the past nine years, I have explored Jingdezhen and have seen the factories and studios do amazing things with porcelain.



This image shows many sections stacked and stored together for creating tall vases. It appears that the decorator is sitting on the rim of a giant form when in fact she is sitting eight feet (2.4 m) in the air on bamboo scaffolding.

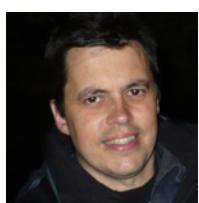
Over the past nine years, I have explored Jingdezhen and have seen the factories and studios do amazing things with porcelain. I have witnessed four workers assisting a master in simultaneously throwing over four hundred pounds of clay. Each section is attached at the dry stage with casting slip, and the sections are stacked upon each other to create vases up to fifteen feet tall. Some factories produce slip-cast bowls in two minutes, with eggshell-thin walls; some others produce three-eighth-inch-thick tiles in sizes up to four feet by twelve feet—perfectly flat! The unique properties of Jingdezhen porcelain allow for both scale and thinness unimaginable in the West.

I have interviewed materials experts, visited historical and contemporary mines, brought students to help in my studio while teaching them about porcelain, and created a unique body of work that could not be made anywhere else in the world. An artist’s relationship with kaolin is very different from that of a scientist. Artists want to know how kaolin might be used in clay, slip, or glaze to enhance their artwork and personal expression. Some artists also study the chemical and structural side of kaolin, leading to new ideas and applications. Through our symbiotic relationship with scientists and their research, artists and industry provide new and creative applications of kaolin. As in my work, the yin combines with the yang.

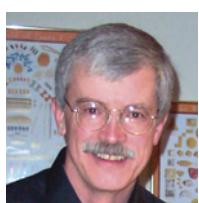


A painter from Beijing was commissioned to paint this 6' x 12' tile in the area known as Lao Ya Tan (old duck pond).

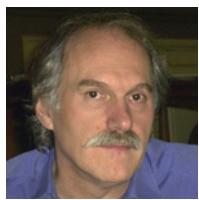
Meet the Authors



Etienne Balan is an IRD research associate at the Institut de Minéralogie, Physique des Matériaux et Cosmochimie (IMPMC, Université Pierre et Marie Curie) in Paris. After graduating in physical chemistry at the École Normale Supérieure de Cachan, he completed his PhD in 2000 at the Université Denis Diderot (Paris) on the crystal chemistry of kaolin and its relation to tropical weathering processes. His research interests are in the geochemical implications of the atomic-scale information recorded by the defect structure of minerals. His approach combines the use of experimental spectroscopic tools and the quantum-mechanical modeling of mineral properties. He is a councilor of the Société Française de Minéralogie et de Cristallographie (SFMC).



David L. Bish is the Haydn Murray Chair of Applied Clay Mineralogy in the Department of Geological Sciences at Indiana University. His research centers on clay and zeolite mineralogy and X-ray powder diffraction. Recently he has focused on the behavior of hydrous minerals under Martian surface conditions. David is a coinvestigator on the CheMin XRD instrument on the Curiosity rover, which has given him the opportunity to analyze the first X-ray diffraction data from Mars. He is the author or coauthor of more than 220 publications, is a fellow of the Mineralogical Society of America, and has been president of the Mineralogical Society of America and the Clay Minerals Society.



Georges Calas is Chair of Mineralogy at the University Institute of France and a professor at Université Pierre et Marie Curie, Paris. His research interests concern how the molecular-scale organization of minerals, glasses, and melts controls their properties and provides invaluable information on the formation conditions of geomaterials; his research combines solid-state spectroscopic and diffraction methods and numerical modeling. His current interests include environmental mineralogy, materials science, nuclear waste management, cultural heritage, and the development of mineral resources in a sustainable manner. He is a member of Academia Europaea, a Geochemical Fellow, and a fellow of the Mineralogical Society of America.



Randall T. Cygan received his PhD in geochemistry and mineralogy in 1983 from the Pennsylvania State University. He then joined Sandia National Laboratories in Albuquerque, New Mexico, where he is now a senior scientist in the Geoscience Research and Applications Group. He was also an assistant professor in the Department of Geology at the University of Illinois. His research includes kinetics, chemical diffusion, mineral dissolution, adsorption, spectroscopy, and molecular simulation. He is a Centennial Fellow of Pennsylvania State University and a fellow of the Mineralogical Society of America. He recently was the recipient of the Brindley Lecture Award by the Clay Minerals Society.



Christian Detellier is a professor of chemistry at the University of Ottawa. After his PhD at the University of Liège (Belgium) and a postdoctoral position at the University of Paris XI, he joined the University of Ottawa in 1980. He was chair of chemistry (1994–1997), dean of science (1997–2006), acting director of the Catalysis Center for Research and Innovation (2007), and associate

vice-president, research (2008–2011), and he is now vice-president, academic, and provost (2012–2015). His research focuses on the design of new types of organo-inorgano nanohybrid and nanocomposite materials from clay minerals. His laboratory is the Canadian partner in the Erasmus Mundus program “International Master in Advanced Clay Science.”



Jessica Elzea Kogel has more than 20 years of experience in the mining industry. She currently leads the geology and mining group for IMERYS's North American kaolin operations and is responsible for exploration, mineral resource development, mine planning, and reclamation. She has authored more than 30 peer-reviewed papers, book chapters, and field guides and holds four US patents. Kogel is past president of the Clay Minerals Society and served as the 2013 president of the Society for Mining, Metallurgy and Exploration. Jessica earned MS and PhD degrees in geology from Indiana University, after completing bachelor's degrees in Earth science and paleontology at UC Berkeley. She is a certified professional geologist.



Gary Erickson received his BA from Hamline University, St. Paul, Minnesota, and his MFA from the New York State College of Ceramics in Alfred, New York. His organic-abstract ceramic sculptures are in private and public collections, including the National Museum of American Art / Smithsonian Institution in Washington, D.C., the Cuban Institute of Friendship in Santiago de Cuba, and the Jingdezhen Sanbao Ceramic Art Institute in Jingdezhen, China. He has received grants from the National Endowment for the Arts, the McKnight Foundation, and the Minnesota State Arts Board. He has traveled to Jingdezhen, China, nine times for art making and cultural exchange. Gary is a visiting assistant professor of art at Macalester College in St. Paul, Minnesota.



Stephen Hillier is a clay mineralogist working in the Environmental and Biochemical Science Group at the James Hutton Institute in Scotland. He completed his PhD at the University of Southampton, which was followed by postdoctoral positions in Paris and Bern. He joined the Macaulay Institute in 1994. Well known for his track record in the Reynolds Cup, he has worked on all the major groups of clay minerals and is particularly interested in the use of quantitative clay mineralogical analysis to understand soil processes and properties. He is a visiting professor at the Swedish University of Agricultural Sciences, Uppsala, and the conference chair for Euroclay 2015 in Edinburgh.



Robert A. Schoonheydt is an emeritus professor at the KU Leuven. His research at the Center for Surface Chemistry and Catalysis deals with transition metal ion chemistry in zeolites and the surface chemistry of clay minerals. His work is concentrated around 4 themes: (1) transition metal ion complexes in the interlayer space, (2) the organization of cationic dye molecules in interlayer space, (3) the construction and characterization of films, and (4) the adsorption of cationic proteins. He was dean of the Faculty of Bioscience Engineering from 1998 to 2004. He was secretary-general (1987–2001), president (2001–2005), and past president (2005–2009) of the AIPEA. Currently he is an associate editor of *Applied Clay Science*.

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The Sea of Japan and Its Unique Chemistry Revealed by Time-Series Observations over the Last 30 Years

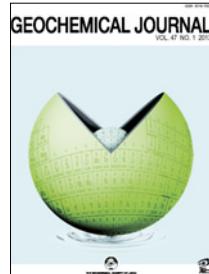
Toshitaka Gamo, Noriko Nakayama, Naoto Takahata, Yuji Sano, Jing Zhang, Eriko Yamazaki, Sachi Taniyasu, and Nobuyoshi Yamashita

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The Sea of Japan, a semi-closed marginal sea in the northwestern corner of the Pacific Ocean, is known as “a miniature ocean” due to its unique geographical and oceanographical characteristics. This paper summarizes water column studies in the Sea of Japan over the last 30 years (between 1977 and 2010) using research vessels *Hakuho Maru* and *Tansei Maru*, in order to better understand the Sea of Japan in its water mass structure, abyssal circulation pattern and their temporal changes from geochemical points of view. Chemical tracers included are: dissolved O₂ and its δ¹⁸O, ³H, ¹⁴C, ³He/⁴He ratio, ²²²Rn, CH₄ and its δ¹³C, and man-made perfluoroalkyl substances such as PFOS (perfluorooctanesulfonate) and PFOA (perfluorooctanoate). A highlight is that the bottom water (depth > 2,000 m) of the Sea of Japan has gradually lost dissolved O₂ by as much as 8-10% per 30 years, suggesting a reduction of the abyssal circulation in scale, to interfere with the O₂ supply from the surface to the bottom water, probably associated with the recent global climatic change.

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Paul A. Schroeder is a professor in the Department of Geology at the University of Georgia, USA. He received his PhD in 1992 from Yale University. He teaches clay mineralogy and Earth surface processes. His research embraces clays in near-surface and hydrothermal environments, and he is particularly interested in the interactions between biological systems and their capacity to record changes in Earth history. He employs novel isotopic, spectroscopic, and crystallographic techniques to characterize clays for discovering paleoenvironmental proxies. His field sites include the southeastern USA, Turkey, and Kamchatka. He is a past president of the Clay Minerals Society and the 2014 recipient of TÜBİTAK's eminent scholar award.



Kazue Tazaki, born in Japan, became interested in geology and clay mineralogy at a young age, visiting mountains, mineral deposits, and radioactive hot springs throughout the world. She obtained a Doctor of Science degree in geology at the Tokyo Kyoiku University. She then went on to work at ISPG in Calgary, McGill University, and the University of Western Ontario in Canada as a clay mineral scientist and electron microscopist, studying uranium mine waste and oil bioremediation using various kinds of electron microscopy. Later, she joined Shimane University as an associate professor and Kanazawa University as a full professor in Japan. She is now a professor emeritus at Kanazawa University. After her retirement, she went to Lac Hong University in Viet Nam and Dodoma University in Tanzania as a visiting professor to teach environmental geology. Her current work involves the Fukushima nuclear power plant accident in Japan and decontamination methods using microorganisms.



Lynda B. Williams is a research professor in the School of Earth and Space Exploration at Arizona State University and manager of the Secondary Ion Mass Spectrometry Facility. A student of R. C. Reynolds (Dartmouth College), she began studying clay mineral chemistry in 1984. Her PhD in sedimentary geochemistry (University of Calgary, Alberta) focused on the stable isotopes of clays in hydrocarbon basins. This led to research on the interactions of clays with fluids, organic compounds, and microbes, with applications in hydrocarbon exploration, environmental issues, the origins of life, and medical geology. She is currently funded by the National Science Foundation to study the antibacterial mechanisms of medicinal clays.

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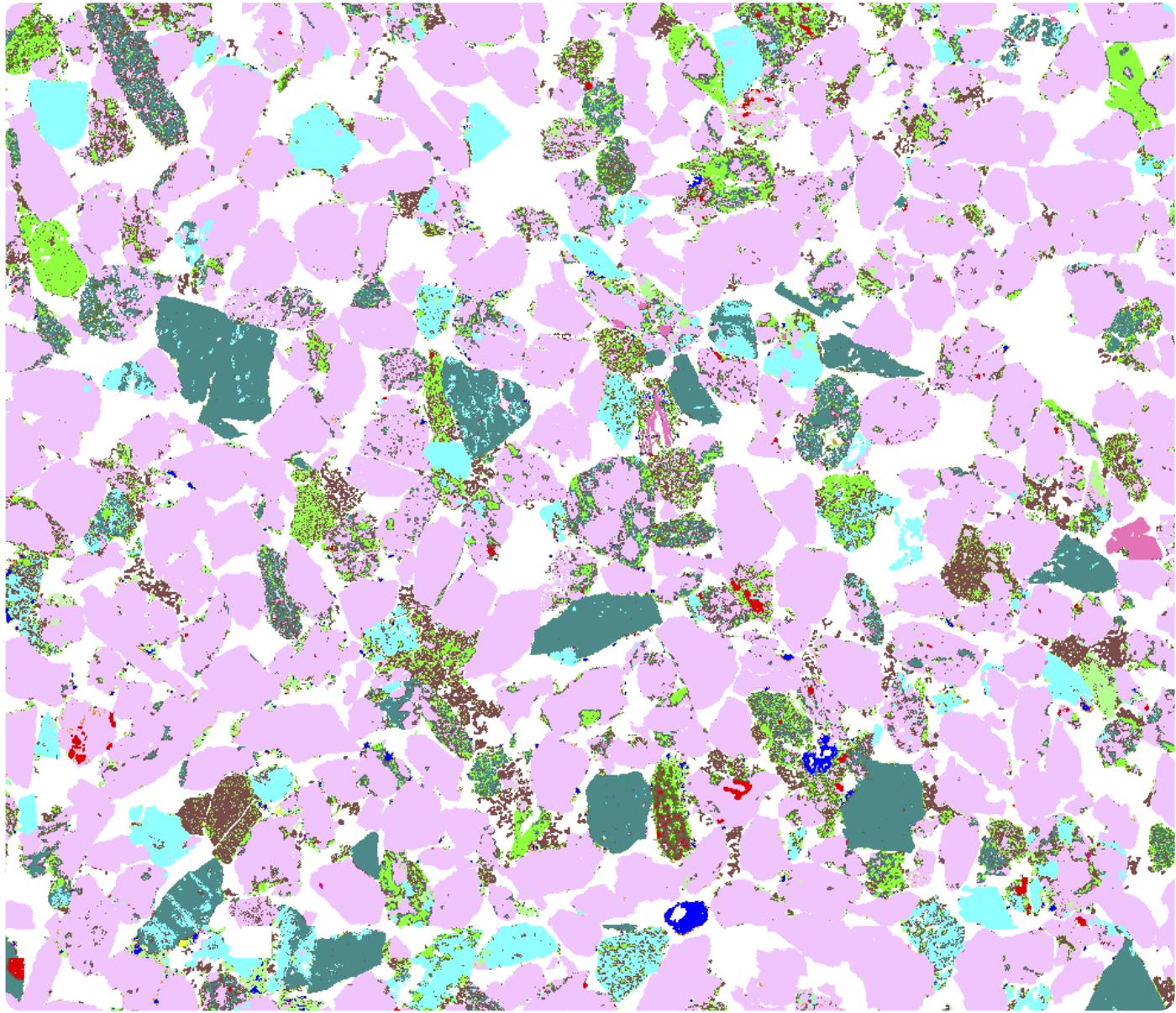


Image courtesy of the ANU and Digitalcore. Color legend: Kaolinite, brown; Quartz, pink; Feldspar, blues; Other Clays, greens; Rutile, red; Purple, apatite; Porosity, white.

Quantify the Micro-Textures of Kaolinite

Some sedimentary rocks are ideal for storing hydrocarbons, which under favorable geological conditions, can make them reservoirs for subsurface oil & gas accumulations. This siltstone contains kaolinite in many different forms including: pore-filling and pore-bridging structures, and as a replacement of detrital feldspar grains. Such knowledge is valuable when assessing a rock's suitability for hydrocarbon production.

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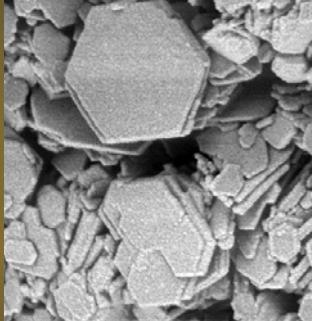
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Kaolin: From Ancient Porcelains to Nanocomposites

Paul A. Schroeder¹ and Gary Erickson²

1811-5209/14/0010-177\$2.50 DOI: 10.2113/gselements.10.3.177



Kaolinite crystals from Twiggs County, Georgia, USA. The largest crystal is 50 µm.

Kaolin has played a prominent role in both Earth and human cultural history, and will continue to do so into the foreseeable future. Its abundance in the rock record has varied according to the waxing and waning of life faunal radiations, crustal differentiation, and climatic conditions. Kaolin-group minerals play an important environmental role in soils of tropical and temperate regions. They also occur in hydrothermal zones, where they form at the expense of felsic rocks through acid hydrolysis, and commonly in episodic geologic events. Kaolin deposits form the basis of many modern materials, but the first sophisticated human use was in porcelains from Jingdezhen, China. From the initial discovery of kaolin and its sculptural use 2000 years ago to today's modern applications in nanocomposites, kaolin has been important throughout cultural history. Art and science are intertwined by the properties and uses of this amazingly small clay mineral.

KEYWORDS: kaolinite, clay minerals, porcelain, Jingdezhen, China, weathering, hydrothermal, hydrolysis

INTRODUCTION

Kaolin is a naturally occurring clay-rich material that has played an important role in shaping Earth history and human culture. Geologically, kaolin is simply the name for a rock dominated by kaolin-group minerals. Minerals in the kaolin group comprise some of nature's most abundant nanomaterials; their unique shapes and layered structures make them important resources in the Earth's near-surface critical zone. Murray and Keller (1993) noted that there are kaolins, kaolins, and kaolins, meaning that kaolin-group minerals are prevalent in many geologic settings. These settings include places where aluminosilicate-rich sedimentary, igneous, and/or metamorphic rocks react with water, acids, and redox-changing solutions to create halloysite, kaolinite, nacrite, or dickite, the minerals constituting the kaolin group (see Table on page 206). Kaolin-group minerals are formed in terrestrial hot springs, in hydrothermal systems, in tropical and temperate soils, and in sedimentary basins, commonly under the influence of microbiologically mediated geochemical reactions.

Worldwide mine production and reserves of kaolin amount to about 37 million tons (Mt), with the United States being a leading producer (5.3 Mt per year). Kaolin's value is nearly \$150 per ton. Compared to other commonly mined clays in the United States (e.g. bentonite and Fuller's earth), kaolin is the largest in tonnage (source: USGS Minerals Commodity Summary, February 2014 production).

Kaolin's economic significance is worldwide, as it occurs in nearly half the manufactured products in daily use. Over the past 100 years, product applications include paper coating, ceramics, rubber, plastics, pharmaceuticals, paints, and cosmetics. Kaolin differs from other clay minerals in that it promotes brightness, opacity, smoothness, viscosity, and printability. New applications include the creation of nano-sized materials for use in the inks of modern printers, nontoxic pesticides in organic farming, and polymer composites used in the packaging industry. The future holds promise for nanocomposites derived from kaolins to improve the rheological, thermal, and organic complexation capabilities

of products used in engineering and medicine. Imagine being able to delay the melting of a steel structure simply by coating it with a clay-polymer coating or to deliver DNA into a cancer cell by using a halloysite nanotube as a Trojan horse. This issue of *Elements* provides insights into kaolins and their unique properties.

Kaolin-group minerals share a basic 1:1 layer structure made of repeating sheets of silica tetrahedra and alumina octahedra; their composition is ideally expressed by the formula $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ (Fig. 1). The combination of the 1:1 structure (including its hydroxyl groups), the variability of site substitutions (e.g. $\text{Fe}^{3+} \rightarrow \text{Al}^{3+}$), and layer stacking disorders gives rise to an array of material properties that benefit countless products. In fact, if you are right now holding a paper copy of *Elements* magazine, your fingertips are likely touching kaolinite. In this article, we briefly review the role of kaolin in Earth's history, including the formation history of different types of kaolin deposits, the cultural uses of kaolin, ancient kaolin mining practices, and ancient and contemporary Chinese influences on the production of kaolin-based ceramics.

KAOLIN IN EARTH HISTORY

Clay minerals probably started forming on Earth immediately after planetesimal formation (Hazen et al. 2013). Given the presence of (1) water, (2) a source of acid, and (3) aluminosilicate rocks on the early Hadean Earth, kaolin-group minerals were likely present and were perhaps the first or second clay group to form, preceded only by smectite-group clays derived from mafic minerals. The abundance of kaolin in the rock record has fluctuated with major events in Earth's evolution (Fig. 2A), particularly as biogeochemical

¹ University of Georgia, Department of Geology
Athens, GA 30602-2501, USA
E-mail: schroe@uga.edu

² Macalester College, Art & Art History
1600 Grand Avenue, St. Paul, MN 55105, USA
E-mail: ericksong@macalester.edu

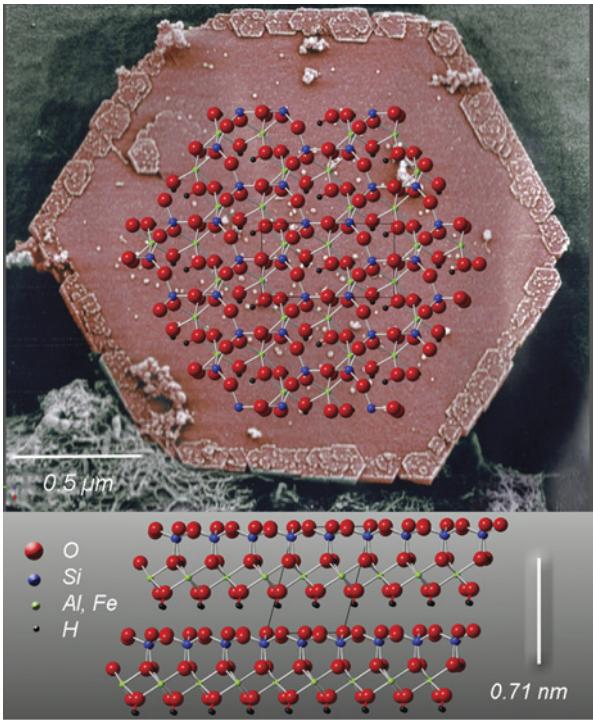


FIGURE 1 (Top) Kaolinite crystal in pseudohexagonal form (false-color image from a scanning electron microscope). Edges are adorned with spiral growth forms, which emphasize the multigenerational nature of kaolin-group minerals. The scale bar is 180 times smaller than the diameter of a human hair. Overlaid on top of the crystal (not to scale) is the atomic structure of kaolinite, showing atom locations parallel and perpendicular (Bottom) to the sheet structure. The bottom image also shows the repeat distance of the 1:1 layer structure. The scale in lower right is about 125,000 times smaller than the diameter of a human hair.

processes on Earth have episodically transitioned their electron acceptors from CO_2 toward O_2 (Lyons et al. 2009; Shock et al. 2010). The exact timing of the first appearance of kaolin is debated; however, it is generally agreed that events such as the emergence of life during the Hadean (Hazen et al. 2008), the Great Oxidation Event during the

Proterozoic, the onset of Paleozoic faunal radiation during the Cambrian, and variations in atmospheric temperatures and CO_2 and O_2 concentrations (Berner 2006, 2009) all influenced kaolin production and preservation rates. The occurrence of kaolin-group minerals on Mars (Bishop et al. 2008) supports the notion of their early appearance on Earth. The modern distribution of kaolinite in ocean sediments shows the importance of climate. Both temperature and rainfall correlate positively with the latitudinal abundance of kaolinite relative to other clay minerals (Fig. 2B).

Kaolin-group minerals are prevalent in well-drained, temperate to tropical soils, where the reaction kinetics favor the formation of halloysite and kaolinite. The occurrence of kaolin-group minerals in soils is environmentally important (Cygani and Tazaki 2014 this issue) and although common, they do not constitute exploitable deposits. The geologic processes that concentrate kaolin-group minerals into economic deposits fall into several categories defined by the parent material and the alteration process that affected them (Murray et al. 1993). Precursor felsic rocks include granites, rhyolitic pyroclastics, and shales. The occurrence of kaolins can be viewed simply as an intermediate stage in a series of hydrolysis reactions involving aluminosilicate rocks (Fig. 2B). Hydrolysis is driven by acidic volcanic/plutonic hydrothermal fluids and/or meteoric water flow influenced by microbial metabolisms, formation hydraulic conductivity, and proximity to the surface. Most economic kaolin deposits form as a result of more than one of these alteration mechanisms. As Earth has evolved toward greater crustal differentiation (i.e. more felsic rocks) and more biological activity on its surface (i.e. more oxidation and organic acid production), the occurrence of large kaolin deposits is generally thought to have increased with time (Fig. 2A). Economic deposits of kaolin are therefore typically hosted in geologically younger rocks (Upper Mesozoic and Lower Cenozoic) and have commonly been modified by Pleistocene to Recent surface weathering (Hurst and Pickering 1997).

Economic kaolin deposits are broadly grouped into (1) primary and (2) sedimentary-rock hosted. Primary kaolins can be subdivided into those that originate in granitic rocks and those that originate in rhyolitic rocks. They are further

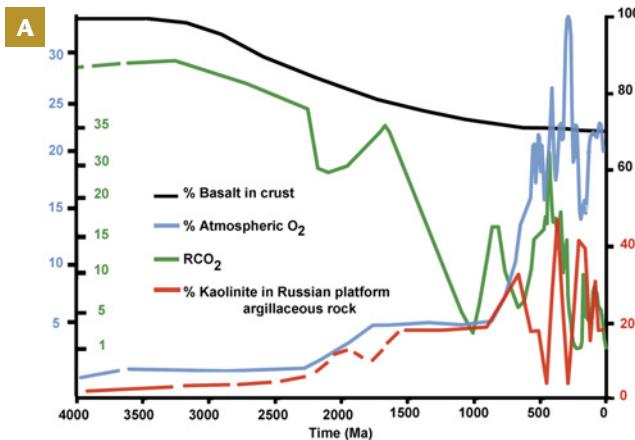
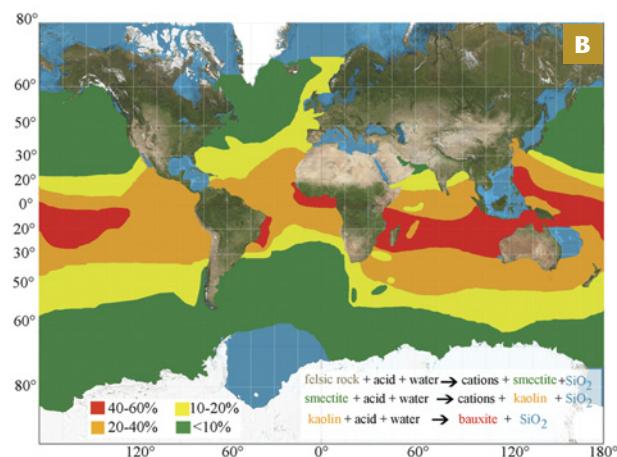


FIGURE 2 (A) Change in abundance (y axis, in percent) of atmospheric and cratonic components compared to the abundance of kaolinite through geological time (Ma = million years). The curves were selected from published works (the dashed lines are interpreted by us): % basalt in crust, Hall and Hughes (1993); atmospheric oxygen, Berner (2009) and Holland (2006); RCO_2 = ratio of CO_2 mass in the past to the present weighted mean for the last one million years, Berner (2006); and % kaolinite in Russian platform argillaceous rocks (Ronov et al. 1990).



(B) Distribution of kaolin-group minerals in modern oceans (modified from Lisitzin 1972). The color-coded zones show percentage relative to the other clay mineral groups, with biogenic and amorphous volcanic sediments not considered. Water, acid, and aluminosilicate-bearing rock are key ingredients to making kaolin. As hydrolysis is dependent on temperature, kaolin-group minerals appear/disappear in a sequence that progressively exports cations and dissolved aqueous silica. Extreme weathering results in bauxite-like deposits, which form under tropical conditions.

subdivided by the extent to which they have been hydrothermally and/or meteorically altered. China and Mexico host large hydrothermally altered granitic residues (Wilson 2004), whereas Japan hosts large hydrothermally altered pyroclastic deposits (Joussein et al. 2005). Primary deposits are located throughout the world and are enhanced by the weathering of volcanic glass, feldspar, and mica by meteoric water. These weathering processes form saprolite extending as deep as 100 m from the surface. Kaolin deposits in Cornwall (England) and Ukraine are perhaps the most widely recognized sources; their origin is attributed to the alteration of granitic rock by hydrothermal and meteoric waters (Murray et al. 1993). A feature common to all these primary deposits is a porous mixture of stack-like kaolinite and tubular halloysite that is low in iron and titania; if buried under appropriate basin conditions, such mixtures can host petroleum deposits.

Sedimentary-rock-hosted kaolins are by far the most concentrated and therefore the most important sources of kaolin ore. Production sites are located in Cretaceous and Eocene shales and sandstones in northern Brazil, the southeastern United States, southern China, and northeastern Australia. The geologic conditions needed to create these unique deposits may not have an exact modern analog; however the deposition of neritic muds proximal to aluminosilicate rocks undergoing intense chemical weathering is likely the first step toward their genesis. Conditions within the sedimentary beds are almost the antithesis of those needed for an economic oil shale deposit. Kaolin shales are extremely poor in organic matter and iron. Postdepositional

uplift of kaolin-bearing shales and sandstones results in further meteoric weathering. The small amount of organic matter and iron sulfides that may be present is oxidized by microbial action (Hurst and Pickering 1997; Shelobolina et al. 2005). During this process the remaining alkali and alkaline earths, iron, and silica are mobilized (Schroeder et al. 2004) and precursor kaolin-group minerals (halloysite and disordered kaolinite) undergo Ostwald ripening (Lowe 1991). Sedimentary kaolins are thus up to 95% pure. Anatase (a titanium-bearing mineral) and iron oxides occur ubiquitously as trace phases in sedimentary-rock-hosted deposits due to the insolubility of Ti^{4+} and Fe^{3+} (Railsback 2003). Variables that affect the final kaolin ore include the initial rock composition, the geologic exhumation history and resulting landscape position (i.e. thickness and permeability of overburden), the hydrologic flux (i.e. climate), and time. These factors conspire to make different types of postdepositional alterations, and industry selectively mines various grades of deposits, often referred to as gray, red, or cream in color and hard or soft in texture (see Kogel 2014 this issue).

KAOLIN IN CULTURAL HISTORY

The first sophisticated cultural use of kaolin dates back over 2000 years to Jingdezhen, which is situated in Jiangxi province in southeastern China. Located thirty miles to Jingdezhen's northeast is Gaoling Shan—translated literally as “high ridge”—and the first mining site for *gaoling tu*, or kaolin clay (Fig. 3). High-tech use of *gaoling tu* started with porcelain production, utilizing what is now known as china clay.



FIGURE 3 (A) Gaoling Shan is a range of mountains in the northern part of Jiangxi province of China. (B) Dongbu Village is a small community situated at one of the entrances to Gaoling National Mining Park. The quaint little village was once a hub for transporting kaolin clay from the mines to Jingdezhen. (C) Off the river small docks once awaited the white kaolin cargo (photo in local kaolin museum © National Geographic Society, 1920). (D) The Tianbao Kiln (dragon kiln), built on the

sloping hillside, is tapered at both ends. Stoking holes progressively preheat successively higher sections, allowing for careful temperature control; three days were often needed to complete a firing. (E) Sculpture of a foreigner and his horse coming from the far west to trade during the Yuan dynasty. Their expressions vividly reflect the cultural and economic exchanges taking place at that time and during the Song dynasty.

The first porcelains were a simple formula consisting of only a feldspathic china stone, or *petunze* in Chinese. *Petunze* was originally found as a weathered, top-layer powder, and the sources were abundant near Jingdezhen. The nonplastic quality of this ground stone made wheel-throwing very difficult and restricted product size. The success rate of kiln-fired pieces was low as they were prone to distortion and collapsed in the kiln due to the instability of the material when shaped into thin objects and fired at 1200°C. The history of ceramics is relatively short compared to traditional Chinese medicine, where one would never use only one herb but rather a combination of ingredients for successful treatment. Applying this principle to ceramics, using only one material when making porcelain was thought to be causing the problem. When the fired porcelain became too soft, they thought that its "yin" was too strong. Ancient Tiwu(体) philosophy focuses on results rather than theory and considers that perception is learned through observation and experience of actions. The application of this philosophy led to one hundred years of experimentation to find the balancing factor—"yang." Near the end of the Song dynasty (1127–1279), a kiln master with the surname He conducted materials experiments in the mountains around the small village of Yaoli. Born into a poor family, Master He was adding a fine-particle-sized white material mined near the surface on Gaoling Mountain. Combining this *gaoling tu* (kaolin) with the china stone (weathered granite) gave the porcelain strength. He did not share his findings but others soon got the same results. During the Yuan dynasty (1279–1368), a dual-formula (binary) porcelain clay body made of approximately 60% china stone and 40% kaolin was developed. These percentages varied depending on the chemical makeup of the material from different mining sources. Alumina-rich kaolin is thought of as the bones of porcelain, while the silica in the china stone is the flesh. Combining the two materials brought the "yang" and "yin" together (FIG. 4).

Near the end of the Southern Song dynasty, exhaustion of the sources for top-layered china stone led to a raw-materials crisis in the porcelain industry. Mining deep into the mountains provided new sources, but artisans could not make porcelain with only this ore, due to its relatively low

sintering temperature. It was the addition of kaolin that allowed the middle- and under-layered china stone to be used, and the porcelain industry flourished. The kaolin allowed the firing temperature to rise, reducing distortion and improving the success rate and quality. The new dual-formula ware became the first true, high-fire porcelain, with firing temperatures exceeding 1300°C. This created great prosperity in the ceramic industry, starting during the Yuan dynasty (1271–1368) and continuing through the Ming (1368–1644) and Qing dynasties (1644–1911). Jingdezhen porcelain was said to be as white as jade, as bright as a mirror, and as thin as paper, and when it was struck, it made a sound as sweet as a *qing*, a musical instrument similar to a chime and made of stone (Ming 2002).

Ancient Mining

Several kaolin deposits were located in the mountains in the Yaoli area, which includes Gaoling Mountain. The first sources were mined, like the china stone, by removing a layer of topsoil. Tunneling and open pit mining were also used. The deep-tunnel mines were triangularly shaped to take advantage of the natural rock strength. Where kaolin resources were plentiful, the cross sections of the tunnel were more irregular, and in mines with large spans, stone poles were used to stabilize the tunnels. The kaolin was brought out of the mountain as damp clumps and was processed near the mine to save costs. Processing required digging a trough into the side of the hill and constructing, on flat ground below, three brick-walled ponds connected by switch gates. The kaolin was first washed down the trough, and the fine kaolin particles overflowed into the first washing pond. There, the coarser particles of quartz, mica, and other impurities settled to the bottom and were held back by the walls as the gate was opened and the water/clay mix drained into the next pond. The overflow from pond to pond continued the purification until only the finest kaolin particles remained. In the last pond the clay was left to partially dry before being pounded into a wooden form to create a *dunzi*, or kaolin brick, weighing approximately two kilograms (kg) each. Similar bricks were made with china stone clay to allow for convenient formulation of the raw materials later, though the china stone was first crushed into a powder using a water-powered trip hammer. Gaoling Mountain workers carried the processed kaolin bricks in baskets seven kilometers down the mountain pathway to docks in the small village of Dongbu (FIG. 3B) along the Yao (East) River, from which it was taken by boat to Jingdezhen and mixed with china stone bricks in the desired proportions.

After He's *gaoling* discovery, news spread quickly and government officials confiscated the Macang mine, which had the best-quality kaolin. During the Yuan and Ming dynasties, this high-quality kaolin was used only for official wares, leaving the lesser-quality kaolin for civil kilns. This monopoly ensured the superiority of imperial ware. During the mid-Qing dynasty, Gaoling Mountain started supplying superior kaolin to both official and commercial kilns, which reenergized the porcelain production and allowed both imperial and commercial wares to flourish. Four large-scale mining sites were managed by four families—the Wang, the Feng, the He, and the Fang. The number-one pit on Gaoling Mountain began production in the Ming dynasty and lasted two hundred years. The largest mine measured 1000 meters in length and 50 meters in width and produced about 1,100,000 tons of kaolin. The Gaoling Mountain operation and other mines around Yaoli village were closed to further mining in 1965, and in 2008 the area was officially reopened as a National Mining Park.



FIGURE 4 The purest kaolin is called *gao bai ni*, or super-white clay, which has limited plasticity. Along with brilliance and whiteness, it can be trimmed to a thinness that allows sculpted walls to be uniquely translucent. This modern porcelain piece was produced from *gaoling tu*. *Yin Yang: Mitosis* by Gary Erickson, H. 20 cm x 38 cm x 28 cm, slipcast porcelain, slip decoration, 2013

Ancient Chinese Influences

The characteristics of Jingdezhen's refined white porcelain were highly sought by Chinese emperors. The first official agency, the Fouliang Porcelain Bureau, was established during the Mongol rule of the Yuan dynasty (1271–1368). At this time, the ceramic centers shifted from the northern to the southern part of China, bringing many experienced ceramic workers to Jingdezhen. The porcelain was mass produced by a very specialized and organized labor force. More than 500 masters and workers were divided among 21 to 23 departments, the most important being kiln masters, potters, painters, and writers of marks. There was also a host of other departments, including clay mixers and sagger makers (Emerson et al. 2000). Soon after, during the late Ming dynasty, there was a dramatic shift towards a market economy, and Jingdezhen began lucratively exporting to India, the Middle East, and Europe. The supply of resources and the location on the Changjiang, a river that connected to Poyang Lake and the Yangtze River, allowed easy and inexpensive transportation to major cities and seaports. At the height of production, there were over one thousand kilns in Jingdezhen.

As Europe had not yet discovered its own sources of kaolin, imported Chinese porcelain was highly admired for its whiteness, thinness, and exquisite painting. In the 17th century, its value exceeded that of gold as a commodity. It was collected only by the aristocracy, which even today feeds the perception that "fine China" is the most precious and expensive, though its production costs may be lower than those using other clays. The French Jesuit missionary priest Francois Xavier d'Entrecolles wrote two letters to his superiors in 1712 and 1722 in which he described Jingdezhen. His letters included detailed descriptions of porcelain-making techniques, which he learned through direct observation, through the help of his converts, and by consulting Chinese printed information. The letters were published in Europe and led to an increased interest in porcelain-making techniques. Soon,

the ceramic industry in Europe was growing by borrowing the Chinese techniques. The export business in China then saw a marked reduction (Emerson et al. 2000).

Contemporary Chinese Influences

Though Jingdezhen kaolin is historically important in the development of porcelain, the quality of its kaolin was actually very poor for ceramics as its alumina content was lower than in other kaolins. Gaoling Mountain kaolin is now only symbolically important because it was used in the first successful experiments of combining china stone and kaolin. Beginning in the Qing dynasty (1644–1911), kaolin began being shipped to Jingdezhen from many places in China. Contemporary kaolin mining sites are located in Fujian, Guangdong, Guangxi, Hebei, Hunan, Jiangsu, Yunnan, and Jiangxi provinces. The majority of kaolin used in Jingdezhen today comes from Fuzhou in Fujian province and from Xingzi town of Jiujiang city, located only 200 km away. Chinese and international ceramic artists still travel to Jingdezhen to utilize the special attributes of its super-white clay (FIGS. 4, 5).

The allure of Chinese porcelain to Europeans promoted efforts to duplicate the production process in places like Cornwall, England. William Cookworthy discovered Cornwall kaolin deposits in 1745. However world-renowned Josiah Wedgwood had actually bought small consignments of kaolin from Georgia, USA, beforehand. It was not until Wedgwood acquired the ability to accurately control and measure kiln temperature that he founded his company in 1759 (Hudson 1969). Major exports from Georgia did not begin until the early 1960s. FIGURE 5 gives a timeline of changing pigmenting and firing technology, each change resulting in more vividly and intricately designed wares. Just as varied occurrences of kaolin and episodical economic deposits formed over Earth time, so have the art and sculpture of porcelain episodically changed with cultural time.



FIGURE 5 Eight ceramic wares depicting the dominance of Chinese influences and stylistic changes through time. (A) Chinese, Northern Song dynasty, late 11th–12th century, Ding ware. (B) Chinese, Song dynasty, 12th century, Jingdezhen ware. (C) Chinese, Yuan dynasty, 14th century, Jingdezhen ware. (D) Italian, Deruta, ca 1520–1525, maiolica, tin-glazed and cobalt blue. (E) Chinese, Ming dynasty, ca 1610–1620, Jingdezhen Kraak

blue underglaze. (F) Chinese, Qing dynasty, 1723–1735, Jingdezhen ware, cobalt blue underglaze and yellow enamel overglaze. (G) German, Meissen factory, ca 1725–1730, hard-paste porcelain with blue underglaze, enamel colors, and lustered. (H) English, modern ca 2011, Wedgwood earthenware. Details of plates in photos A–G (and photo credits) can be found in Emerson et al. (2000).

FUTURE PROSPECTS

The importance of kaolin through human history is intertwined with its place in Earth evolution, and this relationship will continue into the foreseeable future. A Web of Science search using the term *kaolin* for the past sixty years reveals a trend of 103, 204, 570, 871, 2176, 5974, and ~10,000 appearances, respectively, for ten-year increments up to the present. This exponential trend predicts >20,000 articles in the next decade. The fields of publication are also diversifying, from the geological and materials sciences to the environmental and medical sciences. In this issue, Balan et al. (2014) review the styles of kaolin-group layer-stacking defects and how this subject bears on industrial applications and the use of kaolins as environmental recorders. Kogel (2014) discusses concerns about energy efficiency, sustainability, and environmental awareness in the industry and shows how these concerns have led to advances in mining, processing, and reclamation practices. Cygan and Tazaki (2014) examine how kaolin minerals are being probed using computational chemistry and new spectroscopic tools to expand their applications

and to understand their significance in biology and our environment. Detellier and Schoonheydt (2014) note the crystallographic and elemental uniqueness of kaolin and explore how kaolin minerals can be nanocomposited to create material with novel properties. Finally, Williams and Hillier (2014) follow the curiosity of kaolin geophagy and its use in medicine, and they raise the following questions: what long-term health benefits and/or harm are associated with such practices, and what might kaolin offer in the development of new pharmaceuticals and disease treatment? The articles in this issue of *Elements* and the references therein indicate a bright future for kaolin.

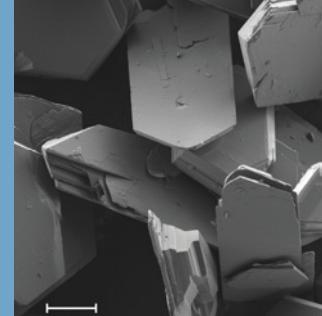
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Kaolin-Group Minerals: From Hydrogen-Bonded Layers to Environmental Recorders



Crystals of
St. Claire dickite.
Scale bar: 40 μm .

Etienne Balan¹, Georges Calas¹, and David L. Bish²

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Kaolin-group minerals typically form as a result of hydrothermal alteration and/or weathering processes. They occur in environments as diverse as tropical soils, continental sedimentary deposits, and altered crustal rocks. They have also been detected on the surface of Mars. Given their prevalence, they have attracted the attention of researchers in materials chemistry, environmental geochemistry, and high-pressure mineral physics. Their structure and related properties have been studied for about a century, and these studies reflect advances in experimental techniques, modeling approaches, and concepts in mineralogy. Among key features of their structure are the predominance of 2-D stacking defects and the peculiar role of H-bonding in the control of their polytypism.

KEYWORDS: kaolin, stacking order, H-bonding, vibrational spectroscopy, weathering processes

INTRODUCTION

Finely divided layered silicates of the kaolin group belong to the “clay minerals” family. However, the high degree of order and chemical purity of many kaolin minerals are unusual characteristics for clay minerals. Kaolin-group minerals have thus been the subject of detailed investigations using modern approaches of mineral physics, ranging from quantum-mechanical modeling to the investigation of phonon anharmonic properties. As all clay minerals, they display variability in their real structure, including styles of layer-stacking defects, differences in particle size and shape, and the occurrence of minor amounts of impurities. This variability bears on a number of industrial applications and can provide information on the physical-chemical conditions that prevailed in diverse geological environments (e.g. Murray 1988). The range of structures within kaolin-group minerals has been extensively investigated, as reviewed by Giese (1988). We summarize some important features and discuss recent advances in our understanding of the structural and spectroscopic properties of kaolin-group minerals.

POLYTYPES OF KAOLIN-GROUP MINERALS IN NATURAL ENVIRONMENTS

The building blocks of the fundamental kaolin layer structure consist of layers of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$ composed of superposed sheets of silica tetrahedra and alumina octahedra (FIG. 1A), as first proposed by Pauling (1930). The cohesion

between these so-called 1:1 layers is ensured by weak H-bonds between three nonequivalent OH groups (inner-surface OH) located on top of the aluminous sheet and bridging oxygens of the basal silicate plane of the adjacent layer. An OH group (inner-OH) is located within the layers, between the Si and Al sheets. Since the original structure solution of Pauling (1930), the determination of the kaolinite structure took more than sixty years to refine. This long interval of time is explained by two factors, namely, (1) the occurrence of hydrogen atoms, whose positions are difficult to determine using X-ray methods, and (2) the small grain size of kaolinite. Using

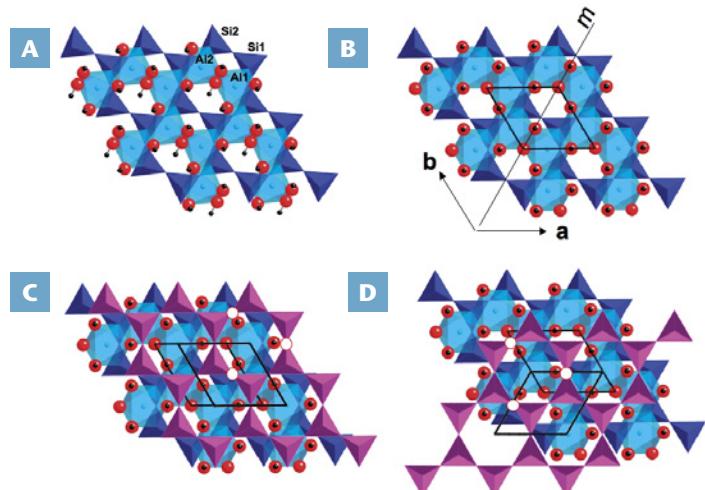


FIGURE 1 Structure of kaolin-group minerals. (A) Dioctahedral layer of kaolinite. Note the two nonequivalent aluminum sites. Oxygen and hydrogen atoms belonging to hydroxyl groups are represented as red and black spheres, respectively. Compared with the ideal layer (B), the Al sites are contracted and the vacant site is expanded. The three inner-surface groups are oriented almost perpendicular to the layer, whereas the inner-OH group is oriented horizontally. (B) Ideal dioctahedral layer constructed by removing one cation from one of the octahedral sites of a trioctahedral layer. The three-fold symmetry decreases to mirror symmetry. Layer translations along the symmetric \mathbf{a} or \mathbf{b} axes lead to enantiomorphic structures. (C) Ideal layer stacking in kaolinite. The adjacent layer is horizontally shifted by $\mathbf{a}/3$. For clarity, the Si sheet of the adjacent layer is represented in purple. (D) Ideal layer stacking in dickite. The adjacent layer is horizontally shifted by $\mathbf{b}/3$ and rotated by $2\pi/3$. In kaolinite and dickite, three H-bonds can form with three Si-O-Si bridging oxygen atoms (indicated as white circles).

1 Institut de Minéralogie, de Physique des Matériaux, et de Cosmochimie, Sorbonne Universités, UPMC Université Paris 06 CNRS UMR 7590, IRD UMR 206, MNHN, F-75005, Paris, France E-mail: Etienne.Balan@impmc.jussieu.fr; Georges.Calas@impmc.jussieu.fr

2 Department of Geological Sciences, Indiana University 1001 East 10th Street, Bloomington, IN 47405-1405, USA E-mail: bish@indiana.edu

X-ray diffraction (XRD) it was recognized that the kaolinite structure is triclinic, and a conventional base-centered pseudomonoclinic unit cell was proposed (Brindley and Robinson 1946). However, the base-centering, which depends on knowing the hydrogen positions, was not reliably established until Bish (1993) used Rietveld refinement and low-temperature neutron diffraction data. Synchrotron XRD performed on micrometer-sized kaolinite single crystals has since confirmed the kaolinite structure (Neder et al. 1999).

The layered structure of kaolinite facilitates the occurrence of ordered polytypes, i.e. structures only differing by their stacking scheme, as well as variations in stacking order. Ordering schemes correspond to the different ways to stack the layers under the constraint that interlayer H-bonding maintains energy efficiency. Dickite and nacrite are two ordered polytypes observed in nature. Both have monoclinic structures based on two-layer repeats. The structure of dickite, including H atom positions, was refined by Bish and Johnston (1993) using neutron powder diffraction. The structure of the less-common nacrite was refined by Zheng and Bailey (1994). Halloysite is a common, naturally occurring kaolin-group mineral (Giese 1988; Joussein et al. 2005) showing characteristic tubular or spherical particle shapes (Fig. 3 in Williams and Hillier 2014 this issue) and H₂O molecules in the interlayer space.

According to Mercier and Le Page (2008), layer stacking in kaolin-group minerals can be understood by considering a more symmetrical trioctahedral-like layer ($31m$ three-fold symmetry), which leads to eight distinguishable stacking schemes. The removal of one cation from this trioctahedral layer leads to an ideal dioctahedral layer that displays a mirror plane (Fig. 1b) and increases to 36 the number of distinguishable stacking schemes. Among these, 20 are energetically distinguishable transformations (EDT), whereas 16 enantiomeric EDT* are mirror-related but not identical to an EDT. Assuming negligible interactions between nonadjacent layers, the low-energy polytypes can be obtained by considering either the repeated application of one EDT or the successive application of an EDT and its EDT*. This leads to 20 structures with single-layer repeats and to 16 two-layer structures. Three of the inferred structures correspond to the naturally occurring polytypes. Starting from the ideal models (Fig. 1a–c), the structures optimized by quantum-mechanical calculations are reasonably close to their experimental counterparts (Mercier and Le Page 2008). Dickite and kaolinite are energetically close to each other, whereas nacrite appears less stable by ~6 kJ/mol. Given their overall structural similarity, it is unlikely that the model approximations affect the relative stability of the polytypes. However, the theoretical values differ from the experimental calorimetric data, which indicate that kaolinite is more stable than dickite by ~18 kJ/mol (Fialips et al. 2003). The discrepancy between theory and experiment remains not understood.

HIGH-PRESSURE POLYTYPES OF KAOLIN-GROUP MINERALS

In addition to crystallographic considerations, the fate of hydrous minerals in subduction processes and related water recycling to the inner Earth has motivated investigations aimed at determining the high-pressure (high-*P*) properties of these H-bonded systems. Johnston et al. (2002) observed that pressure affects the polytypism in kaolin-group minerals and identified a new high-*P* polytype of dickite stable above 2 GPa with distinct structural properties (Dera et al. 2003). The reversible phase transition from dickite to high-*P* dickite corresponds to a layer translation removing Al-Si superposition between adjacent layers and leading to a different H-bonding pattern. Layer translations

appear as a general mechanism of pressure-driven phase transition in kaolin-group minerals (Dera et al. 2003).

More recently, Welch and Crichton (2010) identified two high-*P* polytypes of kaolinite. Kaolinite-II is stable between 3.7 and 7 GPa and corresponds to a theoretically predicted polytype. The transition from kaolinite to kaolinite-II involves an irreversible layer-translation mechanism, geometrically analogous to the low-*P* to high-*P* dickite transformation. Kaolinite-III is observed above 7 GPa and directly transforms on decompression to kaolinite at 1 GPa. It belongs to a different polytypic family, resulting from a different layer-slipping mechanism at high pressure. Remarkably, kaolinite-III was theoretically predicted using *ab initio* methods (Mercier and Le Page 2009) before its experimental observation by Welch and Crichton (2010). In kaolinite-III, two of the inner-surface OH groups are located just below the basal Si atoms of the adjacent layer and adopt an in-plane orientation. Such disruption of interlayer H-bonding is energetically unfavorable at low pressure, but the volume contraction of kaolinite-III of about 3% plays a stabilizing role at high pressure.

HYDROXYL GROUPS AS LOCAL PROBES OF THE LAYER-STACKING PATTERN

Although the H-bonds in the interlayers of kaolin-group minerals are weak, they play a key role in controlling the layer stacking. By providing direct insight into the properties and geometry of OH groups, vibrational infrared (IR) and Raman spectroscopies are important tools for the study of kaolin-group minerals (e.g. Farmer 1974; Johnston et al. 1998, 2008).

The OH-stretching spectrum of kaolinite displays four high-frequency bands (Fig. 2a) (Farmer 1974). These OH-stretching modes are not coupled to lower-frequency vibrational modes and can be interpreted by considering only the displacement of the corresponding oxygen and hydrogen atoms. The lower-frequency band at 3620 cm⁻¹ corresponds to the inner-OH group. This OH group is weakly affected by the layer stacking and leads to a narrow band polarized in the (a,b) plane. The three higher-frequency OH groups are H-bonded to the adjacent layer and are oriented almost perpendicularly to the layer plane. In an idealized layer (Fig. 1a), they are related to each other by three-fold symmetry. As Farmer (1974) elegantly stated, if the three-fold symmetry were perfect, the infrared spectrum would display only two bands: one intense band polarized perpendicularly to the layer, corresponding to the in-phase stretching of the three inner-surface OH groups, and one weaker band with in-plane polarization and related to two degenerate modes involving out-of-phase stretching of the inner-surface OH groups. As the three-fold symmetry is not exact in kaolinite, the degenerate mode splits to give two weaker bands at 3652 and 3669 cm⁻¹. The in-phase vibration occurs at ca 3697 cm⁻¹. Quantum-mechanical calculations of the kaolinite IR spectrum (Balan et al. 2001) confirm this earlier interpretation by Farmer (Fig. 2b).

The modification of layer stacking in dickite and nacrite weakens one interlayer H-bond, and the corresponding OH group is inclined with respect to the vertical. These modifications affect the OH-stretching spectra (Fig. 3). The inclined OH oscillates at higher frequency, and the two remaining OH groups lead to a strongly absorbing in-phase stretching mode and a weakly absorbing out-of-phase stretching mode at lower frequency (Farmer 1974). This interpretation was later confirmed by quantum-mechanical calculations (Balan et al. 2010 and references therein). In the two-layer structure of dickite, coupling of OH motion between adjacent layers due to the long-range character of electrostatic interactions leads to splitting of the high-frequency band ascribed to the inclined OH group (Balan

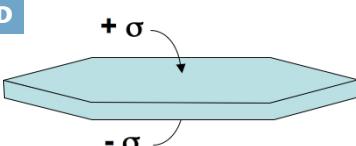
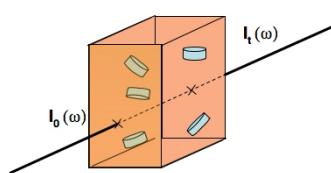
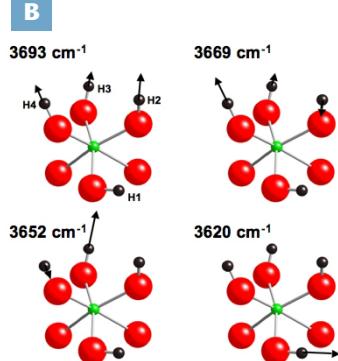
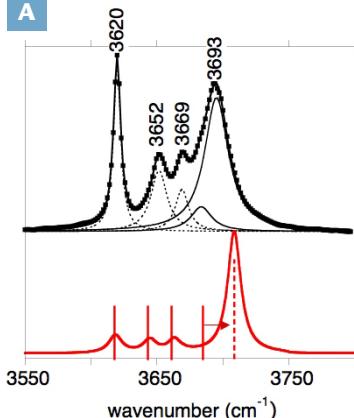


FIGURE 2

Infrared (IR) spectra of the OH-stretching modes of kaolinite. (A) IR absorption spectrum of OH-stretching modes of a well-ordered and coarse kaolinite sample from Decazeville, France (top). The four absorption bands were fitted using an additional contribution to match the broader high-frequency band. The theoretical absorption spectrum computed for a platy particle in a KBr matrix is reported in red (bottom). The assignment of the observed bands in terms of vibrational modes is straightforward. The theoretical high-frequency band is shifted with respect to the vibrational frequency computed with a zero macroscopic electric field (vertical bars). This type of shape-dependent effect explains the broadening of the high-frequency band in experimental spectra (Balan et al. 2001) (B) Atomic displacement patterns of the four OH-stretching modes corresponding to the theoretical spectrum. As predicted by Farmer (1974), the high-frequency mode corresponds to the in-phase vibration of the three inner-surface OH groups. (C) Experimental geometry of a transmission experiment. $I_0(\omega)$ and $I_t(\omega)$ are the frequency-dependent incident and transmitted IR intensity, respectively. Ideally, the sample consists of small kaolinite platelets diluted in a KBr matrix. (D) Vibrational ionic displacements perpendicular to the basal plane of the platelets induce the formation of oscillating surface charges ($+/- \sigma$) on the basal faces, which create a macroscopic electric field in the particle. This field is responsible for the shift of the absorption band observed in (A).

et al. 2010). Although weak, the coupling of the stretching motion of different OH groups is a key feature of the vibrational spectra of kaolin-group minerals.

The high- P polytypes of dickite and kaolinite exhibit characteristic OH-stretching bands (Johnston et al. 2002; Welch et al. 2012). For example, the IR spectrum of kaolinite-III exhibits a characteristic feature at 3595 cm⁻¹, which is related to the single OH group still sharing an H-bond with the adjacent layer (Welch et al. 2012). Simultaneously, the tilting of the inner-OH group with respect to the layer plane weakens the H-bonding interactions and its stretching frequency increases to 3710 cm⁻¹.

Vibrational spectroscopies are thus efficient tools for identifying the polytypes of kaolin-group minerals. In particular, kaolinite's characteristic OH-stretching bands make it detectable in low concentration (<1 wt%). Given the small amount of sample required and coupled with μm -range spatial resolution (e.g. Johnston et al. 1998), these spectroscopic tools are complementary to diffraction-based techniques. The anharmonic character of OH-stretching modes also leads to diagnostic two-phonon absorption bands in the near-infrared range. These combination and overtone bands facilitate the remote sensing detection of kaolin-group minerals, including by satellite on the surface of Mars (Bishop et al. 2008).

PARTICLE-SHAPE EFFECTS ON THE VIBRATIONAL SPECTRA OF KAOLIN-GROUP MINERALS

Interactions between neighboring OH groups lead to coupling of atomic motions in the stretching vibrational modes. However, macroscopic electrostatic interactions related to the collective oscillating motion of ions in the whole clay particle are also observed in the IR and Raman spectra of kaolin-group minerals (e.g. Farmer 1974; Balan et al. 2001, 2010). The collective ionic motions polarize the particle, and an oscillating macroscopic (i.e. constant over the unit cell) electric field is generated by the charge density appearing at the surface of the polarized particle (Fig. 2D). In turn, the induced electric field affects the ionic motion and is responsible for the shape-dependent shift and broadening of specific vibrational bands. Accordingly, these effects also depend on the aggregation state of the particles and on the dielectric properties of the surrounding medium, generally a KBr matrix (Fig. 2C).

For example, the high-frequency IR absorption band of highly ordered and coarse kaolinite is broader than that of more finely divided samples. This somewhat counter-intuitive observation is explained by the fact that in the coarser samples the vibrational frequency ranges from the frequency determined with a zero macroscopic field to that with a maximum induced-depolarization field. The latter case corresponds to a higher frequency observed for a thin platy particle geometry (Fig. 2A). Accordingly, the same band is narrowed and shifted to higher frequency in fine samples also with a platy shape. The quality and chemical purity of many kaolin samples thus make it possible to observe subtle physical effects in their vibrational spectra. These effects cannot be neglected when discussing minor variations among samples.

STACKING DISORDER: A MAJOR FEATURE OF KAOLIN-GROUP MINERALS

Kaolin-group minerals often depart from their ideal structures. They may have a significant amount of stacking defects due to the fact that modifications of the H-bonding pattern change the energy by a few kJ/mol (i.e. comparable to room-temperature thermal energy). Stacking defects are related to the crystal-growth mechanisms and provide information on the physical-chemical conditions during mineral formation. They also influence the thermal stability and surface properties of kaolin-group minerals.

The nature of stacking disorder in kaolin-group minerals has been widely debated (e.g. Brindley et al. 1986; Giese 1988; Bookin et al. 1989; Plançon et al. 1989). The debate stems in part from the complex occurrence, in a single sample, of different kaolin-group minerals that have different degrees of disordering and particle size (e.g. Plançon et al. 1989; Bish and Chipera 1998). Layer-stacking disorder has been examined by XRD and IR spectroscopy, with considerable effort focused on quantitative modeling of XRD patterns (Plançon et al. 1989). XRD models are based on changes in relative layer orientations, modifying the position of the vacant octahedral site, and on specific interlayer translations. For example, stacking defects in kaolinite likely involve enantiomorphism [$b/3$ translation of the ideal layer (Fig. 1), corresponding to the t_2 translation of Bookin et al. (1989)] or the occurrence of dickite-like domains. The narrowing and differential shift of IR absorption bands down to 10 K (Fig. 3) reveal specific features

that can be ascribed to dickite-like or nacrite-like OH configurations (Johnston et al. 2008). At low temperature, even well-ordered kaolinite and dickite samples display minor features due to few short stacking sequences corresponding to another polytype (FIG. 3). The occurrence of less-stable nacrite-like configurations suggests that a large variety of stacking defects with stability intermediate between kaolinite and nacrite (Mercier and Le Page 2008) may occur in disordered samples. Some of these stacking defects could leave the OH configuration unaffected, which is difficult to distinguish using the vibrational spectra characteristics.

A breakthrough in the investigation of stacking defects was achieved by Kogure and Inoue (2005), who directly imaged defects in large crystals from hydrothermal and sedimentary deposits using high-resolution transmission electron microscopy. Their work revealed the occurrence of Bookin's t_2 translation and the t_0 translation [i.e. $2\mathbf{a}+\mathbf{b}/3$] translation of the ideal layer of FIGURE 1]. Dickite or kaolinite domains were also observed among stacking sequences dominantly corresponding to the other polytype (FIG. 4). Importantly, the defect type depends on the sample origin, and the observation of long-period polytypes underlines the role of spiral growth in the formation of stacking defects (see also FIGURE 1 in Schroeder and Erickson 2014 this issue).

KAOLIN-GROUP MINERALS AS RECORDERS OF ENVIRONMENTAL PROCESSES

The structure of kaolin-group minerals depends on the physical-chemical conditions prevailing during their formation. As a result, it can provide important information on past environments on the Earth's surface and alteration processes in the continental crust. The real structure not only includes the stacking defects discussed above, but

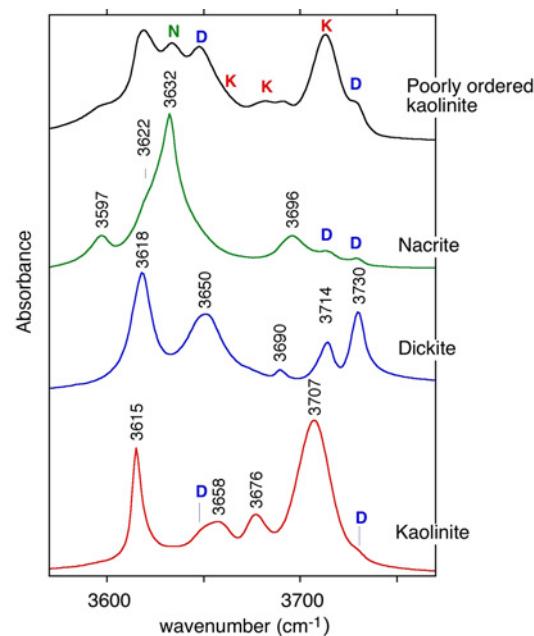


FIGURE 3 Low-temperature infrared absorption spectra of kaolin-group mineral samples: kaolinite (KGa-1) from Georgia, USA; dickite from Nowa Ruda, Poland; nacrite from Sweden; poorly ordered kaolinite from Manaus, Brazil. The spectra were recorded at 10 K in transmission geometry using dilution in KBr disks. The poorly ordered sample reveals contributions from kaolinite-like (K), dickite-like (D), and nacrite-like (N) stacking sequences. The ordered nacrite and kaolinite samples also reveal minor contributions from dickite. The band at 3690 cm^{-1} observed in the dickite sample displays a distinct anharmonic character that has been tentatively ascribed to a kaolinite-like configuration (Balan et al. 2010).

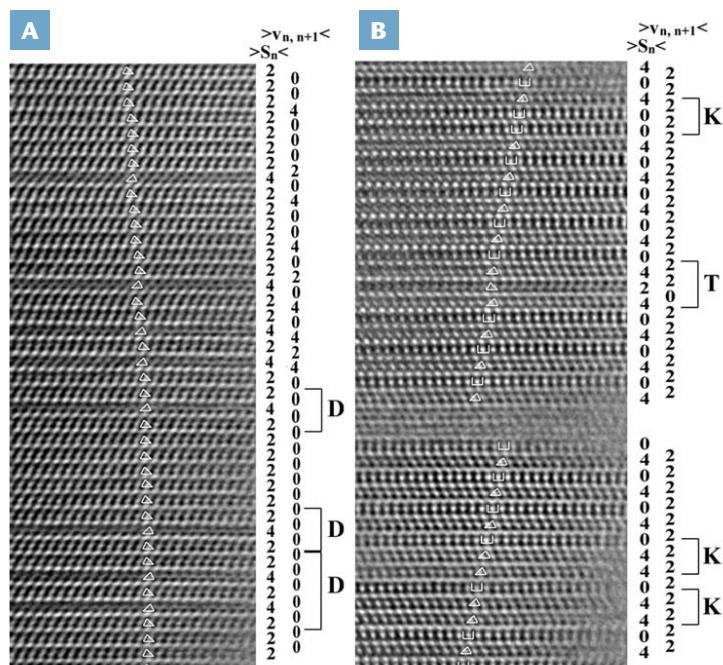


FIGURE 4 High-resolution transmission microscope (TEM) images displaying (A) domains of dickite in a kaolinite-dominant stacking sequence and (B) domains of kaolinite in a dickite-dominant stacking sequence (from Kogure and Inoue 2005). The indices on the right indicate the orientation of the layer ($>S_n<$) and the horizontal shift between the layers ($>V_{n,n+1}<$). D: dickite stacking sequence; K: kaolinite stacking sequence; T: twin fault.

also a diversity of particle shapes and sizes, as well as a number of point defects and chemical impurities (Muller et al. 1995).

Kaolinite particles range from large hexagonal platelets to small anhedral particles (FIG. 5). Lath-shaped particles, elongated along the \mathbf{a} axis, are also observed (e.g. Kogure et al. 2005). Kaolinite platelets are often stacked together to form kaolinite "booklets." Large crystals are usually observed in environments enabling slow crystal growth from slightly supersaturated solutions, such as those in sedimentary deposits, or under the higher-temperature conditions of hydrothermal deposits promoting the development of equilibrium shapes. In contrast, soil kaolinites usually display much smaller particle sizes. Many samples display kaolinite with contrasting particle sizes and shapes (FIG. 5). The relation between the particle size and the occurrence of stacking defects depends on the aqueous environment, reaction kinetics, and precursors. In lateritic soils, topsoil kaolinites are small and disordered, whereas kaolinite samples collected at the bottom of the weathering profiles (saprolite) display larger size and more ordered stacking (Fig. 5). The specific roles of factors such as solution supersaturation, solution composition, soil porosity, and the occurrence of organic matter have still to be determined. In contrast, some hydrothermal samples display an inverse relation between particle size and layer-stacking order. This behavior could stem from the interaction between different spiral hillocks and two-dimensional nuclei on the well-developed basal face of large crystals (Kogure and Inoue 2005). Dickite and nacrite usually display larger particle sizes owing to their specific formation environments (e.g. geothermal fields). Recently, Kogure et al. (2005) and Kameda et al. (2005) used electron backscattered diffraction (EBSD) to investigate the interplay between kaolinite particle shape and stacking pattern. Although restricted to the investigation of large particles, this method opens new possibilities for the investigation of structure versus property relations for single particles.

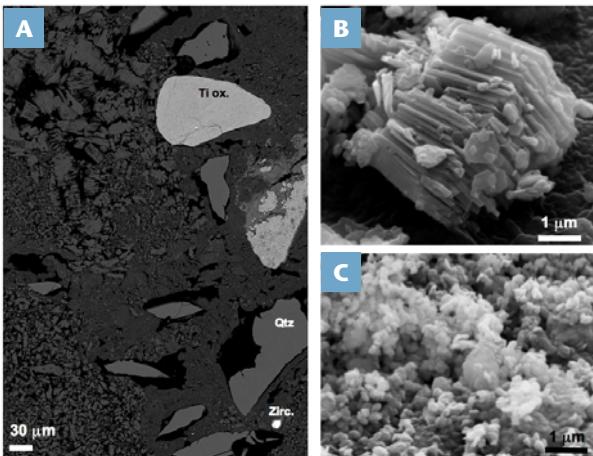


FIGURE 5 Scanning electron microscope images of a kaolin sample from the Manaus area, Amazon basin, Brazil. (A) Image in backscattered electron mode of a section displaying residual minerals (quartz, Ti oxides, zircon) in a kaolinite matrix. The kaolinite matrix displays two types of particles: large kaolinite booklets (e.g. upper left) and fine kaolinite particles in a more homogenous matrix. (B) Image in secondary electron mode of large kaolinite crystals from sedimentary layers at the bottom of a lateritic profile. (C) Image in secondary electron mode of small kaolinite crystals from a lateritic topsoil.

Regarding the chemical impurities in kaolin-group minerals, a number of studies have focused on transition elements, among which iron is the most common. As kaolin-group minerals usually have a greater chemical purity than other clay minerals, it is often difficult to determine whether the impurities occur in the mineral structure or in associated minor phases. To this end, spectroscopic methods are used, including vibrational spectroscopy, electron paramagnetic resonance (EPR), nuclear magnetic resonance spectroscopy (NMR), and diffuse reflectance UV-visible spectroscopy.

For example, the OH-stretching IR spectrum often reveals minor amounts of cationic substitutions at the Al site, lowering the frequency of the inner-OH stretching band. The weakness of the signal attests to the low extent of substitutions, but its quantitative use is made difficult by band overlap as well as by the broadening effects in disordered samples. In contrast, EPR is sensitive and chemically selective. It allows detection of dilute transition elements occurring in paramagnetic valence states (e.g. Fe^{3+} , Cr^{3+} , Mn^{2+} , VO^{2+}). Small magnetic phases display a less-informative broad superparamagnetic EPR signal, but their effects have been detected by solid-state NMR. EPR provides only partial information on the

distribution and speciation of impurities. A number of studies have dealt with iron ions, indicating the substitution of Fe^{3+} for aluminum in the two nonequivalent sites of kaolinite. The Fe^{3+} EPR spectrum is affected by minor structural distortions and indirectly probes the occurrence of stacking defects in disordered samples (Muller et al. 1995). However, no evidence has been found for a direct effect of substituted Fe^{3+} on the formation of stacking defects. Detection of Mn^{2+} or VO^{2+} is less common, and these ions have been interpreted as records of specific redox conditions. The observation of Mn^{2+} ions in kaolinite from lateritic crusts may record fluctuations of the groundwater table, whereas vanadyl ions often observed in sedimentary rock-hosted kaolins may trace kaolin diagenesis and maturation of organic matter (Muller et al. 1995). Crandallite-group minerals and isomorphously substituted anatase are ubiquitous at trace levels in sedimentary rock-hosted kaolins, and each of these is known to bear trace amounts of transition and rare earth elements.

RADIATION DAMAGE IN KAO LIN-GROUP MINERALS, RADIOACTIVE DOSIMETRY, AND KAO LINITE DATING

The sensitivity of EPR spectroscopy enables detection of unpaired electrons corresponding to native radiation-induced damage (Muller et al. 1995; Allard and Calas 2009). These electronic point defects are produced by ionizing radiation, which occurs in the environment due to the decay chains of radioactive isotopes. The EPR spectrum

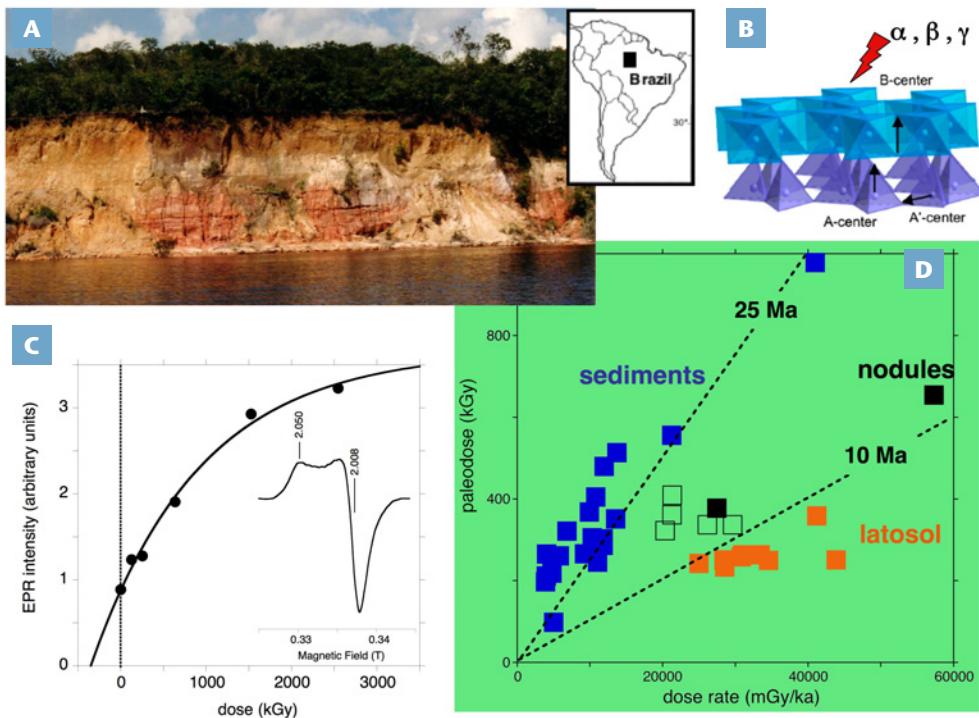


FIGURE 6 Weathering processes and kaolinite dating (after Balan et al. 2005). (A) Lateritic profile developed on sedimentary kaolin on the border of the Rio Negro, Manaus area, Brazil (inset map). The section is ~30 m high. The lateritic soil corresponds to the ~6 m thick yellow-brown layer at the top of the profile. The color of sedimentary kaolin layers varies from white to red, depending on the associated iron oxides (hematite). (B) Orientation of the principal axis of the g-tensor (which relates the magnetic moment of the defect to its electron spin) and assumed location of the paramagnetic radiation-induced defects in kaolinite (after Allard and Calas 2009). (C) Variation of electron paramagnetic resonance (EPR) intensity related to radiation-induced

defects as a function of experimental irradiation dose. Extrapolation of the dosimetry curve to zero makes it possible to determine the paleodose, that is, the radiation dose recorded by the kaolinite sample since its formation. Inset: EPR spectrum of the radiation-induced defects. The g values are indicated. These defects correspond to electron holes located on the oxygen sites of the kaolinite structure. (D) Paleodose recorded by kaolinite as a function of estimated present-day dose rate. Dotted lines represent isochrons at 25 Ma and 10 Ma. Blue: sedimentary layers; open symbols: transition levels; orange: lateritic soil samples; black: kaolinite from iron nodules in lateritic soil.

of the defects depends on their atomic-scale environment (Fig. 6). Isochronal annealing experiments have shown that some of these (A-centers) are stable at ambient temperature, with a lifetime of $\sim 10^{12}$ years. The defect concentration can be calibrated as a function of the radiation dose by artificial irradiation experiments, quantifying the natural dose responsible for the native defects (the paleodose). The paleodose depends on the time elapsed since kaolinite formation and on the environmental radioactive dose rate. This dose rate can be assessed from radionuclide concentrations or directly measured.

Two scenarios can then be envisioned depending upon the sample's geological setting. If the age of kaolinite formation can be independently determined, the paleodose provides information on temporal variations of the dose rate compared with the present-day value. This approach has revealed past uranium migration in natural analogues of high-level nuclear waste repositories, such as the Nopal uranium deposit, Chihuahua, Mexico (Muller et al. 1995). On the other hand, if the dose rate is assumed to be time independent (e.g., when radionuclides are sequestered in resistant minerals), an age can be assessed for kaolinite formation. The timing of kaolinite transformation has been

investigated in lateritic profiles developed on continental, late-Cretaceous sedimentary formations of the Manaus area, Amazon basin, Brazil (Balan et al. 2005). The ages obtained for the sedimentary layers attest to diagenetic processes after sediment deposition. The topsoil samples display more recent ages and low crystal order, indicating transformation of the sediment kaolinite by dissolution/precipitation. However, their defect concentrations indicate that their formation does not correspond to present-day conditions but more likely to older weathering stages.

Determination of their defect structure offers various ways of identifying different generations of kaolinite in a soil section, or even in a single kaolin sample. Combined with stable isotope geochemistry, the defect structure of kaolin-group minerals should provide original information on the conditions that prevailed over time in the alteration environments of the Earth's surface.

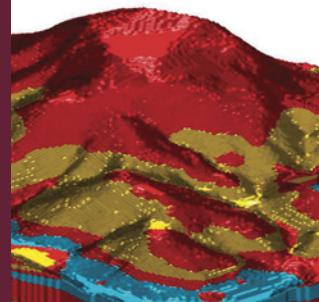
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Mining and Processing Kaolin



Jessica Elzea Kogel*

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Kaolin is used in many consumer products and as a functional additive and process enabler in manufacturing. It is typically extracted from open-pit mines that range from small to very large scale (tens to hundreds of thousands of dry metric tons produced per year). Ore processing consists of removing impurities, engineering particle size and shape, and enhancing certain properties through thermal and chemical treatment. In addition to the technical aspects of mining and processing, the social, environmental, and economic impacts of kaolin production are managed at each stage of the mining life cycle. Discussed herein are aspects of the history of kaolin mining, the classification of kaolin mines, the processing of kaolin, and the life cycle of mining.

KEYWORDS: kaolin mining, sustainable development, mining life cycle, mineral processing

A HISTORICAL VIEW OF KAOLIN MINING, PROCESSING, AND USES

Kaolin, a highly versatile industrial mineral, is mined and processed for diverse end-use markets. Its versatility derives from its naturally occurring range of crystal shapes, sizes, and layer structures. These attributes, along with desirable rheological, chemical, and optical properties, give kaolin its value as an industrial raw material. Kaolin has limited utility in its raw form, and the majority of end-use applications require a refined product derived from a combination of controlled mining and selective processing to engineer specific properties.

Kaolin mining began in the Neolithic when early humans discovered that the material could be used as a white pigment for painting and decoration. These miners devised a simple process to transform the raw mineral into a form that could be more readily applied to surfaces. The process started with digging kaolin from river banks, drying it, grinding it into a fine powder, and finally mixing it with various binders, including animal fat, saliva, water, and blood. For thousands of years after the first kaolin-based paint was placed in the hands of prehistoric artists, kaolin mining and processing barely changed. Small advances were made as new applications were discovered, but the basic process remained more or less the same. In some parts of the world, the same small-scale mining methods that provided clay for cave art are still employed today to extract clay for mud huts, earthenware pottery, and handmade tile. About 2000 years ago the Chinese exploited kaolin for higher-tech, small-scale porcelain production (Schroeder and Erickson 2014 this issue).

It wasn't until the industrial revolution that the first significant technological changes took place and large-scale mechanized methods became available. These new technologies led eventually to the development of the most important commercial kaolin-mining districts in operation today. They are in the southeastern United States, northern Brazil, and the United Kingdom (Cornwall). Kaolin from these regions is shipped worldwide. Many small kaolin mining operations can be found on most every continent. The vast majority of these small mines serve local markets.

Over the past 50 years there have been continuous advances in the way we mine and process kaolin. Much of this has been market driven as more technically demanding uses for kaolin have evolved. The most significant markets today in terms of value and volume are paper, ceramics, fiberglass, and paint. Recently the use of kaolin as a raw material for ceramic proppants has emerged as a rapidly growing market that will likely surpass paper, which has declined over the last decade. In addition to these commodity markets, there are new highly technical applications such as specialty packaging, energy-efficient building materials, and lightweight paper coatings.

On the mining side, many of the advances have been driven by sustainable development and corporate social-responsibility principles. These principles incorporate social, environmental, and economic considerations into each phase of the mining life cycle. There are many ways to define sustainable development (SD); in the context of mining, however, its meaning is not always clear. This is because SD is a broad and complex concept especially as it applies to mining. The most universally accepted definition is "*development that meets the needs of the present without compromising the ability of future generations to meet their own needs*" (Brundtland Commission United Nations 1987).

In 2003, the International Council of Mining and Metals took this concept and drafted 10 SD principles to provide a roadmap for implementing SD practices into mining operations (ICMM 2003). Since then many mining companies, including those that mine kaolin, have integrated SD into their business models and new management strategies have emerged as a result (Boltin 2009). These include improving mine efficiency and process recovery. Efficient use of energy and water are also key aspects of sustainable mining operations (Kogel et al. 2014).

* IMERYS, 380 Smyrna Church Road
Sandersville, GA 31082, USA
E-mail: jessica.kogel@imerys.com

KAOLIN ORE DEPOSIT CLASSIFICATION

Kaolin ore deposits are classified as either primary or secondary depending on their origin. Primary kaolins formed in situ through hydrothermal and/or weathering alteration of feldspathic rocks such as granite and arkose. Secondary kaolins are sediment-hosted, where materials transported from their point of origin were deposited as kaolinite-rich sediments. Some of the most economically important secondary kaolins were further altered after deposition by microbially mediated processes that naturally removed iron-bearing ancillary minerals (Hurst and Pickering 1997). The largest and purest kaolins are the fluvial, neritic, and near-shore marine Coastal Plain deposits in the southeastern United States and the fluvial and lacustrine deposits mined in the Amazon region of northern Para State, Brazil. The best-known primary kaolins are found in Cornwall, UK.

THE LIFE CYCLE OF A KAOLIN MINE

Mining is a wealth-generating activity that creates significant economic and social benefit through the responsible extraction of valuable mineral resources. A range of industry professionals skilled in the technical, business, legal, environmental, safety, and social aspects of the mining sector work together to manage each stage of the mining life cycle (FIG. 1). This life cycle applies to all mined materials, including coal, industrial minerals, metals, and precious metals. It provides a framework for implementing sustainable development practices at the operations level (Laurence 2011) and will be used here to discuss each step in developing and operating a kaolin mine.

Exploration

Following Clues

Exploration focuses on the discovery of new mineral deposits and typically takes place in two phases. The first phase involves searching for a deposit on the surface. It may begin with a geologist using his or her training to identify promising areas and then searching them, sometimes on foot, for signs of kaolin mineralization. Prospectors rely on outcrops, stream beds, and road cuts for clues to subsurface geology. Stratigraphic position, topographic elevation, and geomorphologic features are also commonly employed prospecting tools. For example, the Capim kaolins in Brazil were discovered when geologists realized that the kaolin deposits form low-elevation plateaus. In addition to these simple tools, more sophisticated approaches, such as geophysical surveys and remote sensing, may be used to gather indirect information about potential kaolin deposits.

Subsurface Sampling

Once a kaolin deposit has been located, the second phase of exploration is to directly sample and test the deposit. The most widely used methods for sampling kaolin are rotary core drilling and auger drilling. Both methods yield good sample recovery and have become standard for sampling kaolin and other industrial clays. Typically a small number of test holes are drilled on a random or widely spaced grid pattern to confirm the discovery.

Social and Environmental Considerations

Prior to drilling, access to the land must be secured and, in the USA, all required local, state, and federal permits must be obtained. Access to private land usually involves a legal contract between the landowner and the mining company. At this point the mining company must also consider the social and environmental impacts of exploration drilling, such as noise, water contamination, soil erosion, distur-



FIGURE 1 The mining life cycle

bance of wildlife habitat, disruption of land use for other activities (i.e. farming, hunting, timber, community recreation), and the disturbance of culturally significant sites. These impacts are important because, if mismanaged, the company risks losing its reputation and social license to operate. This license is not a physical document but refers to acceptance of the mining company and its projects by the local community. This license is earned by developing and maintaining good relationships with all stakeholders and is based on open dialogue, transparency, timely responses to community concerns, and ethical behavior.

Resource Development

The next step towards bringing a deposit into production involves drilling the deposit on an increasingly dense grid pattern. This close-spaced drilling is required for mineral resource estimates. A mineral resource is defined as a mineral deposit of sufficient size and quality to have "reasonable prospects for economic extraction." Based on this definition, which is used by most codes governing resource and reserve estimation, three pieces of information are needed to evaluate the resource potential of a kaolin deposit. These are tonnage and grade, estimated from drill hole data, and economic viability. Economic viability is assessed based on deposit depth (i.e. overburden thickness), clay thickness, continuity, quality, distance to the processing plant, and other cost factors. The economic assessment completed at this stage is very preliminary and is not nearly as detailed as the economic assessment completed during the full-blown feasibility study typically done at a later stage in the project.

Grade, Tonnage, and Classification

Methods used to estimate tonnage and grade fall into two categories. One is based on conventional approaches such as maps, cross sections, and spreadsheets. The other utilizes 2-D and 3-D, computer-driven geostatistical modeling techniques (FIG. 2). Both methods produce valid results as long as high-quality geological and test data are used for estimation. Increasingly, 3-D models combined with GPS data are required to both efficiently and selectively extract

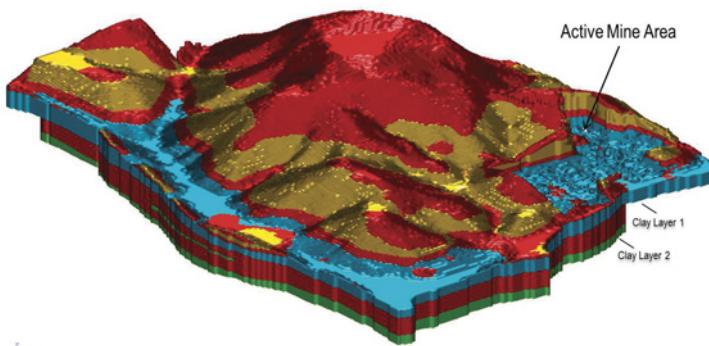


FIGURE 2 A 3-D geologic model constructed from drill core data

the range of valuable kaolin materials that can occur within a clay deposit. Decades ago, it was not uncommon to mine only the highest-grade portion of a deposit. This practice, known as high-grading, increases mining costs and goes against the principles of sustainable mining.

Mineral resources are classified as inferred, indicated, or measured using a common classification system that has been adopted by most major mining regions, including Canada, Australia, Europe, South Africa, Chile, and the United States. The classification is based on increasing geological knowledge and confidence, which is generally related to drill hole spacing (FIG. 3). Once the resource estimation has been completed, the results are reviewed and the project may be abandoned or, if the results are promising, drilling will continue.

Feasibility Studies and Reserve Development

Feasibility studies are detailed engineering and economic analyses that include mine design, cash flow analysis (capital cost, operational cost, and revenue), mineral-processing flow sheets, closure plans, reclamation plans, and plant design. Feasibility studies are used to delineate the portion of the measured or indicated resource that is economically minable. This is called the reserve. For kaolin resources to be converted to kaolin reserves, the deposit must not only be economic to mine but it must also pass certain other "modifying factors." Any one of the modifying factors listed in FIGURE 3 could prevent a resource

from being converted to a reserve. For example, if the site cannot be permitted for mining, the resource cannot be converted to a reserve.

Mine Design, Construction, and Production

Mine design and planning encompass a broad range of activities that are mainly concerned with determining the size of the mine, mine layout, mining method, production requirements, and equipment needs. This stage often includes permitting as well. For example, the Georgia Environmental Protection Division regulates all mining in the state of Georgia in the United States, and a land-use permit must be secured before mining can begin. The permitting process requires the submission of a mine plan that shows the mine layout (pits, overburden stockpiles, roads, ramps, sediment ponds) and reclamation plans for the site. Local and federal permits may also be required.

Typically, kaolin is extracted from open-pit mines (FIG. 4). The mining process begins with designing a mine that takes into account the geotechnical aspects of the site. The mining engineer designs the highwall slopes to reduce the risk of wall failure and ensure safe working conditions. The next step is to remove overburden using scrapers, excavators, or loaders. Once overburden is relocated, kaolin mining begins.



FIGURE 4 A typical kaolin mining operation in Georgia, USA

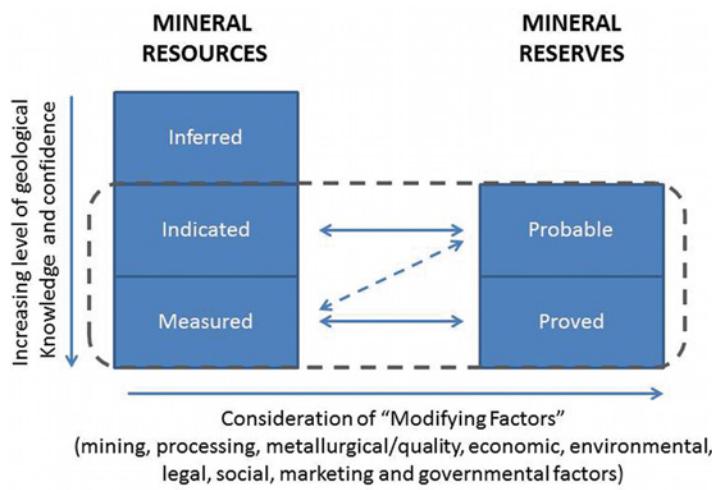


FIGURE 3 Classification scheme for mineral reserves and resources

In Georgia and Brazil, a standard cut-and-fill mining process is used. Overburden removed from the first cut is stockpiled, and then the overburden from each subsequent cut is placed in the previously mined-out cut. The in-filled area is then sloped and graded in preparation for revegetation and final reclamation. The active mine area of open-pit kaolin mines in Georgia and South Carolina are generally relatively small, with footprints of 1 to 5 acres (0.4–2 hectares) for individual cuts and depths typically ranging from 6 to over 30 meters. Open-pit mines in Brazil are much larger, with footprints of 10 or more hectares and depths averaging 12 meters. The much higher grit (i.e. coarse-mineral-bearing) primary kaolins in Cornwall are mined using wet methods. The vastly different designs and production modes reflect geometric differences between primary and sediment-hosted kaolin deposits (Pruett and Pickering 2006).



FIGURE 5 Stages of postmining wetland reconstruction starting with grading subsoil (upper left), planting trees (upper right), and establishment of final wetland (bottom)

Closure and Restoration

Mining is a transitional land-use activity. During the mining operation, minerals are extracted and wealth is created for the local community through jobs, taxes, and royalty payments. After the mineral has been removed, the land is graded and revegetated (Fig. 5). Mined-out land is then developed for a variety of postmining uses that bring long-term value to the local community. Some common examples of land use after kaolin mining include wildlife habitat creation, community recreation areas, timber plantations, farming, hunting, and fishing. Community engagement is important throughout this process because communities are left with the land after it has been mined and the best outcomes occur when communities have a role in deciding how to repurpose the land.

Companies focus significant resources on this critical phase of the mining life cycle. They commonly employ sustainable land-management practices to ensure that there are no long-term environmental issues after the mining project has finished. Mismanagement at this stage puts a company's reputation at risk.

PROCESSING

Kaolin ore is processed to enhance or control various properties within a specified range as determined by the end-use application. Processing may be divided into three basic types: wet, dry, and thermal. Typically, wet processing is used to produce kaolin products for paper, specialty, and

functional filler applications. Dry processing is commonly used for ceramic- and fiberglass-grade products. Thermal processing is used for specialty ceramic, paint, refractory, and paper grades. Chemical treatment after firing is used to make products that are suitable for functional filler applications.

Wet Processing

Wet processing begins with the preparation of a dispersed mineral–water suspension that is then passed through screens, hydroseparators, or hydrocyclones to remove coarse mineral particles (grit). The degritted kaolin suspension is then classified into specific particle size fractions using various types of centrifuges depending on the feed material and the desired final particle size cut. After fractionation, the slurry undergoes brightness beneficiation to remove discoloring mineral impurities, such as iron oxides, iron hydroxides, anatase, mica, and tourmaline. Typical methods for enhancing kaolin brightness include high-intensity magnetic separation, selective flocculation, froth flotation, and reductive leaching. Wet grinding is used to engineer particle shape by delaminating stacked kaolinite crystals to create single particles with a high aspect ratio. Prior to shipping, the kaolin slurry is dewatered or dried depending on how the product will be delivered to the customer.

Dry Processing

Dry processing, also called air flotation, involves fewer steps and is less expensive than wet processing. The crude kaolin is milled, air classified to remove grit, and dried to reduce moisture prior to shipment to the customer. The dry-processed product generally has poorer color and higher grit content compared to wet-processed kaolin. This

is because the lower level of processing produces a less refined product. Consequently the properties of the crude ore are more critical for final-product quality, and higher-quality ore is generally required to meet final-product quality specifications.

Thermal Processing and Chemical Treatment

Thermal processing (calcination) consists of high-temperature firing of wet- or dry-processed kaolin in either a rotary or a vertical kiln. Calcination increases whiteness and hardness, improves electrical properties, and alters the size and shape of the kaolin particles. Firing temperature and residence time are varied depending on the desired product outcome.

Lower-temperature firing drives water from the kaolinite crystal structure to produce metakaolin, which is used in paint and certain paper applications that require a high-bulk, optically superior aggregated particle. Products produced at this temperature are also used in PVC cable insulation to improve dielectric properties and in concrete as a pozzolanic additive.

Firing at high temperature causes mullite formation. Products fired in this temperature range are used in rubber compounds and may be coated with silane to enhance mechanical properties and chemical resistance. Silane treatment also improves rigidity, toughness, and dimensional stability in polyamide moldings. High-temperature firing is also used to manufacture high-strength ceramic proppants for hydraulic fracturing.

CONCLUSION

Although at first glance kaolin appears to be a simple material, sophisticated analytical techniques have revealed its complexity and allowed researchers to more fully explore its many novel characteristics. In parallel with this improved understanding of the material properties of kaolin, there have been advances in kaolin mining and processing methods. These advances have led to innovative approaches for extracting and engineering kaolin to further enhance its commercial utility and unlock its value as an important raw material for many consumer products.

Along with technical advances, there has been a movement towards adopting management practices that integrate environmental, economic, and social considerations into all phases of the mining operation. By adopting these practices, companies demonstrate a commitment to creating long-term value for all stakeholders, including future generations. Businesses also realize certain benefits, such as an enhanced reputation, improved operational efficiency, extended life of mineral reserves, and a more secure social license to mine.

ACKNOWLEDGMENTS

The author acknowledges the contributions of IMERYS colleagues Monty Sanders, Mining and Lands Manager, and Lee Roberts, Minerals Resource Development Manager. Their contributions include the figures for this article as well as providing a sounding board for many of the ideas captured here. Many of my fellow miners have contributed by sharing their passion for practicing community engagement, corporate social responsibility, and environmental stewardship every day and at every step of the mining process. ■

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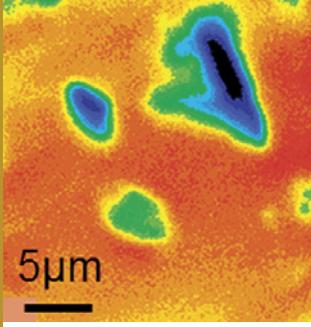
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Interactions of Kaolin Minerals in the Environment



Randall T. Cygan¹ and Kazue Tazaki²

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The interactions of ions, organics, and microorganisms at the aqueous interface with kaolin-group minerals control many important geochemical processes in the environment. Kaolinite has both hydrophilic and relatively hydrophobic external surfaces that exhibit different adsorption phenomena. Our understanding of kaolin minerals in the environment is advancing as a result of molecular simulation and field studies. Molecular dynamics simulations reveal the structure and behavior of adsorbed ions and water molecules at the interface. The presence of microorganisms affects the formation and surfaces of kaolinite and halloysite. Mechanisms by which kaolin-group minerals complex, adsorb, and desorb radioactive pollutants in the subsurface can be understood by combining theory with observation.

KEYWORDS: adsorption, biomineralization, kaolinite, molecular dynamics, radioactivity, surface chemistry, weathering

INTRODUCTION

The adsorption of contaminants onto the surfaces of clay minerals is an important geochemical process for protecting the quality of groundwater. The fine-grained nature of clay minerals and their correspondingly high surface area promote relatively large adsorption capacities and allow clays to be used as efficient migration barriers at contaminant sites and nuclear waste repositories. The negative layer charge associated with most clay minerals is effective in controlling the adsorption of metal cations and other positively charged species (e.g. UO_2^{2+} and organic cations) under most pH conditions. Unlike 2:1 clay minerals, which can also exchange cations in the interlayer, the 1:1 kaolin-group minerals primarily adsorb species onto their external surfaces. Although impurity substitutions may impart a local charge site, kaolin-group minerals are typically neutral phases and are unable to swell in nature and develop intercalated structures like the smectite and vermiculite varieties of clay minerals. Nonetheless, kaolin-group minerals make a significant contribution to adsorption in the environment and are involved in many other important geochemical processes (Newman 1987; Dixon and Schulze 2002). Kaolinite, in particular, strongly interacts with microorganisms and can nucleate and precipitate on cell walls. Biomineralization processes—in which living organisms produce or induce minerals—can be extensive in the natural environment and could be employed in the remediation of radioactive environments, including the region near the recent Fukushima nuclear accident in Japan.

¹ Geoscience Research and Applications Group
Sandia National Laboratories, Albuquerque, NM 87185-0754, USA
E-mail: rtcyan@sandia.gov

² Department of Earth Sciences, Kanazawa University
Kanazawa, Ishikawa 920-1192, Japan
E-mail: kazuet@cure.ocn.ne.jp

KAOLIN-GROUP MINERALS IN THE ENVIRONMENT

Kaolin-group minerals include kaolinite, dickite, nacrite, and halloysite, each having the common ideal formula of $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$. FIGURE 1 presents the basic structure of the mineral group as represented by the structure of kaolinite (Brindley and Brown 1980; Bish 1993). The 1:1 designation denotes the combination of a single tetrahedral sheet and a single octahedral sheet to form a kaolinite layer. The octahedral sheet is comprised of edge-sharing $\text{Al}(\text{O},\text{OH})_6$ octahedra, with vacant sites occurring once

for every two occupied sites and with Al coordinated by four hydroxyl groups and two bridging oxygen atoms. This sheet structure is similar to that of the mineral gibbsite, whose formula is $\text{Al}(\text{OH})_3$, and is often referred to as the gibbsite-like sheet. The tetrahedral sheet incorporates corner-sharing SiO_4 tetrahedra, which form a ditrigonal structure on the basal plane of the layer, and is often referred to as the siloxane sheet. The other basal plane, as expressed by the gibbsite-like sheet, is saturated with hydroxyl groups that form hydrogen bonds across the interlayer with the oxygen of the siloxane surface. The basal *d*-spacing of 0.72 nm (7.2 Å) is diagnostic of most kaolin minerals.

The polymorphs dickite and nacrite have the same basic structure as kaolinite but with different stacking sequences of the layers (Balan et al. 2014 this issue). Typically, kaolin-group minerals occur with plate-like morphologies. The

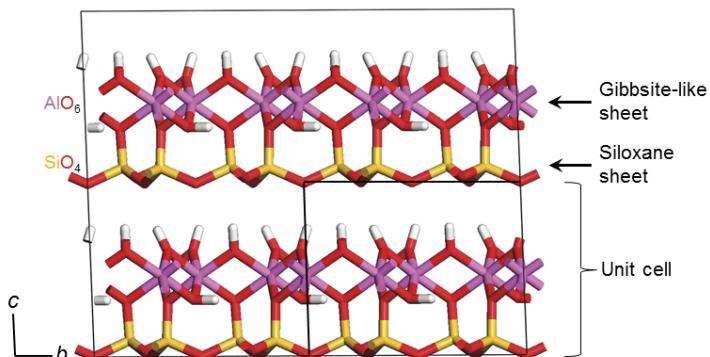


FIGURE 1 Molecular model of kaolinite, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as a periodic simulation cell ($1 \times 2 \times 2$ unit cells) showing the gibbsite-like and siloxane sheets and the inner and interlayer hydroxyl groups

lone exception, halloysite, has the same fundamental structure but occurs in cylindrical form when hydrated with a single water layer between sheets; the cylinders are typically 30 nm in diameter. Although all kaolin-group minerals are the result of aqueous-solution weathering or hydrothermal alteration of micas and feldspars at low-pH conditions, only kaolinite and halloysite are found in modern soils and sediments.

SURFACE CHEMISTRY OF KAOLINITE

Kaolinite, as the most common of the kaolin-group minerals, has been the focus of several studies of adsorption phenomena concerning clay minerals in the environment. On or near the Earth's surface, adsorption onto mineral surfaces is primarily determined by the surface structure, composition, and surface charge, although this conventional approach is complicated by the strong structural anisotropy (dipolarity) of the 1:1 layers. In addition to its occurrence on the basal planes of kaolinite, adsorption takes place on its edge surfaces, which are controlled by exposed $-Al-O$ and $-Si-O$ sites, where the interaction with water is different from that on basal surfaces. Using titration experiments, Brady et al. (1996) distinguished different pK values for protonation and deprotonation reactions for two aluminol edge sites and one silanol edge site and derived the corresponding site densities. By combining this information with atomic force microscopy observations of the high percentage of edge surface area for kaolinite compared to smectite and illite and with molecular models of kaolinite charge distribution, they demonstrated the significant role of surface aluminols in controlling adsorption. The basal surface makes a smaller contribution, compared to the edge sites, to the total adsorption of inorganic cations, especially at neutral- to high-pH conditions, although the adsorption of neutral species and organic compounds will involve both basal and edge surfaces.

MODELS OF KAOLINITE-WATER INTERFACES

The details of the adsorption mechanisms for kaolinite at the molecular level are poorly understood. The fine-grained nature of clay particles (typically less than 2 μm in diameter) and the difficulty in obtaining accurate crystal structures for layered phases with stacking disorder, severely limit physical observations of structure–property relationships (Balan et al. 2014). Particle-size and sample-preparation issues affect the quality of kaolinite images obtained using optical, electron, and atomic force microscopies, as well as the interpretation of measurements from many spectroscopic and diffraction methods. In the last decade, however, new molecular simulation methods have been used to supplement these experimental approaches by offering a theoretical probe of clay mineral structure, surfaces, and the clay mineral–water interface.

Adsorption Mechanisms through Simulation

Molecular simulation has been used to develop a basis for understanding adsorption on clay surfaces, with particular success in evaluating the adsorption of metal cations on the basal surfaces of kaolinite. Two general modeling approaches are used in these types of studies: (1) classical simulation methods involving an empirical description of how atoms interact with each other and (2) quantum approaches that provide a first-principles description of the electronic structure and that require approximate solutions to the Schrödinger equation. The classical approaches include molecular dynamics (MD) and Monte Carlo (MC) simulations, which incorporate many thousands of atoms and, in some cases, more than a million atoms (Thyveetil

et al. 2008). Energy force fields, such as Clayff (Cygan et al. 2004), provide an accurate set of potential energy expressions for modeling a variety of environmental phases (including clay minerals and aqueous solutions). Potential energy and atomic configurations are monitored during the simulation (time steps for MD; sample steps for MC) and used to evaluate optimized or equilibrium states. Quantum methods can be computationally expensive and therefore are limited to applications involving less than several hundred atoms. Advances in high-performance computers and quantum chemistry software, however, are allowing for more efficient, accurate, and computationally affordable quantum chemistry simulations.

Adsorption on Kaolinite

Several computational studies have examined water adsorption onto kaolinite using either classical or quantum methods. These include the recent investigations of wettability (Šolc et al. 2011), the adsorption of a water monolayer on the basal surfaces (Tunega et al. 2004), and the viscosity of nanoconfined water in a kaolinite nanopore (Haria et al. 2013). As with most simulations of kaolinite–water systems, molecular dynamics models of the adsorption of aqueous cations have usually focused on a comparison of the adsorption behavior of both basal surfaces since they offer contrasting hydrophilic and hydrophobic structures (Vasconcelos et al. 2007). Similarly, quantum methods have been used to examine the binding of organics, such as formamide ($HCONH_2$) (Scott et al. 2012) and glucose-related molecules (Lee et al. 2013), on both basal surfaces.

The molecular dynamics investigation of Vasconcelos et al. (2007) offers a comparison of the adsorption behavior at 300 K and one atmosphere for several monovalent and divalent cations interacting with the two kaolinite basal surfaces. FIGURE 2 presents the initial and equilibrated configurations for a CsCl solution in a kaolinite nanopore as represented by a modest-sized system of about 20,000 atoms. The simulation cell has periodic boundaries in all directions and cell lengths that are allowed to shorten or lengthen as the system equilibrates during the molecular dynamics simulation. The equilibrated simulation cell exhibits a smaller pore dimension, which results from contraction of the aqueous solution as the ions in solution diffuse to either of the kaolinite surfaces. In this example, Cs^+ ions migrate toward the negatively charged oxygens of the siloxane surface while Cl^- counterions are attracted to the gibbsite-like surface. Atomic density profiles traversing the nanopore are calculated by averaging the trajectories of each species over 500 picoseconds (ps) (5000 total structures) following the equilibration period (Fig. 3).

The density profiles graphically depict the equilibrium distribution of atoms in the aqueous solution and in the kaolinite substrate, and provide insight into the structure and mechanisms of ion adsorption. Inner- and outer-sphere adsorption complexes exist at both basal surfaces depending on whether water molecules are intermediate between the ion and the surface. Cesium ions bind strongly at the siloxane surface as an inner-sphere complex (Cs^+ has the lowest hydration enthalpy of the ions), whereas Na^+ , Cd^{2+} , and Pb^{2+} behave predominantly as outer-sphere adsorption complexes and are fully coordinated by water molecules. At equilibrium, all cations display finite atomic density in the bulk-solution region, illustrating the dynamics of element partitioning between being adsorbed onto kaolinite or remaining in solution. In similar fashion, Cl^- occurs as an inner-sphere complex adsorbed on the gibbsite-like surface. Interestingly, Cd^{2+} and, to a lesser extent, Na^+ exhibit ion pairing with Cl^- , which allows for some indirect adsorption of cations to the gibbsite-like

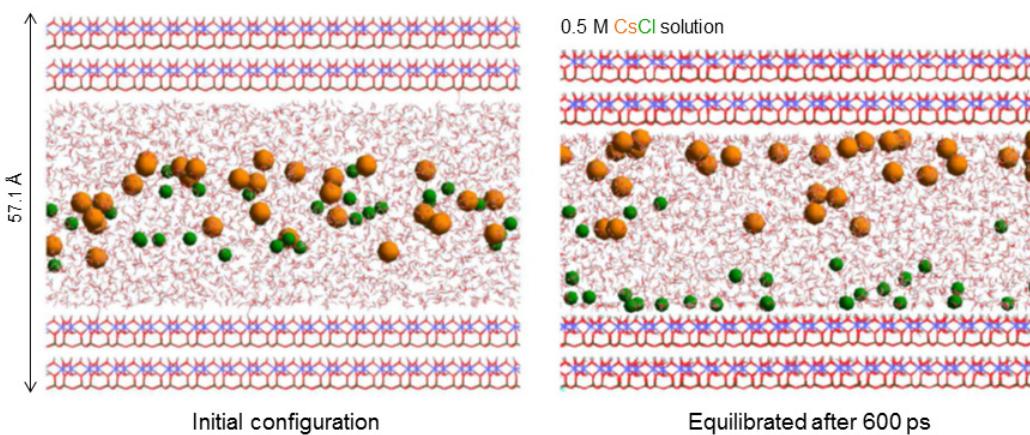


FIGURE 2 Periodic simulation cells of a kaolinite nanopore with a CsCl solution exposed to the gibbsite-like and siloxane basal surfaces of kaolinite. The equilibrated configuration from molecular dynamics shows Cs^+ (orange spheres) mostly adsorbed

to the siloxane surface and Cl^- (green spheres) bound to the gibbsite-like surface ($\text{ps} = \text{picoseconds}$). ADAPTED WITH PERMISSION FROM VASCONCELOS ET AL. (2007). COPYRIGHT 2007, AMERICAN CHEMICAL SOCIETY

basal surface. Site densities for ion adsorption derived from these results can help improve surface complexation models for thermodynamic and reactive transport models currently being used to simulate the fate of pollutants in the Earth's surface environment.

Density profiles for water H and O (Fig. 3) readily show the formation of ordered water layers at each kaolinite surface, with the hydrophilic gibbsite-like surface exhibiting more tightly bound water than the relatively hydrophobic siloxane surface. Up to three ordered water layers occur near the gibbsite-like surface; the ordered water layers transition into a diffuse water region in the central part of the nanopore. The combination of Clayff and MD simulation offers amazing insight into the molecular details of adsorption behavior that is beyond the reach of laboratory experiments.

The present challenge in the molecular simulation of kaolinite, and of clay minerals in general, is in obtaining accurate models of edge sites, especially for variable

protonation states. Quantum chemistry simulations have been used successfully to evaluate possible kaolinite edge structures and their reactivity (Liu et al. 2012), but these have not yet been applied to examining adsorption phenomena with large-system models. Research on developing improved classical models and force field parameters for kaolinite edges is ongoing. Although one would hope that all molecular simulations are accurate depictions of real materials, it is important to stress that the validation of models by experimental findings is crucial, and perhaps their best contribution lies in helping to design or interpret the next experiment.

BIOMINERALIZATION, REDOX, AND KAOLINITE-WATER INTERFACES

Microorganisms play an important role in the concentration of elements, the crystallization of kaolin-group minerals, and the transport and sedimentation of most elements in the environment. Microbial mats of bacterial colonies complex with clay minerals in many environmental systems. Bacterial biomineralization contributes to the remediation of toxic heavy metals at abandoned mining sites (e.g. uranium and cadmium, and mercury mud ponds in gold mines) and in polluted soils and water systems (e.g. pesticides, tar sand spoils, and petroleum spills).

The occurrence of kaolin-group minerals produced in the presence of microorganisms depends on temperature, pH, oxidation-reduction potential (Eh), and the amount of dissolved ion. At the high temperatures and strongly acidic conditions associated with hot springs, microorganisms produce various clay minerals external to and within the living cell. Understanding the mechanisms of bacterial biomineralization is crucial to our understanding of the redox potentials of electron donors (fuels) and acceptors (oxidants) commonly used for microbial respiration.

Perhaps the best-known example of biomineralization is the colorful microbial mats observed in hot springs, geysers, and geothermal areas, which form at high-temperature and low-oxygen conditions (e.g. Yellowstone National Park, USA). The colored microbial mats surrounding geysers clearly exhibit specific pH-Eh-temperature dependencies. Other examples include reddish *Halobacterium* and *Halococcus* bacteria occurring in high-salinity lakes and red algae occurring on snow surfaces during winter in the Arctic. The biominerals assemblages include not only

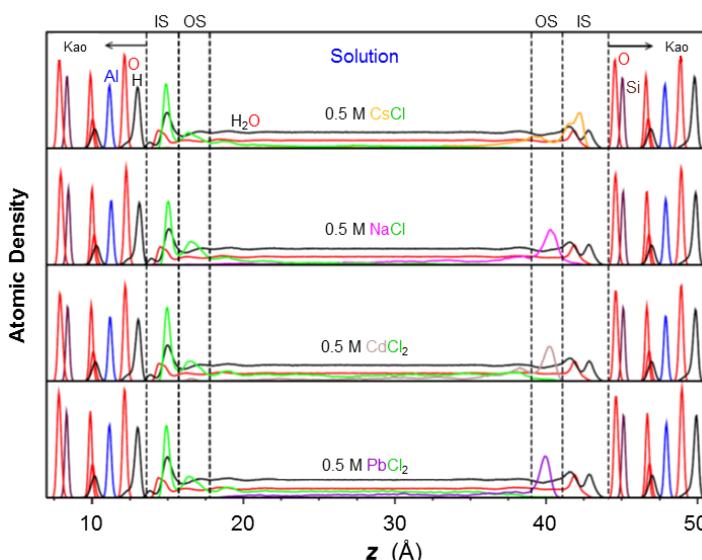


FIGURE 3 Atomic density profiles for various solution compositions at the basal surface of kaolinite (Kao) derived from an equilibrated molecular dynamics simulation. The interfacial regions for adsorption are denoted by IS for inner sphere and OS for outer sphere, as indicated by water intermediate between the ion and the surface. ADAPTED WITH PERMISSION FROM VASCONCELOS ET AL. (2007). COPYRIGHT 2007, AMERICAN CHEMICAL SOCIETY

kaolin-group minerals but also carbonates, silicates, Fe–Mn oxides, hydrated phosphates, and sulfides formed through bacterial activity (Tazaki 1997a, b).

Bacterial Biomineralization of Kaolin

In nature, the degree of order and disorder within kaolin-group minerals ranges from poorly crystalline kaolinite granules to well-oriented crystalline phases. Polymeric substances secreted by microbial cells include the crystalline surface-layer proteins, polysaccharides, and capsules that often provide nucleation sites and possibly a favorable chemical microenvironment for biomineral formation. Bacterial cells can act as nucleation sites for clay minerals. The layer of extracellular polymeric substances surrounding microbial cells can therefore act as a template in the formation of hydroxides (Tazaki 2005). Cation bridging is one mechanism in which multivalent metal cations complex with a functional group such as carboxylate (e.g. COO^-), which in turn bridges with ionic silicate species to form large aggregates. Multivalent cations may serve as cation bridges in the interaction between clays and microbial extracellular polymeric substances. The coccus- and bacillus-type bacteria transfer electrons via the pilus—a hair-like appendage—to the metal that they feed from. Transferring the electrons provides the bacteria with energy. This also changes the ionization state of the metal, producing a form that can potentially precipitate from solution.

Evidence for kaolin mineral production via bioweathering is supported by experiments with iron bacteria (*Toxothrix* and *Gallionella*) carried out using thin sections of granite. Samples of bacteria were collected from microbial mats in river freshwater. Cavities and fissures with bacilli and filamentous bacteria were immediately observed on the surface of feldspars and biotite in the granite samples, and during two months of treatment K and Si were released into solution. The Si content of the altered material was reduced at the grain edges (Si:Al modified from 3:1 to 3:2), and the material was identified as kaolinite by electron diffraction. Compared to an abiotic experiment, microorganisms associated with the release of nutrients such as K^+ accelerated the weathering of granite. The biokaolinite exhibits almost the same X-ray diffraction and energy-dispersive X-ray (EDX) patterns as hydrothermal kaolinite. Fourier transform infrared spectra exhibit absorption bands of kaolin, which is an additional indicator of organic origin (FIG. 4A) similar to that of primary kaolinite from Cornwall, UK (FIG. 4B). Optical and electron microscope observations of cultured microbes reveal that thin clay films cover areas of the bacterial cell wall after two years, and these display the 7.13 Å *d*-spacing of a halloysite-like phase, $\text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4$, as determined by X-ray diffraction (Asada and Tazaki 2000; Tazaki 2005).

Kaolinite and Bioremediation of Radioactive Environments

Tanzania is endowed with a variety of industrial minerals, such as kaolinite, diatomite, and rock salt, which are occasionally associated with uranium deposits. One such occurrence is the Bahi swamp area in central Tanzania, which is a dry lake or playa. Uranium is known to have variable degrees of mobility depending upon its redox state, and it accumulates in poorly oxygenated aquifers. Uranium is observed on the margins of regional uplands of uraniferous granites. The Bahi uranium mine is located in weathered granite and clays characterized by a high γ -ray radioactivity, with indurated-sediment cores having U_3O_8 contents of 0.23 wt%. Salt soils with Th/U ratios ranging from 2.9 to 3.7 are also found associated with abundant

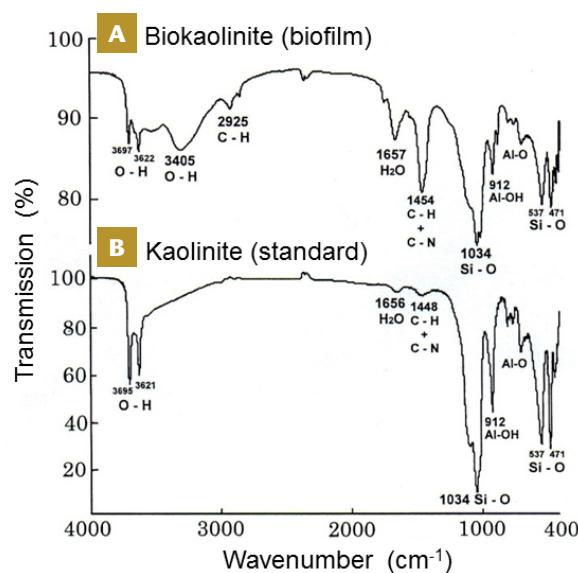


FIGURE 4 Fourier transform infrared (FT-IR) spectra of (A) biokaolinite compared with (B) standard kaolinite for reference material API62 (Cornwall, UK). The peaks at 3697 cm^{-1} and 3622 cm^{-1} are due to the structural water O–H stretch of kaolinite, whereas the peaks at 1454 cm^{-1} to 1420 cm^{-1} are due to abundant organics (C–H and C–N stretch) in the structure of kaolinite.

microorganisms. Nearby, rice paddy soils are composed mainly of halloysite, micaceous clays (10 Å), smectite (14 Å), feldspar, tridymite, and quartz.

Scanning electron microscope (SEM) imaging provides elemental maps of kaolin grains in the Bahi soils, and these show abundant Al resulting from weathered feldspar and the presence of clay components (FIG. 5A). The maps indicate a nonuniform distribution of elements within 100 µm sized grains. Elemental maps of 5 µm sized bacteria show regions of concentrated Na, Cl, S, Ca, and Sr (FIG. 5B). Some coatings on bacteria are rich in S and Ca whereas others are dominated by Ca and Sr, suggesting the occurrence of SrCO_3 and SrSO_4 nodules in the sediments. The elongated and spherical shapes suggest the presence of bacillus and coccus bacteria, respectively. Transmission electron microscopy (TEM) observation of paddy soils confirms the survival of many microorganisms under radioactive conditions. Among the microbes are filamentous bacteria (FIG. 6A) covered by submicron hexagonal precipitates of kaolinite (FIG. 6B, c). TEM micrographs and electron diffraction analysis show the initial stages of biomineralization involving coccus-type (FIG. 6D) and bacillus-type (FIG. 6E) bacteria. All bacteria observed in the radioactive paddy soils are lightly covered with kaolinite grains on the cell walls and occasionally within the cells themselves. These results suggest that kaolinite grains play an important role as a screening tool for radioactive pollutants and as a potential repository for containment.

Clay minerals are a significant component of the radioactive soils and tsunami sediments contaminated by the Fukushima Daiichi nuclear power plant accident in 2011 (Murakami and Ewing 2012). The destruction of the Fukushima power plant was the world's worst nuclear accident since the Chernobyl disaster in 1986. Kaolin minerals associated with the weathered-granite soils near Fukushima are now contaminated with high levels of radioactive material. The interaction of soils with ^{131}I , ^{134}Cs , ^{137}Cs , ^{129m}Te , ^{110m}Ag , ^{238}Pu , ^{239}Pu , and ^{90}Sr pollutants is controlled by a complex interplay of surface organic chemistry, redox, pH, and microbiology. Especially

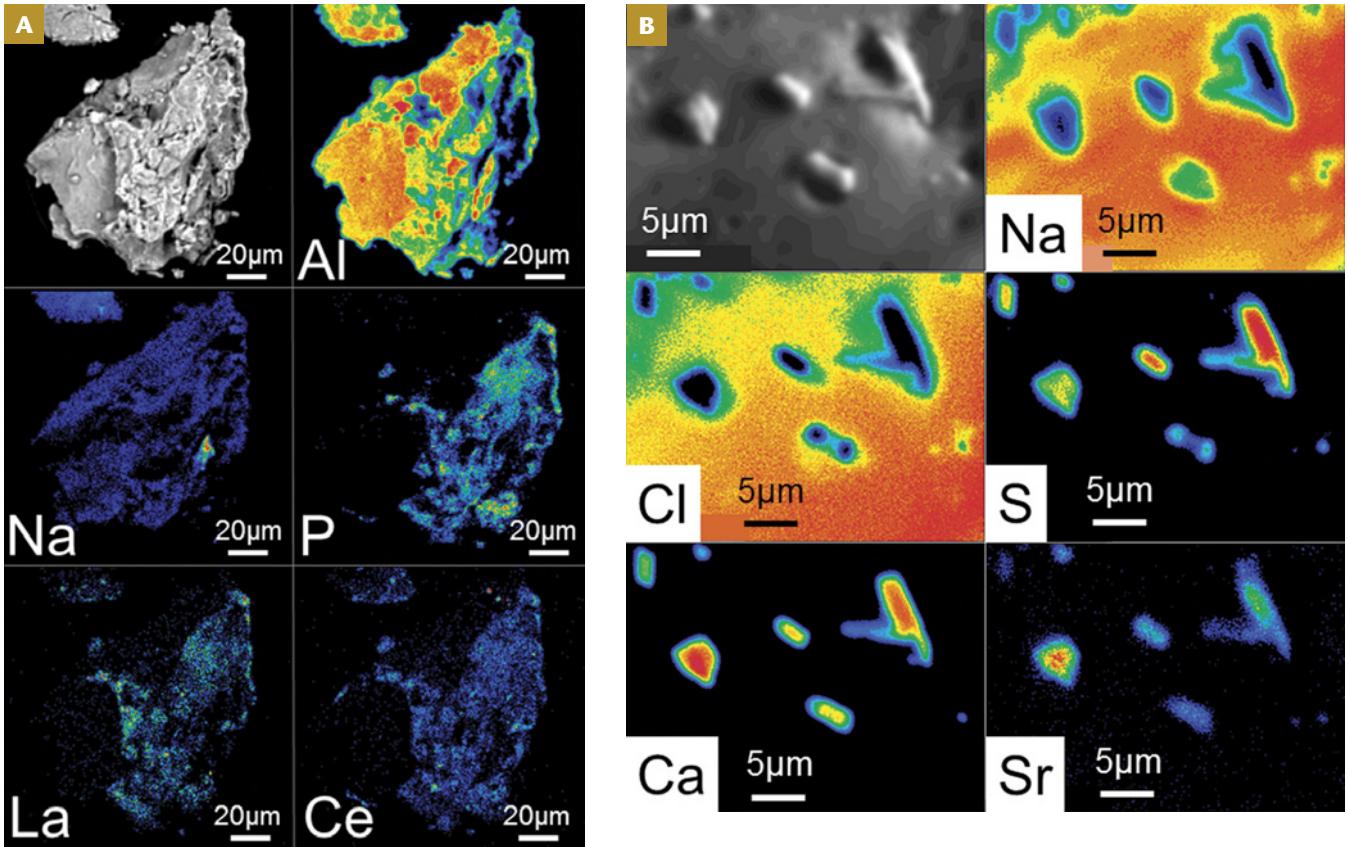


FIGURE 5 (A) Scanning electron microscope elemental color-coded maps of kaolinite grains from Bahi, Tanzania, indicating a major component of Al, lesser amounts of Na and P, and traces of La and Ce. (B) Elemental, color-coded maps of bacteria from Bahi indicating S- and Ca-rich regions in coccus-type (round shape) and bacillus-type (elongated) bacteria and a Sr-rich region in coccus-type bacteria. The background surrounding the bacteria is rich in Na and Cl because of the salty paddy soil surfaces in Bahi during the dry season. The colors indicate elements contents, red corresponding to the highest content.

common is the adsorption of 134 , ^{137}Cs and K onto the edge and interlayer sites of illite and mica-group minerals (McKinley et al. 2004; Pusch 2006; Asami 2013).

Salty microbial mats on the rice paddy soils at Minami Soma were exposed to radioactivity after the tsunami event at Fukushima. Electron microscope observations indicate abundant microorganisms, such as diatoms, foraminifera, and bacteria, in the severely contaminated environment (Tazaki 2013; Tazaki et al. 2013). After one year of exposure, quantitative analyses using SEM-EDX showed that diatoms and kaolin minerals held discernible concentrations of radionuclides (such as I, Cs, Ba, Nd, Th, U, Np, and Pu), indicating a capacity for adsorbing both radionuclides and stable isotopes from paddy soils polluted by radioactive materials (^{137}Cs , some ^{90}Sr , and a trace of Pu) dispersed by the Fukushima accident. The microorganism–clay–radio-nuclide interactions as observed in the contaminated paddy soils at Fukushima could be potentially effective in moderating the transport of low-level radioactive waste from geological repositories. Microbe–clay interaction is of concern for mediating the risk in contaminated sites for longer periods, such as the concentration of ^{90}Sr at various radioactive hot spots in Japan. This is significant for health issues, and especially for the safety of food sources (Steinhausser et al. 2013).

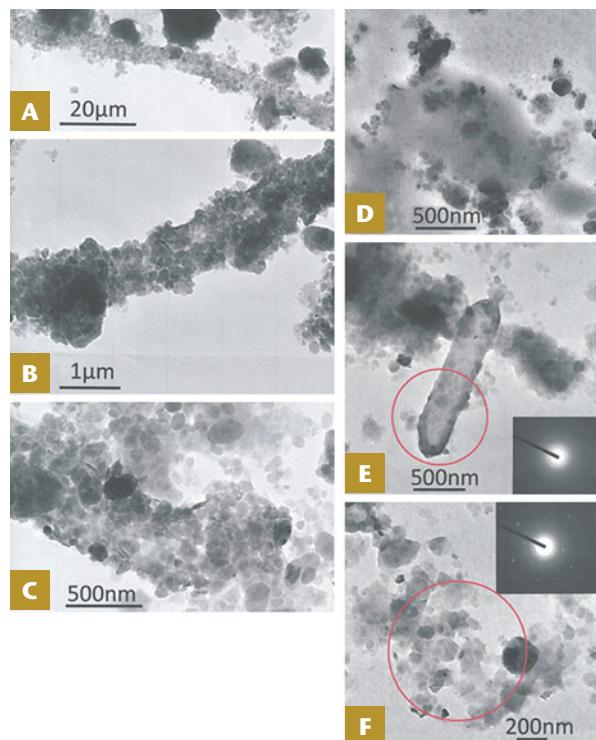


FIGURE 6 Transmission electron microscopy (TEM) micrographs. (A) Filamentous bacteria 1 μm wide and more than 100 μm long, which are (B) densely covered with hexagonal granular grains of kaolinite on the cell surface. One large hexagonal kaolinite crystal can be seen in the lower left. (C) Nanometer-sized kaolinite grains adhere to the bacterial surface, showing the initial stage of biominerilization. (D) Coccus-type bacteria. (E) Bacillus-type bacteria with an electron diffraction pattern (inset) for the circled area. (F) Nanometer-sized kaolinite grains with an electron diffraction pattern (inset) indicating 7 Å and 4.5 Å d-spacings.

OUTLOOK

Kaolinite and other kaolin-group minerals are prevalent environmental phases that control many geochemical processes, such as adsorption, nucleation and growth, redox, and induced biomineralization. The fate of heavy metals, radionuclides, pesticides, organics, and other contaminants in the environment will be partly determined by their physical and chemical interactions with kaolin and other clay materials. New developments of natural gas resources and the efficient extraction of methane from kaolin-bearing beds may potentially be improved by determining the fundamental mechanisms of gas-clay interactions. Similarly, the extraction of oil from deep sedimentary reservoirs is limited by our understanding of the wetting properties of clay mineral surfaces. The design of a geological repository for radioactive waste requires the assessment of geomicrobiological factors to better evaluate the chemical and biological reduction of radionuclide species. Within these contexts, the properties

of kaolinite are important for understanding the behavior of microorganisms in natural environments. It is clear that investment in research toward improving our understanding of such complex interactions at many spatial scales and timescales would benefit our global society.

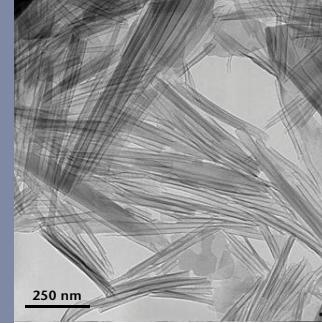
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From Platy Kaolinite to Nanorolls



Christian Detellier¹ and Robert A. Schoonheydt²

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Kaolinite is one of the most important industrial clay minerals, with a worldwide consumption in the millions of tons per year and applications in a wide range of industrial areas. Traditionally, its most important use has been in the paper and ceramic industries. New, innovative techniques are being developed that are based on intercalation and grafting of kaolinite's unique dipolar layer structure. Such techniques are leading the way to the synthesis of kaolinite–polymer nanocomposites, including bionanocomposites that might have value-added properties benefiting industry and the health sciences.

KEYWORDS: kaolinite, intercalation, grafting, exfoliation, delamination, nanocomposites, nanohybrids

INTRODUCTION

Crystalline order/disorder and layer stacking are the properties most important in determining the use of kaolin-group minerals in industrial materials. For most industrial applications, mined kaolinite has to be refined and processed to achieve the desired properties, such as viscosity, whiteness, purity, and crystal size and shape (Kogel 2014 this issue). It is advantageous that kaolinite readily disperses in water at high solid contents—up to 70%. Common impurities, such as quartz, micas, illite, montmorillonite, goethite, hematite, anatase, and rutile, can adversely affect the use of kaolins and commonly must be removed.

Beyond the traditional uses of kaolins, much effort has been devoted to the synthesis of clay–polymer nanocomposites and the development of their applications (Ruiz-Hitzky and Van Meerbeek 2006). Much work has been done on the smectite-group minerals, or “swelling clays,” because cationic molecules can be easily intercalated via the ion-exchange reaction. Kaolinite in contrast has a negligibly small cation-exchange capacity.

Intercalation, the reversible insertion of a molecule or ion into layered compounds, is difficult in the case of kaolinite because the H-bonding between the layers has to be broken up. However, in recent years our knowledge of the intercalation of kaolinite has increased significantly. One might expect that kaolinite–polymer nanocomposites will be developed that can compete with smectite–polymer nanocomposites in specific applications. This paper gives an account of how kaolin-group minerals can be modified and nanocomposited with other materials to develop new materials.

Kaolinite is a 1:1 clay mineral. The notation 1:1 means that one layer of kaolinite is composed of a tetrahedral silica sheet and an octahedral alumina sheet. The tetrahedral and octahedral sheets share a layer of oxygen atoms (FIG. 1A). One basal surface of the layer is composed of oxygen atoms bonded to Si and is called the siloxane surface. The basal surface on the opposite side of this sheet is composed of OH groups bonded to Al (FIG. 1A). This surface is called the aluminol surface. There are three important consequences of this arrangement: (1) each kaolinite layer is a strong dipole; (2) the kaolinite layers are strongly held together by H-bonding and by dipolar interaction; and (3) the siloxane surface is hydrophobic, while the aluminol surface is hydrophilic.

Kaolinite is the most common kaolin-group mineral, and it occurs in nature as particles composed of stacks of several layers. Often they have a hexagonal shape (FIG. 1B). The ideal formula of the pseudohexagonal unit cell is $\text{Si}_2\text{Al}_2\text{O}_5(\text{OH})_4$. Dickite and nacrite are less common polymorphs in the kaolin group. Halloysite is a hydrated 1:1 structure and occurs in nature as spheres and tubes; the latter are typically 30 nm in diameter and 0.5–10 μm in length (Brigatti et al. 2006). The kaolinite structural formula is electrically neutral. However, very small amounts of isomorphous substitution occur: most commonly Fe^{3+} for Al^{3+} (up to 1:30) and rarely Al^{3+} for Si^{4+} and Fe^{2+} for Al^{3+} . Thus, the structural formula can be slightly negatively charged, and a weak cation-exchange capacity, typically less than 2 cmol/kg, has been measured (Murray 1999). The edges of kaolinite particles are terminated by O atoms and OH groups. Interactions depend on the pH of the surrounding solutions. The OH groups take up a proton from the solution to form $-\text{OH}_2^{2+}$ in an acidic medium, or release a proton to the solution to form O^- in basic conditions. The pH at which the edge surface is neutral, or at which the number of positive charges equals the number of negative charges, is the isoelectric point or the pH of zero charge, pH_{zero} . In typical waters, this pH is 3.6 for kaolinite (Lagaly 2006).

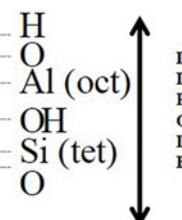
INTERCALATION

Up until the end of the 1950s, almost nothing was known about the intercalation of any compound, be it organic or inorganic, neutral or ionic, between the layers of clay minerals of the kaolin family. In 1959, Wada described what he called “the oriented penetration of ionic compounds between the silicate layers of halloysite, resulting in

¹ Department of Chemistry and Center for Catalysis Research and Innovation, University of Ottawa, Ottawa, ON K1N 6N5, Canada
E-mail: Christian.Detellier@uottawa.ca

² Center for Surface Chemistry and Catalysis, KU Leuven, Kasteelpark Arenberg 23, 3001 Leuven, Belgium
E-mail: Robert.Schoonheydt@biw.kuleuven.be

Hydroxyl Surface



Siloxane Surface

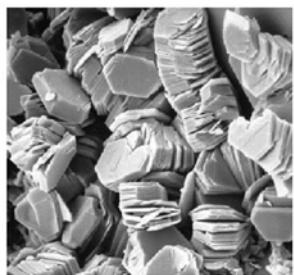


FIGURE 1 (A) Structure of a layer of kaolinite (B) Scanning electron microscopy (SEM) image of typical stacks of hexagonal particles of kaolinite. These aggregates show neither intercalation nor ion exchange.

reversible one-dimensional swelling.” He showed conclusively that the 10.1 Å basal spacing of hydrated halloysite was affected when this mineral was treated by a group of salts, mainly with K⁺ and NH₄⁺ cations, indicating intercalation between the 1:1 layers. Washing with excess water restored the 10.1 Å spacing of hydrated halloysite (Wada 1959), demonstrating that the intercalation was reversible.

At the time, the identification of 7 Å minerals in soil clays posed a problem because dehydration of halloysite was considered irreversible. Consequently, based on his 1959 conclusions, Wada formulated the working hypothesis that “formation of the salt complexes and regeneration of hydrated halloysite might be utilized as a criterion for differentiation of halloysite from kaolinite” (Wada 1961). However, when he submitted kaolinite to the same dry-grinding treatment with potassium acetate (KOAc), as he did for halloysite, to his great surprise (“*contrary to expectation*”), a strong and sharp reflection appeared at 14.2 Å, indicating an expansion along the *c*-axis similar to the case of halloysite (Wada 1961).

This experiment defeated the working hypothesis and constituted a major breakthrough in the whole field of clay mineral science: kaolinite was expandable! The observed expansion to 14 Å resulting from dry grinding with KOAc became a characteristic of all members of the kaolin group, since dickite had been shown previously to expand (Andrew et al. 1960). A few months later, in a short note, Weiss (1961) reported the intercalation of a neutral molecule, urea, between the layers of kaolinite. He indicated also that a few other neutral molecules could be intercalated, such as formamide, acetamide, chloracetamide, and thiourea.

The urea-kaolinite intercalate was the basis of a highly cited paper published by Weiss (1963). He demonstrated that the extremely thin-walled porcelains manufactured

in China as early as the 9th century, and whose secret of fabrication had been lost in the 13th century, resulted from urinary ageing of kaolinite under well-defined conditions. Anecdotally, his conclusion was reinforced by the accidental observation that a kaolinite-like mineral that had been for a long time below a pit of dung and liquid manure was indeed a urea-kaolinite intercalate (Weiss 1963).

These independent discoveries, made almost simultaneously by groups in Japan and Germany, were opening the way to new directions in clay minerals chemistry: kaolinite interlayer surfaces were accessible.

MOLECULAR INTERCALATIONS IN KAOLINITE

Why did it take so long to start the intercalation chemistry of kaolinite when smectites were known for a long time to be expandable and swellable? The individual layers of kaolinite are linked together through H-bonds between the aluminol groups of the octahedral sheets and the siloxane macrorings of the tetrahedral sheets. In addition, due to the asymmetric structure of the layers, strong dipole interactions add to the strength of the layer packing (Fig. 1A). Consequently, access to the interlayer spaces of kaolinite is not favored, and only a select group of guest compounds can directly intercalate (Lagaly et al. 2013). These guest compounds are divided into three groups: (1) compounds containing both H-bond donor and acceptor functions, such as hydrazine, urea, and formamide; (2) compounds with high dipole moments, such as dimethyl sulfoxide (DMSO); and (3) salts of short-chain fatty acids with a limited number of cations, such as potassium or ammonium acetate (Lagaly et al. 2013). These intercalates are not stable in water or under heating: the intercalated molecules are desorbed and generally the starting kaolinite is recovered.

Why is direct intercalation limited to a small number of compounds? The strong attractive forces linking the octahedral and the tetrahedral sheets are responsible. On the external surfaces a highly dipolar compound can interact with OH groups at the edges of the mineral, causing an elastic deformation of the layer that results in an opening of the interlayer space (Lipsicas et al. 1986). Recent studies on the adsorption of indole, a nitrogen heterocycle, on the surfaces of kaolinite have indeed shown that the density of the nitrogen heterocycle is larger on the octahedral side through interactions of the N–H group with the aluminol surface (Figs. 2, 3) (Fafard et al. 2013). Once the first step, the deformation, is completed, the intercalation becomes a cooperative and synergistic process that completely fills the interlayer space. A corollary of this mechanism of intercalation is counterintuitive: larger kaolinite particles do intercalate more readily than smaller ones, in contrast to what is generally observed in solid-state reactivity. The basis of this unusual behaviour can be found in the misfit existing between the tetrahedral and the octahedral sheets, creating a structural stress. If a particle is larger, its lateral dimensions increase, and consequently the cumulative degree of misfit increases. A result of the intercalation is to reduce the stress (Deng et al. 2002). In other words, the resistance to intercalation decreases in the case of larger particles. It is energetically more favorable to break the attraction forces between the stacked layers in the case of coarser particles.

Once direct intercalation is achieved, it becomes possible to replace the first intercalate (DMSO, KOAc, or urea, for example), which we call the preintercalate, by a much larger choice of compounds, and a large number of secondary intercalates have been reported (Lagaly et al. 2013), including bulky organic cations such as imidazolium

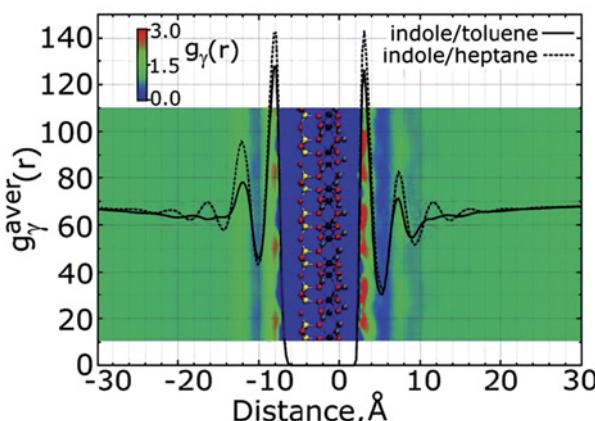


FIGURE 2 Multilayer adsorption of indole on kaolinite in toluene and heptane along the vector perpendicular to the kaolinite surfaces. The map highlights the maxima of adsorption (in red) near the Al-OH surface of kaolinite, which correspond to the first adsorption layer of indole, as well as the first and second depletion layers (in dark and lighter blue) at 5 Å and 8 Å. The density of the nitrogenous heterocycle is larger on the octahedral side. FROM FAFARD ET AL. (2013), REPRINTED WITH PERMISSION OF THE AMERICAN CHEMICAL SOCIETY

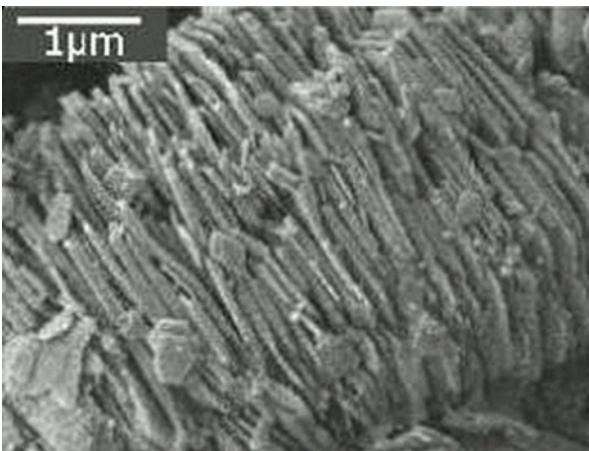


FIGURE 3 SEM image of the aggregation of kaolinite in the presence of adsorbed indole. FROM FAFARD ET AL. (2013), REPRINTED WITH PERMISSION OF THE AMERICAN CHEMICAL SOCIETY

derivatives (Letaief et al. 2008) and long-chain alkylamines. In the latter case the basal spacing increases linearly with the length of the alkyl chain (Komori et al. 1999a).

INTERLAYER GRAFTING

Intercalated compounds are readily displaced by water when the kaolinite intercalate is dipped in water, and their thermal stability is low. This prohibits applications of organokaolinates in aqueous media. The aqueous and thermal stabilities would be greatly enhanced if the intercalated compounds were covalently grafted on the interlayer surfaces. The Al-OH sheet is a candidate because of the reactive OH groups. The first interlayer grafting of kaolinite was achieved by intercalating and thermally grafting ethylene glycol (EG) and a series of alcohols and diols from a DMSO-kaolinite preintercalate to form an aluminum alkoxide sheet (Tunney and Detellier 1993). The grafted intercalates, resulting from the esterification of the aluminol groups, are characterized by a strong resistance

to extensive water washing, even under reflux for a long period of time. This was clearly described in the case of diethanolamine and triethanolamine (Letaief and Detellier 2007). Extensive washing can be used as a test to probe the grafting and to separate ungrafted and grafted intercalates. Intercalated nongrafted molecules will be removed, leaving only the grafted ones, and a slightly shorter basal spacing.

The formation of the Al-O-C bonds in EG-kaolinite was conclusively demonstrated by ^{27}Al solid-state nuclear magnetic resonance (NMR) studies showing a specific signal for the grafted Al-O-C unit. The ^{13}C - ^{27}Al distance of the grafted EG was measured by more sophisticated echoing double resonance NMR studies, which indicated a distance of 3.1 Å between the bonded ^{13}C nucleus of the EG molecule and the ^{27}Al nuclei of the kaolinite layer (Hirsemann et al. 2011). This distance is in excellent agreement with that of a covalent Al-O-C bond.

Rheological studies of aqueous dispersions of kaolinite modified by interlayer grafting of alcohols, diols, and glycol monoethers showed an exponential increase of the apparent viscosity with increasing alkyl chain length of the grafted molecules (Gardolinski and Lagaly 2005a). Some of these covalently modified kaolinates were then intercalated with long-chain amines (Gardolinski and Lagaly 2005b). The largest basal spacing ever obtained was for n-docosanamine and was reported as 64.2 Å. The aim of the study was to delaminate kaolinite in the thinnest-possible particles. The octadecylamine-kaolinite intercalate (basal spacing of 53.2 Å) was used for the delamination. These basal-spacing values indicate that the alkyl chains are in an all-*trans* conformation, perpendicular to the plane of the basal surface, in arrangements similar to what is observed with other layered materials, such as the layered double hydroxides. After dispersion and ultrasound treatment in toluene, the intercalates were recovered by repeated toluene dispersion and centrifugation. Although some thicker particles were still present, the sample contained thin lamellae forming hollow tubes (Fig. 4); the smallest one was formed by a single kaolinite layer (Gardolinski and Lagaly 2005b). The lateral misfit between the octahedral and tetrahedral sheets, mentioned above, was compensated by curling of the layers. This happens because the attractive forces between the layers were sufficiently weakened.

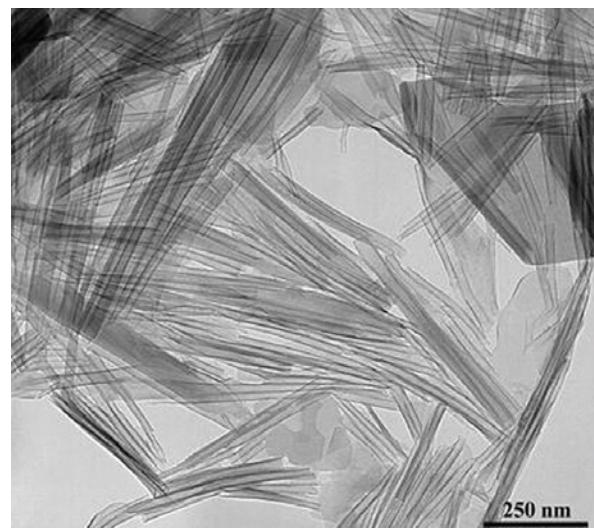


FIGURE 4 Transmission electron microscopy (TEM) image of the deintercalated kaolinites grafted with di(ethylene glycol) 2-ethylhexyl ether. FROM GARDOLINSKI AND LAGALY (2005B), REPRINTED WITH PERMISSION OF THE MINERALOGICAL SOCIETY OF GREAT BRITAIN

NANOCOMPOSITES

In the middle of the 1980s, Roy, Komarneni, and their colleagues (Roy et al. 1986; Komarneni 1992) introduced the generic term *nano*composites to recognize the regular heterogeneity, at the nanometer level, of some materials. The next two decades saw a spectacular increase in the use of this term, following the discovery that the properties of these materials could be significantly and synergistically improved with respect to the properties of each individual component, sometimes in a dramatic way (Sanchez et al. 2005). Since clay minerals had been largely used as fillers in polymers and other materials, it is not surprising that one would try to exfoliate clay minerals in single layers and disperse them in polymers. This was successfully achieved by Toyota researchers who were the first to report exfoliated montmorillonite–nylon nanocomposites, with strong improvement of the polymer mechanical properties (Kojima et al. 1993). The prolific field of clay-based polymer nanocomposites (CPN) was born (Carrado and Bergaya 2007). Essentially, two main types of CPNs can be considered: intercalated and exfoliated (Alexandre and Dubois 2000). If an increased basal spacing is observed after intercalation of the polymeric chains, the stacking of the layers is maintained and an intercalated nanocomposite is obtained. In contrast, if there is a complete loss of crystallographic orientation, the layers are dispersed randomly in the polymeric matrix and an exfoliated nanocomposite is formed. There is a range of intermediate situations.

Because of their swelling properties, smectites have typically been the clay minerals used for the preparation of these nanocomposites. What about kaolinite? If exfoliated, its intrinsic asymmetric structure, resulting in single layers with strong dipoles and functional surfaces covered by hydroxyl groups, could potentially lead to nanocomposites with properties differing significantly from those obtained with smectites.

KAOLIN–POLYMER INTERCALATED NANOCOMPOSITES

After the first major breakthrough in the chemistry of kaolin minerals by Wada and Weiss in 1961, a second came in 1988 with the first intercalation of a polymer in the interlayer space of kaolinite (Sugahara et al. 1988). The ammonium acetate of a kaolinite–ammonium acetate preintercalate was displaced by acrylonitrile. Subsequently, the intercalated monomer was polymerized to yield a kaolinite–polyacrylonitrile intercalated nanocomposite, characterized by a basal spacing of 1.3–1.4 nm. Essentially, three methods have been used to prepare CPN from kaolinite: (1) as exemplified in the case above, intercalation then polymerization of a monomer; (2) an approach largely used in the case of smectites, the direct intercalation of the polymer from its melt by displacing preintercalated molecules; this was successfully achieved in the case of polyethylene glycol (PEG) to produce kaolinite–PEG intercalated nanocomposites (Tunney and Detellier 1996); and (3) displacement of a preintercalate by a dissolved polymer (Komori et al. 1999b; Turhan et al. 2010). These methods were applied to a number of systems (Letaief and Detellier 2013). The nanocomposites obtained were invariably of the intercalated type. Strong attractive forces remain in effect after intercalation of a monolayer of polymer, resulting in ordering in the *c*-axis direction.

EXFOLIATION

As described above, hollow tubes can be formed after appropriate modifications and treatment of the kaolinite internal surfaces (Gardolinski and Lagaly 2005b; Matusik et al. 2009) or of the dickite internal surfaces (Matusik et al.

2012). The misfit between the tetrahedral and octahedral sheets of kaolinite was further exploited to transform the platy mineral into a curled one. Nanorolls or nanotubes (Fig. 5) were obtained in a one-step route from methoxy-modified kaolinite. Intercalation of alkyltrimethylammonium salts and exfoliation proceeded concurrently (Kuroda et al. 2011). Yuan et al. (2013) showed that the reaction conditions, such as the temperature, significantly influenced the formation of these nanorolls.

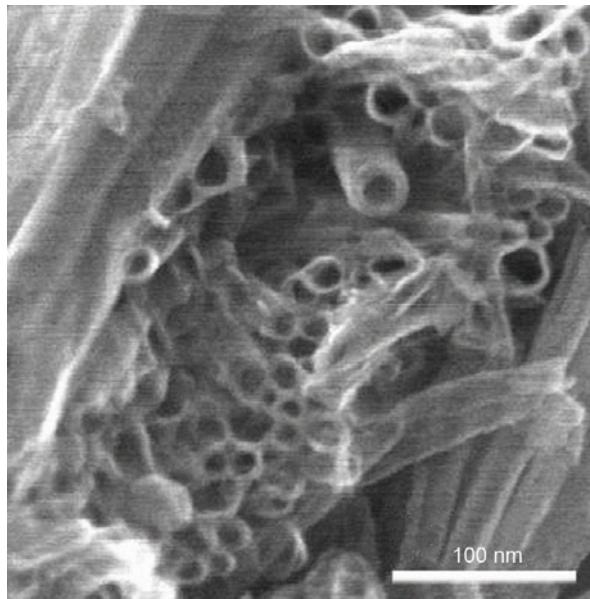


FIGURE 5 High-resolution scanning electron microscopy images of methoxy-kaolinite-cetyltrimethylammoniumchloride (C16TMACl) after heat treatment at 600°C. FROM KURODA ET AL. (2011), REPRINTED WITH PERMISSION OF THE AMERICAN CHEMICAL SOCIETY

Can kaolinite be exfoliated in a polymer matrix? A route to achieve this, based on the intimate mixing of two polyelectrolytes of opposite charges, has been reported by Letaief and Detellier (2009). Kaolinite was first modified by grafting triethanolamine on its internal surfaces and transformed into a quaternary ammonium ion, R₄N⁺, so that an extended lamellar hybrid polycation was obtained. An organic polyanion, polyacrylate, was mixed with this modified kaolinite inorganic polycation. Morphological changes were then obtained (Fig. 6): curved structures similar to previously reported nanorolls or nanotubes were observed, dispersed in the polymeric matrix. A simple chemical route has also been reported for the exfoliation of kaolinite in polymerized ionic liquids (Letaief et al. 2011).

The dispersion of individual layers of kaolinite opens the way to new types of clay nanohybrid materials, with improved interactions between the polymer and the clay mineral components in the exfoliated nanocomposite.

CONCLUSIONS AND FUTURE PROSPECTS

Significant advances have been made in the intercalation and interlayer grafting of kaolinite particles. These have allowed for the preparation of kaolinite–polymer nanocomposites. This field of research is in its infancy. Further developments will depend on the answer to the question of whether the kaolinite–polymer nanocomposites have advantageous properties compared to those of smectite–polymer nanocomposites. The properties to be considered include fire resistance, mechanical strength, deformation,

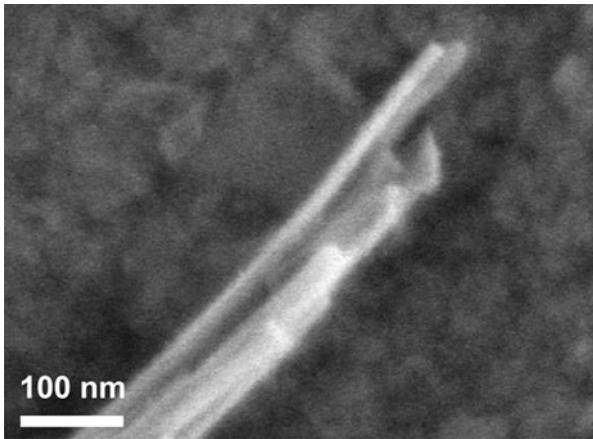


FIGURE 6 Scanning electron microscopy image showing the partial morphology of kaolinite exfoliated in sodium polyacrylate. FROM LETAIEF AND DETELLIER (2009), REPRINTED WITH PERMISSION OF THE AMERICAN CHEMICAL SOCIETY

and point-impact strength. They depend on the particle size and shape, the degree of exfoliation, and the amount of clay mineral needed to achieve the desired properties.

On a more fundamental level, there is a mismatch between the octahedral and tetrahedral sheets in both kaolinite and smectites. This mismatch is due to the difference in

bond length of the Si–O and Al–O (or Mg–O in the case of smectites) bonds. Planar layers are obtained in the case of kaolinite because of the strong interlayer interactions (dipolarity and H-bonding). If the kaolinite particles are exfoliated up to the individual layers, this interlayer interaction is minimized/disappears and the planarity of the kaolinite layers is lost: they curl, and a new type of material is obtained. The impact of curling on the properties of kaolinite–polymer nanocomposites has not yet been studied. This curling of the layers does not occur in smectites, or does so only partially, because the octahedral sheet is sandwiched between two tetrahedral sheets. It seems to be a good strategy to exploit this difference in behavior of kaolinite layers and smectite layers for the preparation of specific nanocomposites, such as ultrastiff nanocomposites and bionanocomposites (Podsiadlo et al. 2007).

ACKNOWLEDGMENTS

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TABLE SUMMARY OF NOMENCLATURE AND CLASSIFICATION OF KAOLIN-GROUP MINERALS

Properties	Kaolinite	Halloysite	Nacrite	Dickite
Crystal shape (SEM image)				
Space group Unit-cell parameters (reference)	C \bar{I} $a = 0.5154 \text{ nm}$ $b = 0.8942 \text{ nm}$ $c = 0.7402 \text{ nm}$ $\alpha = 91.69^\circ$ $\beta = 104.61^\circ$ $\gamma = 89.92^\circ$ Bish (1993)	Cc $a = 0.51 \text{ nm}$ $b = 0.89 \text{ nm}$ $c = 2.07 \text{ nm}$ $\alpha = 99.7^\circ$ Joussein et al. (2005)	Cc $a = 0.8906 \text{ nm}$ $b = 0.5146 \text{ nm}$ $c = 1.5664 \text{ nm}$ $\beta = 113.58^\circ$ Zheng and Bailey (1994)	Cc $a = 0.5137 \text{ nm}$ $b = 0.8918 \text{ nm}$ $c = 1.4389 \text{ nm}$ $\beta = 96.74^\circ$ Joswig and Drits (1986)
Structural views of hydroxyl orientations in octahedral sheet H = black, O = red Al = green				
Environmental occurrences	Weathered volcanic ash, pumice, granite, laterites, shales, sandstones	Weathered volcanic ash, pumice, granite, hot springs, hydrothermal systems	Hydrothermal systems (rare)	Diagenesis, hydrothermal systems

The differences among the kaolin-group minerals result from the distribution of vacancies in the octahedral sheet and nature of stacking shifts (Kogure et al. 2005). In kaolinite and halloysite, the directions of the 1:1 interlayer shift are easily disordered, which results in a wide range of stacking order (informally referred to as high to low crystallinity). Disorder is commonly distinguished in X-ray diffraction by peak broadening of the $k \neq 3n$ region of the pattern, but it is also seen in infrared spectra, electron diffraction patterns, and dehydroxylation temperatures.

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Halloysite is influenced by the substitution of larger Fe^{3+} for Al^{3+} , creating a misfit of the 1:1 layers and causing them to curl into tube- and sphere-like forms (Joussein et al. 2005). Halloysite expands and accommodates interlayer H_2O molecules (schematically shown above). Most importantly, the kaolin-group minerals display a wide range of crystal shapes and surfaces, all affecting their hydroxyl-group orientations and hence their physical-chemical properties.

Kaolins and Health: From First Grade to First Aid



Lynda B. Williams¹ and Stephen Hillier²

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The use of kaolins in health has its origins in prehistoric times. Humans and other animals consume kaolin for gastrointestinal ailments, digestive enhancement, and possibly nutritional supplementation. Kaolins are effective as hemostatic wound dressings, because they can clot blood from traumatic injury, with little damage to tissue. Various forms of kaolin have been shown to be antibacterial, and increasingly kaolins are being utilized in drug delivery. While nanoparticles of kaolin can have deleterious effects on human tissues, modern understanding of the mineralogy of kaolins and their interactions with human cells allows many health applications, reaching far beyond the prehistoric "first aid" uses.

KEYWORDS: kaolin, health, geophagy, drug delivery, antibacterial, wound dressing

INTRODUCTION

Anthropologist Berthold Laufer (1930) introduced his research on the medicinal uses of clays with the observation that "*Earths used as medicines...are almost without exception fine, fat and usually ferruginous clays.*" Clays are certainly fine in texture (<2 µm particles); smectites and many mixed-layer clays may be called fat, due to their ability to swell when hydrated (Fig. 1); and iron is a common substituent in clay minerals and plays a central role in human health. So it makes sense, perhaps, that humans looking for a natural substance to aid their well-being might seek these characteristics in clays used medicinally.

Because of their ubiquity, clay minerals have a long history intertwined with matters of human health (Reinbacher 2003). Medicinal uses of clays were recorded in antiquity by Greek philosopher Aristotle (4th century BC), by Pliny the Elder and Dioscorides (1st century AD), and in the writings of Galen of Pergamon (2nd century AD). The latter was an influential Roman doctor, whose visit to the Greek island of Lemnos did much to publicize the use of "Lemnian earth." The material was made into small stamped clay troches (Fig. 2) and used as a remedy for a variety of ailments and poisons. The practice resurged in the medieval period with the availability from various localities of *terra sigillata*, literally "signed earth," a measure to assure the authenticity of sources of medicinal clay.

The health benefits of clays have been documented on all continents (Laufer 1930). Most fascinating is **geophagy**, the eating of clays by man and animals. Indeed, kaolinitic clays recovered from the Kalambo Falls prehistoric site

in Zambia provide evidence that *Homo habilis* practiced geophagy over 2 million years ago; and this behavior remains widespread across the world today (Young 2011). Medicinal uses of clays have evolved from the common consumption in "first grade" to pharmaceutical uses in "first aid," and now go beyond, to antibacterial applications and as vehicles for drug delivery and cancer treatment. Here we review this evolving interface between kaolins and human health.

CLAY INGESTION

Geophagy

Historically, geophagy has often been viewed from outside with disdain, but in some cultures it is strongly linked to religion and healing beliefs (Ferrell 2008). Demographically, geophagy is consistently most prevalent among pregnant women and children. Geophagy is typically associated with a craving, and practitioners are highly selective when choosing the earths they consume.

From a health perspective, geophagy may have both positive and negative outcomes (Wilson 2003; Ferrell 2008; Young 2011). Its potential as a vector for heavy metal ingestion (e.g. some kaolins contain Pb, Cd, Hg, and As; Bonglaisin et al. 2011) or as a cause of infection due to soil geohelminths (intestinal parasites) are examples of negative effects. The typical quantity eaten is ~30 g and, given the absorbent nature of some clays, its consumption may give a feeling of satiety. Indeed, it has been suggested that hunger may motivate geophagy, but there is little evidence to support this. On the contrary, the widespread occurrence of geophagy among animals suggests that there may be an adaptive benefit.

The two most common hypotheses for the consumption of clays are that they (1) are a source of micronutrients and (2) offer protective effects against pathogens and toxins. Some researchers report a correlation between clay consumption by animals and craving for nutrients (e.g. salt, Fe, Ca), and it is well known (Wilson 2003) that many subsistence cultures add clay minerals to foods where dietary staples are toxic (e.g. acorns, tubers, some fruits). Geophagy may provide a dietary supplement for Fe, Zn, Ca, and micro-nutrients (Young 2011). An association between anemia and geophagy has been recognized since Roman times. However, geophagy does not appear to correlate with life cycle nutritional needs, and nutrient supplementation does not cause geophagy to cease. Furthermore, the low bioavailability (ease of absorption) of micronutrients in

1 School of Earth & Space, Arizona State University
Tempe, AZ 85287, USA
E-mail: Lynda.Williams@asu.edu

2 The James Hutton Institute, Aberdeen, AB15 8QH, Scotland;
Department of Soil and Environment, Swedish University of
Agricultural Sciences (SLU), SE-750 07, Uppsala, Sweden
E-mail: Stephen.Hillier@hutton.ac.uk

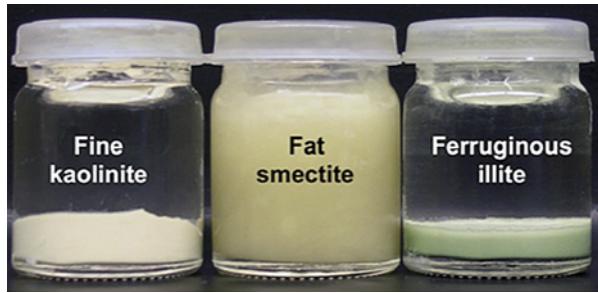


FIGURE 1 Examples of fine, fat, and ferruginous hydrated clays; <2 µm fraction, equal clay:water ratios.
PHOTO: STAN WILLIAMS, ASU

most geophagic earths makes it unlikely that they function as dietary sources. In fact the clays may adsorb and bind nutrients, making them less available to the body (Young 2011). Compared to normal food, many clay minerals are very rich in total Fe, but this does not mean that the Fe is bioavailable (Seim et al. 2013). Few studies have focused on the bioavailability of nutrients and toxins in clay minerals as they pass through the low-pH environment of the stomach (pH <2) to the small intestine (pH ~6.8). This is where mineral structure (Detellier and Schoonheydt 2014 this issue), composition, solubility, cation-exchange capacity, and surface-energy studies must be combined with clinical research. According to Young (2011), protection and detoxification is perhaps the most plausible hypothesis to explain geophagy. Indeed, from a mineralogical and geochemical point of view, it is clear that the composition of clays consumed is quite diverse (Wilson 2003; Ferrell 2008).

Gastrointestinal Medicine

Dr. Julius Stumpf (1865–1932) pioneered the modern use of clays via his *Bolus alba* (Fig. 2) treatment for gastrointestinal disorders, most famously for the treatment of cholera. Stumpf's extraordinary journey of medical discovery began with his observation of the preservation effects of clay on exhumed cadavers (Reinbacher 2003). Rather than any direct bactericidal effects, the action of kaolin in the gut has been related mainly to its ability to adsorb toxins, thus preventing their transmission to the patient, and to mechanical effects such as enclosing and carrying bacteria through the gut (Fig. 3) and forming an adherent coating on the walls of the bowel, like a "filter bed." Kaolins taken orally may interact with the digestive tract, coating the epithelial cells lining the small intestine villi and mixing with and modifying the physical and chemical properties of the gastrointestinal mucus layer.



FIGURE 2 (LEFT) Troche of ancient terra Lemnia (diameter 15 mm), showing Philoctetes, leader of the Greek fleet that sailed against Troy, bitten by a snake on Lemnos and cured by the application of Lemnian clay. PHARMAZIE-HISTORISCHES MUSEUM DER UNIVERSITÄT BASEL, SWITZERLAND, COURTESY OF CORINNE EICHENBERGER. (RIGHT) The modern equivalent, *Bolus alba*, in powder form, was pioneered by Dr. Julius Stumpf.

Notably, the morphology of the kaolin (platy, tubular, or spherical; Fig. 3) will affect the surface interaction between the clay and cells. The clay's high surface attraction to cell walls can provide a physical barrier for toxins, and the kaolin may bind bacteria or viruses (Lipson and Stotzky 1983) and absorb excess water for efficient removal from the digestive tract. The surface area of the kaolin crystallites is several orders of magnitude greater than the surface area of the villi; therefore, the mineral surface chemistry, in particular the exchangeable ions of the clays, can act as a source or a sink for both nutrients and toxic compounds.

As well as demonstrating that the clay mineral attapulgite (palygorskite) was more effective than kaolinite for the adsorption of alkaloids, bacteria, and toxins, Barr and Arnista (1957) found that halloysite was up to five times more adsorbent than kaolinite for alkaloid and toxin adsorption. This is interesting in the context of animal geophagy since there is a suggestion that halloysite is a "favored" clay. In the southeastern United States, Georgia has long been hailed as the primary producer of kaolin, producing >60% of the world's most pure kaolinite (Kogel 2014 this issue); it is locally known as "down home Georgia white-dirt" or by the misnomer "chalk." Kaolinite was originally the active ingredient in Kaopectate™, and it was shown to be mineralogically similar to "eko," a Nigerian clay sold for indigestion (Vermeer and Ferrell 1985). More highly adsorbent, attapulgite replaced kaolinite in Kaopectate but was in turn abandoned in 2003 in favor of synthetic bismuth subsalicylate (www.drugtopics.com). These modern uses of clay are in effect extensions of the use of *terra sigillata* in ancient pharmacopeia as an antidote to poisons and a treatment of disorders of the gastrointestinal tract. The composition of the famed and ceremoniously extracted Lemnian earth remains unknown, but it is reasoned to have contained a significant amount of kaolin (Hall and Photos-Jones 2008). The related ancient clay from the island of Samos is also thought to have been a compact form of kaolin, and four of the seven troches of *terra sigillata* preserved in the Hans Sloane collection in the British Museum are kaolins (Robertson 1996).

ANTIBACTERIAL CLAYS

The attraction of the kaolin surface to microbes and human cells is the basis for its use in many health applications (Cygani and Tazaki 2014 this issue). Antimicrobial clays—clays that kill human pathogens on contact—have been identified from hydrothermal clay deposits (Morrison et al. 2013). In these clays, redox-sensitive transition metals

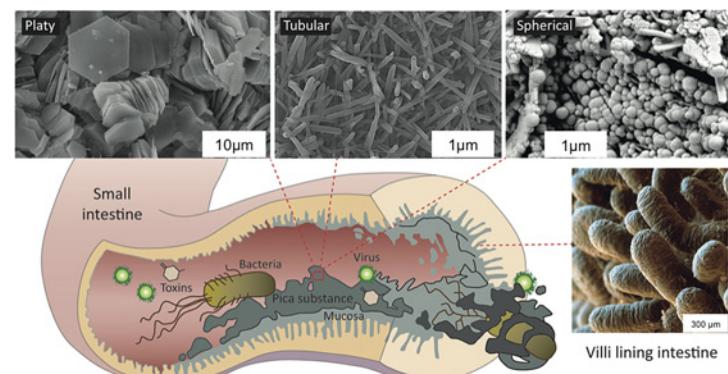


FIGURE 3 Geophagic clays are commonly kaolins with various morphologies (left to right: platy, tubular, spherical; white boxes indicate variable scale) and absorbent capabilities. In the small intestine they bind to endothelial cells, thus (1) reduce permeability of toxins across membranes, (2) bind pathogens directly, and (3) absorb excess water. The image on the lower right shows the comparative scale of villi (www.sciencephoto.com). CARTOON MODIFIED FROM YOUNG (2011)

appear to play a role in the bactericidal action. Recently, a lacustrine deposit from the Colombian Amazon basin has been shown to be antibacterial against *E. coli* and *B. subtilis*. This clay primarily contains kaolin (kaolinite, 30%; halloysite, 16%), along with smectite (31%), quartz (16%), and muscovite (7%). Compared to a nearly pure kaolinite standard (API #5), which has no effect on bacterial growth, the Amazon clay reduces the viability of the Gram-negative and Gram-positive bacteria tested by 3–5 orders of magnitude. Any of the minerals in this deposit may be ultimately responsible for the bacterial reduction, but it is clearly the geochemistry of the clay, in particular the surface energy and exchangeable cations, that is key to the bactericidal process. Notably, the aqueous leachate of this clay (50 mg clay / ml water), equilibrated over 24 hours, reaches pH ~4 but is not bactericidal; nor is the clay bactericidal after it has undergone cation exchange. The K-exchange either removes cations involved in the bactericide or changes the surface charge of the clays, affecting their interaction with cell walls. Certainly, a physical attraction of clays to the cell wall could cause suffocation or prevent nutrient intake. However the zeta potential (a measure of the degree of repulsion or attraction between particles in a colloid) of the Amazon clay and bacteria indicates no physical attraction. Transmission electron microscopy images show a few random clay particles adhering to the cell walls and intracellular Al^{3+} and Si^{4+} (S. C. Londoño, pers. comm.). Aluminum toxicity to cell membranes is possible, and nanoparticulate kaolins clearly cause lipid peroxidation and metabolic distress (Cervini-Silva et al. 2013).

PELOTHERAPY AND TRANSDERMAL TRANSFER

Pelotherapy is the therapeutic use of peloids, or muds, which are usually applied in baths with water of various compositions at temperatures approaching 45–50 °C (Tateo et al. 2009). The therapeutic effect may be from the thermal treatment, water chemistry (saline), and clay properties. Kaolin and smectite are most commonly used in pelotherapy, and are mixed with waters of various salinities and additives in a process referred to as “maturation.” Maturation is a period of time (months) that allows chemical equilibration between the clay and water. The mud is then applied topically, most commonly in spas for periods of normally 20–30 minutes. The medicinal effects have been studied extensively and were recently reviewed (Tateo et al. 2009) with reported evidence that chemical exchange through the skin is mostly effective for osteoarthritis. The major elements identified in the transdermal delivery from spa muds were Na, K, Ca, Mg, P, S, and Cl, as well as trace elements of unknown health effect.

In addition to the transfer of elements through the skin, the transdermal delivery of nanoparticles has been a recent focus (Buzea et al. 2007), and kaolins in certain soils may take this route. Thus entry into the dermis through the skin on the soles of the feet and translocation of soil particles within the lymphatic system are identified as the primary pathogenic events in the disease known as podoconiosis (*podos*, of the foot; *konion*, dust) (Price 1990), and a shared etiology is suggested for endemic Karposi sarcoma. Both are noncommunicable diseases of barefoot agriculturalists working fertile, clay-rich soils formed on volcanic parent materials. During the barefoot cultivation of wet soil, nanometric clay particles enter the dermis via sweat ducts, possibly aided by microtrauma from larger abrasive silt. Biopsies have demonstrated the presence of soil particles, many up to 0.1–0.2 µm in size, in tissues and phagosomes, in the feet and in the femoral lymph nodes of barefoot people in areas where the disease is endemic. Electron microprobe analysis indicates that the particles are composed of Si, Al, and Fe. In the absence of biological

systems for metabolizing silica, the residues of kaolinite particles accumulate in the tissues following differential dissolution of the alumina at the acidic pH of hydrolytic enzymes in the phago-lysosome. The accumulation results in chronic lymphatic irritation, inflammation, fibrosis, and collagenesis, causing an obstructive lymphopathy by interruption of the normal peristalsis of the lymphatic vessels, the malfunction clinically expressed as lymphedema and “elephantiasis.” The usually red or brown soils in such areas have long been recognized as rich in kaolinite and iron oxides, and recent analysis suggests that ultrafine mixed-layer kaolinite-smectites and paracrystalline allophanes are common components of these soils. The nanometric size of the clay components may explain their propensity to penetrate the dermis and further translocate in the lymphatic system.

HEMOSTATIC WOUND DRESSINGS

The use of clays as wound dressings dates back to the work of surgeon Dr. Addinell Hewson (1828–1889) in the USA and of Dr. Julius Stumpf in Germany (Reinbacher 2003), but their work was not widely accepted at the time. In the last decade, however, interest has been rekindled and various clays, including kaolinite, have been applied as hemostatic wound dressings, primarily in the treatment of soldiers wounded in battle. It is estimated that >80% of casualties in the Iraq and Afghanistan wars died from hemorrhage (Lawton et al. 2009). Commercially, zeolite, smectite, and kaolin are sold as absorbents and to promote clotting of bleeding arteries. When dry zeolite is hydrated, it produces enough heat (~100 °C) to cauterize blood vessels (Baker et al. 2007), but unfortunately it causes severe damage to vascular tissue, requiring post-trauma grafting. The use of smectite on wounds has also proven problematic as it can cause severe endothelial injury, massive thrombosis (lung, brain), and occlusion of the injured blood vessels (Lawton et al. 2009). Among the natural clays tested in hemostatic wound dressings (Fig. 4), kaolinite closely matches the clotting time (~2 minutes) of the dry, exothermic zeolite and is faster than the hydrated zeolite, montmorillonite, saponite, and hydrotalcite samples tested (Baker et al. 2007). The surface charge of kaolinite, which is negative at the pH of blood and human plasma, is positively correlated with its blood-clotting potential. Kaolinite applied to sterile

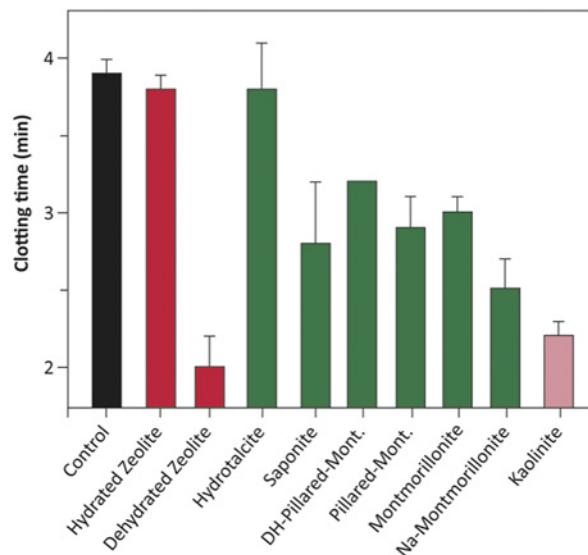


FIGURE 4 Examples of clays used in hemostatic wound healing and their effectiveness. DH = dehydrated. Mont. = montmorillonite. FROM BAKER ET AL. (2007), REPRINTED WITH PERMISSION

gauze (10% of total weight) was shown to be most effective at stopping bleeding and presented least difficulty during later debridement (removal of unwanted tissue).

CYTOTOXICITY

Clays may enter the body by respiration, ingestion, or transmission through the skin, and once in contact with cells, interactions are likely to be complex. Early studies of the cytotoxicity of kaolin towards various cell lines were driven by a desire to understand the pulmonary effects of kaolin inhaled into the lungs. Jaurand and Pairon (1990) reviewed ~30 studies on red blood cells and macrophages, and they concluded that kaolinite particles showed a variety of membrane interactions and metabolic impairments. Differences in cytotoxicity may be related to different origins of kaolins, including natural variation in size, surface properties, and coatings. Ghio et al. (1990) demonstrated that a kaolinite from Georgia was an extremely potent Fenton catalyst in the production of hydroxyl radicals from hydrogen peroxide, causing hemolysis. They further demonstrated that hemolysis was inhibited by iron chelators, and implicated Fe^{3+} present as an adsorption complex on the surface of the kaolin as the Fenton catalyst. In this context it should be noted that Fe^{3+} is a common though minor structural component of many kaolins, especially the more disordered kaolinites and particularly many of those formed in soils by pedogenic processes. Oxidative stresses appear to be one of the main cytotoxic effects of clay particles, and it is relevant that the ability of Fe in smectites to induce oxidative degradation of lipids has been documented (Morrison et al. 2013). The effects of various halloysites along with observed differences in cytotoxicity assays have been related to the availability of surface reactive sites on halloysites, dependent on marked differences in specific surface area among specimens (Cervini-Silva et al. 2013). Variation within and among different halloysite deposits may be a significant factor in their suitability for specific medicinal applications and performance.

CARRIERS FOR DRUGS

Due to their adsorption and surface interactions, clays have a long history of use as coatings or carriers for drugs. Patterns of drug release by desorption and pharmacological action in the gastrointestinal tract may be affected by changes in pH, ionic strength, or dilution, and therefore careful analysis of both the clay mineral and the drug is required to evaluate their interaction (White and Hem 1983). Most recent attention has focused on the use of nanotubular halloysite for controlled release of high drug loadings, 10–15% being typical. Halloysite may entrap molecules in various ways, including adsorption to the external and internal walls of the tubes, intercalation into the interlayer, and most particularly, loading into the central tubular pore or “lumen,” sometimes accompanied by condensation or crystallization. Halloysites have similar morphology to, but larger lumen than, carbon nanotubes, which, besides being prohibitively expensive for most pharmaceutical applications, have shown evidence for toxic effects (Buzea et al. 2007).

Compared to planar kaolinites, tubular halloysites have much higher surface areas and therefore significantly greater potential for binding, especially of cationic drugs. In addition, halloysite is amenable to many processing steps to further modify drug release. Poorly soluble drugs may be loaded from nonaqueous phases, and the variable and different surface-charge characteristics of the outer silanol and inner aluminol halloysite surfaces (see Detellier and Schoonheydt 2014 for structure) may be manipulated by controlling pH to optimize loading. Most drug molecules

DID YOU KNOW?

Look! I can't vomit but...
I am good at tasting food



Rats can't vomit!

Researchers who study kaolin consumption by animals have long known that rats are ubiquitous consumers of clay because of their opportunistic diet and common ingestion of toxins. Rats are not capable of emesis (vomiting), but eat kaolin to alleviate stomach distress. Rats have been used to study the emetogenic effects of cancer drugs because the amount of kaolin that rats eat is proportional to the severity of nausea induced by cancer treatments.

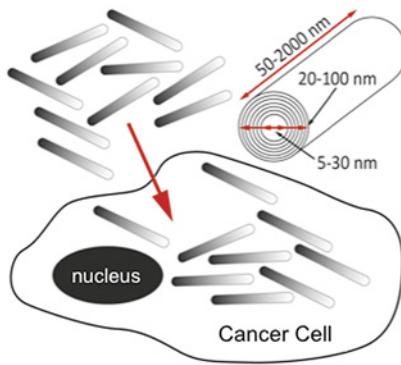
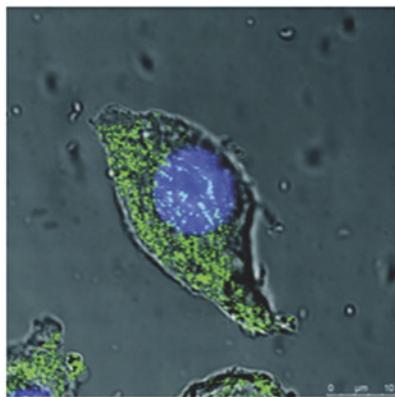
are too large to enter the halloysite interlayer space, but edge-exposed hydrated interlayer sites may influence the binding and release of many compounds via surface functional groups present on the drug molecules. In contrast, even larger molecules like proteins may enter the lumen. Smaller enzymes may also be encapsulated to shield them from degrading proteolytic macromolecular agents, hence maintaining biocatalytic functionality for a longer time. Depending on binding and the specific architecture, extended drug-release rates of hours to days have been obtained (Veerabadrin et al. 2009).

Other applications include targeted delivery (Fig. 5) of highly reactive compounds—such as Resveratrol, a polyphenol known for having antioxidant properties—that inhibit growth of malignant cancer cells; without encapsulation, these compounds would be rapidly metabolized (Vergaro et al. 2012). Even more remarkable are emerging applications of halloysite as a carrier for gene-therapy drugs, whereby functionalized halloysite tubes are used as vectors for drug delivery, via endocytosis (halloysite nanotubes are enveloped by the cell), enhancing antitumor activity (Shi et al. 2011). Procedures for the collection and treatment of circulating tumor cells from blood using halloysite as a substrate are also in development. Captured cancer cells remain viable, which allows testing for the effectiveness of different therapies, but the arrangement may also be used more directly for targeted delivery of therapeutic drugs (Hughes and King 2010).

CONCLUSIONS

Kaolins have been used in the most ancient medicinal practices because of their fine particle size, making them palatable, and their absorptive properties, which can alleviate nausea and indigestion by coating the stomach and small intestine. Kaolins can buffer the gastrointestinal pH and absorb toxins, bacteria, and viruses. Where nutrients (e.g. Ca, Mg, Fe) are bioavailable on exchangeable sites or in soluble phases, kaolins may contribute to human and animal nutrition. Kaolins are used for hemostatic wound dressings because their surfaces are adsorbent and promote blood clotting. Tubular halloysite has been used as a template for layer-by-layer assembly of drugs,

FIGURE 5 (TOP) Confocal laser scanning image of halloysite nanotubes (HNTs) inside a cervical cancer cell (HeLa). Green fluorescence shows HNTs surrounding the blue-stained HeLa nucleus. FROM VERGARO ET AL. (2012), REPRINTED WITH PERMISSION. (BOTTOM) Cartoon showing the internalization and typical dimensions of HNTs.



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for time-released drug delivery, and for the capture and targeted treatment of cancer cells. Finally, kaolins and other clays can be antibacterial when they act as reservoirs of exchangeable elements that are toxic to human pathogens.

Understanding the mechanisms by which clays deliver antibacterial components and catalyze reactions that lead to bactericide may be important in producing new antibacterial agents to fight drug-resistant bacteria. Caution is warranted when using any natural mineral for health applications because, like a Trojan horse, the delivery method may be a gift or an enemy and the complex interactions that occur between cells and clays are just beginning to be understood. Toxins may be adsorbed on clay, as well as nutrients. Clays can be nanoparticles that may pass through human membranes and lodge in tissues (lung, brain, lymphatics) where damage may occur. Inhalation of kaolin is not as toxic as silica, but cases of fibrosis have been associated with long-term exposure. As with any substance, the significant factor controlling whether kaolin acts as a nutrient or a toxin is the dose, whether eaten in first grade or used in first aid.

ACKNOWLEDGMENTS

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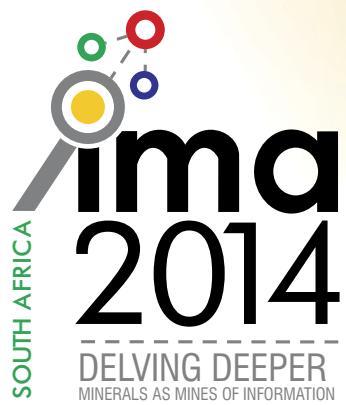
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INVITATION

The IMA 2014 Organising Committee invites you to participate in the 21st General Meeting of the International Mineralogical Association. This is the first time that this quadrennial conference will take place in Africa, with South Africa being the proud hosts. The overall theme of the conference is "Minerals as Mines of Information", in recognition of South Africa's resource wealth and mining heritage.

IMA 2014 promises to be an exciting experience, in bringing the world's leading mineralogists to Africa and exposing mineralogists from around the world to the latest research in various fields.

We look forward to welcoming everyone to South Africa in September!

Dr Sabine Verryn (Chairperson)

Dr Desh Chetty (Scientific Programme Chair)

Dr Craig Smith (Finance Chair)

PROGRAMME

IMA 2014 comprises 57 scientific sessions, grouped into ten parallel oral sessions per day, as well as poster sessions. The main themes included in the programme are:

- Clay Science
- Deep Earth
- Environmental Mineralogy / Geochemistry
- Economic Geology / Mineralogy, Applied Mineralogy
- Geochemistry and Petrology
- Mineralogical Crystallography
- Methods and Applications
- Minerals, Museums, Culture and History
- Planetary and Cosmic Mineralogy

Eight plenary speakers have confirmed in the fields of process mineralogy and geometallurgy, ore genesis, computed tomography, environmental mineralogy, petrology and crystallography. The latter pays tribute to the United Nations-declared International Year of Crystallography, 2014.

FIELD TRIPS

Bookings are still open for a number of field trips, including day tours that run during the conference. These include:

Pre-conference:

- Pilanesberg Alkaline
- Northern Bushveld
- Various mine visits
- Local Wits Geology

During conference:

- Anglo American ARC Labs
- SGS Laboratory
- Ceramic Factory
- Mintek
- Exxaro
- PPC Cement Factory

Post conference:

- Witwatersrand Golden Geology
- Pilanesberg Geology, Fauna and Flora
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PRESIDENT'S CORNER

The Need for Diversity



Chris Ballantine

Diversity in a biological context is always reported as a system's strength, our oceans and rainforests being amongst the richest of our planet's ecosystems if measured in terms of biodiversity. Diversity also provides strength in science, whether it is in the educational base of scientists starting their career or in the science environment that supports academic endeavour. Science societies have an important role to play in providing an academic environment. This

includes organising discipline conferences, making publications available, promoting workshops, ensuring outreach and providing an outward-facing profile for the public, industry, politicians and funders alike. But why does geochemistry need more than one society? It is a question I have been asked several times, and I always respond with the same answer – the need for diversity. After all, no one would expect all geochemistry publications to appear in only one journal, with one editorial structure and one set of editors; this would be unhealthy in the extreme, and the same is true for our community's societies.

Smaller societies can be focused on one scientific discipline and operate effectively to enhance their field. Larger societies can encompass more areas within the broad umbrella of geochemistry, help coordinate these fields and often have the resources to host larger conferences and organise publications. All are subject to the personalities who run them and, for longer-established societies, to the culture that has grown up with them. Societies are all different, and each has its own focus and strengths. It has been one of the pleasures in my role as EAG president to discuss and work with my counterparts in other societies to coordinate our respective activities; these colleagues have the same goal as EAG: to promote and enhance geochemistry and the Earth sciences. The richness of the many activities around us attests to the vigour of our community, and *Elements* provides a superb example of what can happen when societies pool their resources.

The smooth running of a society nevertheless has some associated risk. Large science societies can sometimes seem more like a corporate entity and risk losing a sense of ownership by their members. Any society that slumbers or becomes complacent will soon find its meetings and members diminish as other organisations respond better to the ever-changing community needs; but this happens only if there are active, healthy societies operating in related areas. In this sense both diversity and a level of friendly and supportive competition among societies is essential to keep the vigour of our community's science environment.

EAG supports society diversity through the Goldschmidt conferences, which it organises with the Geochemical Society (GS). Goldschmidt provides a forum for other societies to meet, conduct their business and present their awards under the greater umbrella of the meeting. EAG and the GS have been helped by the Geochemical Society of Japan over many years to bring this meeting to the community, and the GS and the Geochemical Society of Japan now have a formal memorandum

of understanding that cements our support of each other's interests through Goldschmidt. EAG has just signed a similar agreement with the Mineralogical Society of Great Britain and Ireland. EAG is working with several other societies at present to forge similar agreements. If you are reading this and think such an arrangement might be useful for your society, please contact us. We won't charge you corporate rates to have a booth at the Goldschmidt meeting; EAG will provide support to organise booths and workshops and to host society functions at cost. I don't want our community to be dominated by a monolithic society culture as some have become; rather, I want to celebrate and support the diversity of societies that provides the richness and strength we see today in our geochemical community.

Chris Ballantine, EAG President

EAG LECTURE TOUR 2013



Thomas Röckmann

Being nominated as an EAG Distinguished Lecturer was a great honor, but also a challenge. The Earth's atmosphere, my area of expertise, is not the classical geochemical topic. So the goal of my lectures was to show how our common tools – isotope measurements – are applied in atmospheric research to get information about biogeochemical cycles of atmospheric trace gases.

My tour started in Budapest, where Csaba Szabo and his group hosted my lectures at the Eötvös University. The visit was perfectly organized, except for the weather. So no sightseeing, but an intensive and interesting science-seeing program! I was impressed by the university's mineral collection, and I got a nice tour of the atmospheric aerosol-measurement observational program run by Imre Salma's group. Finally, I visited the Hungarian Academy of Sciences and Attila Demény's group, where we had some real isotope talk.

The same evening I continued my trip to Babeş-Bolyai University in Cluj Napoca, Romania, where I was warmly welcomed by Calin Baciu and Alida Timar, who took great care of me during my stay. I was very interested to learn about the research activities related to the emissions of methane from mud volcanoes in Romania, a natural source of this important greenhouse gas that is still not well understood. My hosts took me on a tour through town and for lunch and dinner, so I got to see quite a lot of the town and the picturesque landscape. The venue for my two lectures the next day was a beautiful old theatre at the university, and the lectures were attended by what seemed like the entire student population of the department.



Attentive audience at Babeş-Bolyai University, Cluj Napoca, Romania

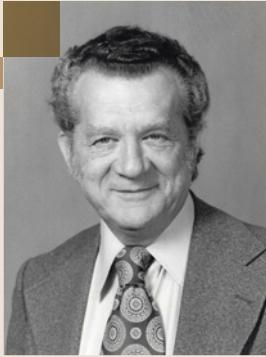
The following stop was the University of Science and Technology in Krakow, where I was more on home terrain, because Kazimierz Rozanski's group has an active research program on atmospheric trace gases. Jaroslaw Necki was my local host and made my first trip to Krakow a memorable experience. He took me to several

THE LIVES OF GREAT GEOCHEMISTS

Samuel Epstein (1919–2001)

Sam Epstein's career can be viewed as a thread linking the first developments in stable isotope geochemistry with its evolution into the mature science we know today. Born in 1919 near Kobryn in what was then Poland, Samuel Epstein emigrated with his family in 1927 to Winnipeg, Canada. He graduated from the University of Manitoba in 1941 with a BSc in chemistry and geology and in 1942 obtained his MSc in chemistry. His PhD (1944) in chemistry at McGill involved an investigation of the reaction kinetics of the high explosive nitroamine (RDX).

Sam's subsequent research took him into the field of rare gas fission products whilst working on the Canadian Atomic Energy Project in Montreal. During this period he met his wife, Diane, and Harry Thode, who proved to be a lifelong friend and great influence on his subsequent career. It was Thode who persuaded him to move to McMaster University, stimulated his first interest in isotope geochemistry, and, perhaps most importantly, in 1947 recommended him to Harold Urey at Chicago as the ideal scientist to work on a new isotopic palaeotemperature project he had initiated.



Sam and Diane moved to Chicago, renting an apartment above the garage of Harold Urey's home. The next few years proved to be a seminal period as Sam and his group, including John McRea, Charles McKinney, Heinz Lowenstam and Toshiko Mayeda, solved the instrumentation and analytical challenges of making oxygen isotope palaeotemperature measurements. It is a testament to his leadership, intellectual rigor, hands-on approach and technical expertise that today we still use the same sample preparation and analytical techniques for oxygen isotope thermometry measurements of carbonate minerals. At this time Sam also produced the first surveys of the isotopic compositions of

natural waters. In 1952 he moved to Caltech, where he established one of the most innovative isotope geochemistry groups of the time. Together with numerous students, many of whom also became world leaders, entirely new areas of isotope geochemistry were initiated. These include the oxygen isotope composition of meteorites; carbon isotope fractionation and processes in plants, including studies of the isotopic composition of plant cellulose and lipids; oxygen isotope variations in coexisting minerals in igneous rocks and applications to geothermometry and fluid-rock interactions; the first major isotopic studies of dolomites and cherts; the preservation of the oxygen isotope record in ancient sedimentary rocks; and isotopic studies of glaciers and Antarctic snow, ice and firn. In the 1970s Sam also worked on the isotopic composition of lunar samples returned as part of the Apollo missions. Sam Epstein remained at Caltech, working until his death in 2001.

This list is just a partial reflection of the breadth of Samuel Epstein's interests, and serves to highlight the unique part he played in the development of stable isotope geochemistry and his role as a teacher and mentor, inspiring generations of isotope geochemists.

Paul Dennis, University of East Anglia

interesting spots inside and outside the city, away from the typical tourist routes. The next day, we discussed in detail possible collaborations, and two of them have actually been started. My lecture in Krakow was part of a seminar series for the physics and computer sciences faculty, quite a different audience from the student-dominated talks before.

Two weeks later, I made another visit to the Czech Geological Survey in Prague. I landed in thick fog, and luckily Petr Dobes picked me up at the airport and brought me safely to the institute. I got an interesting tour of the impressive laboratory facilities there, and then went to an enjoyable lunch with Martin Novak, a gifted science entertainer. My two lectures in Prague were separated by a short coffee break, so I shortened them a bit, and I hope that I managed not to overload the audience with too much "atmosphere".

What I will remember from this lecture series is the excellent organization and the warm hospitality of my hosts at each location, and the wide variety of science topics I learned about during the discussions and visits. And finally, it brought to mind again how nice it is to be able to travel, in such a short period of time and without any complications, to many countries in Europe and experience the differences – but also the strong similarities – among the various cultures.

Thomas Röckmann, EAG Distinguished Lecturer 2013

Videos of the lectures given by Thomas Röckmann are available on the EAG YouTube Channel (the link is provided on the EAG website).

EAG AT EGU GENERAL ASSEMBLY 2014

At the EGU General Assembly held in Vienna, Austria, 27 April to 2 May, EAG was proud to co-sponsor six sessions highlighting the importance of geochemistry in various fields such as mineralogy, biogeoscience, the water cycle, atmospheric science and sedimentology, as well as present the 2014 EAG Eminent Speakers Award to Dan Yakir, professor at the Weizmann Institute of Science (Rehovot, Israel). Dan Yakir developed very early on the use of stable isotopes to trace carbon and water fluxes at the scale of the leaf and soil, up to the global scale, and is now one of the best-known experts dealing with ecosystems and the carbon cycle. EAG also had a booth and wishes to thank all the delegates who visited us, and we particularly welcome our new members.



Dan Yakir (right) receives the EAG Eminent Speakers Award from Marie-Aude Hulshoff, EAG Business Manager.



Association of Applied Geochemists

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26th INTERNATIONAL APPLIED GEOCHEMISTRY SYMPOSIUM – ROTORUA, NOVEMBER 2013

The 26th International Applied Geochemistry Symposium (IAGS), incorporating the 35th New Zealand Geothermal Workshop (NZGW), was held at the Rotorua Convention Centre on 18–21 November 2013. Registrations included 536 delegates attending the technical programme (275 IAGS and 261 NZGW, including 104 students), 22 exhibitors and 34 accompanying persons, representing 31 countries.



Audience at the opening session in the Rotorua Convention Centre Theatre

The technical programme commenced with a plenary session of four keynote presentations on the geology, geothermal systems and geothermal mineralisation of the Taupo Volcanic Zone. Subsequently, the programme split into separate IAGS and NZGW plenary and concurrent sessions, with a total of 32 keynote, 222 oral and 55 poster presentations. There was a maximum of three concurrent IAGS sessions. The IAGS sessions included 6 sessions sponsored by the Society of Economic Geologists with some notable international speakers, such as Richard Arculus, Stephen Cox (both Australian National University), Rich Goldfarb (U.S. Geological Survey), David Groves (University of Western Australia), Iain Pitcairn (Stockholm University), Terry Seward (Victoria University of Wellington) and Stephen Turner (Newmont). The conference ended with a keynote presentation on wine terroir by Larry Meinert (U.S. Geological Survey), who explained why the Gimblet Gravels area in Hawkes Bay produces great wine. Apparently Gimblet Gravels is the only appellation in the world defined by a geological unit.

Eight short courses and workshops and 11 pre- and post-conference field trips were run in association with the IAGS/NZGW. All field trips were blessed with great weather. Short course registrations ranged from 8 to 29, whereas field trip participation ranged from 5 to 31 with the low numbers of the range representing the helicopter trips to White Island. An accompanying-persons programme provided tours on five days, beginning on Sunday.

The meeting had social functions on each evening, providing plenty of opportunity for networking. Sunday was the Powhiri and Welcome function. Monday was a 'Students Meet Industry' evening, but open to all. More than 320 attended the Tuesday night conference dinner held at the Blue Baths, a very attractive and historic venue. Wednesday night provided a choice of three activities: the Tamaki Maori Village Hangi and concert, attended by more than 80 of the overseas delegates, a pub crawl with more than 100 participants, and the Hydrothermal Fluid Society wine tasting attended by 27, with 83 bottles of wine up for tasting! Eighty delegates attended the Thursday evening farewell dinner poolside at the Millennium Hotel.



More than 320 attended the conference dinner at the Blue Baths.

The 2013 conference was a real departure from the norm for the biennial IAGS, because of the incorporation of the NZGW and SEG sessions. Positive responses from the delegates indicated that the combined conference was a great success.

Tony Christie (T.Christie@gns.cri.nz)
GNS Science, 26th IAGS Convenor

RECENT ARTICLE PUBLISHED IN EXPLORE

YULIA A. UVAROVA, JAMES S. CLEVERLEY, AARON BAENSCH, MICHAEL VERRALL (2014) Coupled XRF and XRD analyses for rapid and low-cost characterization of geological materials in the mineral exploration and mining industry. EXPLORE 162 (March 2014)

A set of 200 pulps from a diamond drill hole at the Brumunga pyrite mine, South Australia, was analysed by portable X-ray fluorescence (pXRF) spectrometry and portable X-ray diffraction (pXRD). The corresponding diamond drill core was logged and the analytical data were interpreted in light of the logging data. The rocks intersected by the drill hole are fine-grained greywackes, quartzites, siltstones and pyrite- and pyrrhotite-bearing siltstones of the Nairne Pyritic Formation, in places intruded by dolerite dikes. The drill hole intersected the main pyrite-pyrrhotite ore body from 130 to 280 m and a number of thin zones with iron sulfide veins. Portable XRF and XRD analyses were performed on powdered material using an Olympus Delta Premium pXRF and Terra pXRD instruments. The pXRF data show that sulfide veins and main mineralisation are evident as sharp increases in Fe and S contents, whereas dolerite dikes are distinguished by well-defined peaks in Ca. The assemblage quartz-feldspar-biotite-muscovite ± actinolite ± chlorite ± pyrite ± pyrrhotite was identified in all samples studied with pXRD, and mineral percentages were quantified. Sulfides were identified in samples from the mineralised zone and veins, and actinolite was identified in samples from dolerite dikes. Our study shows that coupled portable XRD-XRF analysis offers rapid and low-cost characterization of geological materials for mineral exploration and the mining industry and delivers elemental and mineralogical information of high quality. The integrated data can then be used to constrain lithologies and contacts between various units, hydrothermal alteration and ore types.

Yulia A. Uvarova (yulia.uvarova@csiro.au)
CSIRO Earth Science and Resource Engineering, Australia



Japan Association of Mineralogical Sciences

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

PREMIER RESEARCH INSTITUTE FOR ULTRAHIGH-PRESSURE SCIENCES (PRIUS) – A NEW NATIONAL JOINT USAGE / RESEARCH CENTER AT GRC, EHIME UNIVERSITY

The PRIUS, operated by the Geodynamics Research Center (GRC) at Ehime University, has been approved as a Joint Usage / Research Center by the Japanese Ministry of Education, Culture, Sports, Science, and Technology. The main purpose of PRIUS is to effectively utilize (1) advanced high-pressure apparatus and analytical instruments, (2) techniques of ultrahigh-pressure experiments and numerical calculations, and (3) ultrahard nanopolycrystalline diamond (NPD, HIME diamond) products at GRC via collaborative research to further develop ultrahigh-pressure research in mineral/materials sciences and related scientific fields. PRIUS is calling for the following types of collaborative research in the ultrahigh-pressure sciences and any related fields.

1. Use of PRIUS facilities

This type of collaborative research project mainly utilizes research facilities at GRC, including high-pressure apparatus and analytical instruments, and some facilities in other institutions installed and run by GRC. The following experimental apparatus are applicable:

- Ultrahigh-pressure apparatus and related equipment, such as multianvil apparatus (FIG. 1) and diamond anvil cells
- Analytical instruments and processing equipment such as ATEM, FE-SEM, FIB, XRD
- Measuring instruments and ultrahigh-pressure apparatus at synchrotron radiation facilities



FIGURE 1 High-pressure apparatus at GRC

2. Collaborative research

This is a collaborative research project without utilizing any GRC facilities (supplementary use of the facilities is applicable). The following are examples of the subject areas:

- Utilization of HIME diamond (FIG. 2)
- Theoretical simulations such as *ab initio* calculations and computational fluid calculations, etc.
- Analysis and ultrahigh-pressure synthesis of samples on request



FIGURE 2 Nanopolycrystalline diamond (NPD, HIME diamond) synthesized at GRC

3. Meetings

A research meeting is to be organized and held, in principle, at Ehime University. If necessary, it may also be held at another domestic institution or university, but a statement of this necessity in the application form is required in this case. It is also acceptable to organize a training (internship) program combining lectures and practical training for the purpose of improving the research techniques of researchers and students.

Once the application is approved, we may cover some travel expenses (*domestic* travel costs and accommodation) of successful applicants, depending on the financial situation at PRIUS. For further details, please see the following website: www.ehime-u.ac.jp/~grc/prius/index_eng.html.

If you are interested in collaborative research at PRIUS, please send an e-mail to prius@stu.ehime-u.ac.jp or directly contact corresponding researchers at GRC.

Professor Tetsuo Irfune

Director of PRIUS and GRC, Ehime University, Japan

JOURNAL OF MINERALOGICAL AND PETROLOGICAL SCIENCES

VOL. 109, NO. 2, APRIL 2014

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- Formation of iron mineral fine particles by acidic hydrothermal alteration experiments of synthetic Martian basalt
Hiroshi ISOBE and Miwako YOSHIZAWA

Letters

- Adachiite, a Si-poor member of the tourmaline supergroup from the Kiura mine, Oita Prefecture, Japan
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- Formation process of olivine-clinopyroxene cumulates inferred from Takashima xenoliths, Southwest Japan arc
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- Secondary phosphates in montebrasite and amblygonite from Nagatare, Fukuoka Prefecture, Japan
Yohei SHIROSE and Seiichiro UEHARA

www.dmg-home.de


SCIENTIFIC PROGRAM

Petrology and Geo/Cosmochemistry

- Meteorites and the early Solar System
- The mineral record of impact events
- Stable and radiogenic isotopes – clocks and tracers of rocks
- Magmatic petrology – from melt to rock
- Metamorphic rocks: petrology, geochemistry, geochronology
- Minerals – fluids – rocks
- Minerals in the environment – from geo- to biosphere

General Mineralogy and Crystallography

- Microstructures, textures, and interfaces of minerals
- Mineral physics and the deep Earth's interior
- Crystal structures and properties of materials
- Mineralogical crystallography
- Modern techniques for mineralogical research
- Mineralogical museums and collections

Applied Mineralogy

- Functional materials
- Technical mineralogy – cements, ceramics, and glasses
- Economic minerals: formation, characterization, and applications
- Archeometry and monument conservation

Plenary Talks

- Prof. Dr. G. Diego Gatta
Università degli Studi di Milano (Milano, Italy)
- Prof. Dr. Mihály Pósfai
University of Pannonia Veszprém (Veszprém, Hungary)
- Dr. Hella Wittmann-Oelze
Helmholtz-Zentrum-Potsdam (Potsdam, Germany)
- Prof. Dr. Klaus Keil
University of Hawaii (Honolulu, USA)

Website: www.dmg2014.de

22nd ANNUAL MEETING OF THE GERMAN CRYSTALLOGRAPHIC SOCIETY (DGK)

Most minerals are crystalline, and if in some of them the ordering of atoms is in doubt, the degree of crystallinity of those minerals is an important topic of mineralogical research. Historically, when ideas about the inner structure of crystals and its correspondence with macroscopic crystal morphology emerged, the study of crystals was the study of minerals. During the 20th century crystallography became an important part of biological sciences as well, especially in the subdisciplines of microbiology and structural biology, and also in highly applied branches like pharmacology.



Susan Schorr and members of her organizing team at the booth of a sponsoring company. The persons to the left and right of the support team are officials of this company, which sponsored more than just the team T-shirts.

Stereotypic thinking thus creates tension in the study of crystals among geological science, materials science, and biological science, and this tension led to an ironic schism in Germany in the early 1990s. Just after the reunification of East and West Germany, the mineralogically and crystallographically inclined community dissociated into the German Mineralogical Society (DMG, now with more than 1700 members) and the German Crystallographic Society (DGK, now with more than 1000 members). Many scientists are members of both societies!

The German Crystallographic Society held its 2014 annual meeting in Berlin in the convivial ambiance of Freie Universität's Henry Ford Bau. Some 516 participants were part of this successful meeting, directed by Susan Schorr and her supporting team from FU Berlin and Helmholtz Centre Berlin. As usual, the meeting consisted of about one-third organic and two-thirds inorganic crystallography. In Berlin a new session theme, "Crystallography in Geology," was convened by Rainer Abart (Vienna) and Claudia Trepmann (Munich). The topics covered the entire geosphere, from near-surface conditions (e.g. ancient and recent marine-carbonate cements) to the Earth's crust (e.g. slip systems in zircon) and down into the mantle (e.g. inclusions in diamond). The most used techniques in geologically inclined crystallography seem to be modern single-crystal and powder X-ray diffraction, including synchrotron methods, as well as electron diffraction, especially electron backscatter diffraction. The transmission electron microscopy community was probably underrepresented in this session. Still, polarized-light microscopy remains an indispensable complement to the more recent (and much more expensive) research tools.

The session was very useful in highlighting the approaches followed by crystallographers from various subdisciplines. In "Crystallography in Geology," there was strong emphasis on texture formation, surface crystallography, and the crystal's response to outer forcing, like applied or reaction-induced pressure. Thus, there was a strong interest in the ways crystalline substances interact with their surroundings. This contrasts with crystallographic research that places the focus on the synthesis and structural characterization of isolated substances, often in search of technical applications or improvements. It seems that both traditions could profit from close interaction. Moreover, there is an obvious need to close the gap between structural biology and inorganic materials science, and this could easily be done by mineralogists who have adopted "biomineralogy" as a centerpiece of modern mineralogical science. Consider that ordinary limestone is in large part a product of biomineralogical processes, not to speak of phosphates and the bones, teeth, and other mostly undesired crystalline precipitates in our own bodies. Along with "Crystallography in Geology," which should be continued, I suggest that colleagues in the DGK make "Crystallography of Biominerals" a topical session in the coming years.

Ralf Milke (FU Berlin)

DMG JOINT WORKSHOP

A joint workshop of two German Mineralogical Society (DMG) sections – Chemistry, Physics, and Crystallography of Minerals (CPKM) and Applied Mineralogy in Technique and Environment (AMiTU) – was held on 26–28 February 2014 in Bad Windsheim, in the northern region of Bavaria. The workshop was organized by the section leaders, Christoph Berthold from the University of Tübingen and Gert Klöß from the University of Leipzig. Some 35 graduate students, postdocs, and senior scientists attended 23 lectures, which were mostly given by the students. The aim of this workshop was to bring the students into contact with experienced scientists in order to start discussions about the students' recent and future scientific work.

At the start, Claudia Weidenthaler from the Max-Planck-Institute für Kohlenforschung introduced the audience to a new section of the German Crystallographic Society (DGK) with the translated title Crystallography in Materials Science. Due to the very similar topics, a discussion started about combining the annual workshops of the previously mentioned sections of the DMG and DGK. Afterwards, several young scientists from the Helmholtz-Zentrum Berlin (HZB) gave an overview on the synthesis and microstructural analysis of thin films used in photovoltaic

Participants in the 2014 CPKM/AMiTU workshop



cells. Subsequently, students from the University of Göttingen gave an introduction to the analysis of pressure-induced phase transitions and the behavior of microalloys. After a short break, students from the University of Jena and LMU Munich presented their studies on the chemistry of crystals, hydrothermal phase relations, and the Raman spectroscopy of sodalites, which were followed by interesting talks from students from the universities of Tübingen and Leipzig about non-destructive XRD, XRF, and thermal analysis. The lectures of the first day were complemented by an excellent plenary talk given by Helmut Mayer (Friatec AG Mannheim) about oxide ceramic materials for high-performance products.

On the second day, the topics of the talks were again diverse and very fascinating. Students from the University of Würzburg, the University of Tübingen, and the Federal Institute of Materials Research and Testing (BAM) in Berlin presented their results from the high-resolution *in situ* analysis of the hydration of bassanite, cementitious materials, and glasses. The lectures closed with topics related to geoscience, environmental science, and materials science.

The next workshop is expected to be held at the end of February in 2015. Please mark your calendar accordingly. I hope to see you next year!

Moritz-Caspar Schlegel
(Helmholtz Zentrum Berlin)

International Diamond School
THE NATURE OF DIAMONDS AND THEIR USE IN EARTH'S STUDY

Bressanone-Brixen (Italian Alps)
27-31 January 2015

FIRST ANNOUNCEMENT

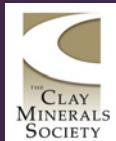
The school will provide a general overview of the most recent advances in diamond research as well as an introduction to modern techniques for diamond exploration.

Committed speakers:

Steven Shirey (geochemistry, Carnegie Institution Washington) -
Graham Pearson (geochemistry, University of Alberta) - Andy Davy (diamond exploration, Rio Tinto) - Dan Frost (petrology, Bayerisches Geoinstitut) -
Pierre Cartigny (geochemistry, Institut de Physique du Globe de Paris) - Jeff Harris (geochemistry, mineralogy, University of Glasgow) - Ross Angel (mineral physics, University of Padova) - Mike Walter (petrology, University of Bristol) - Bruce Kjarsgaard (diamond exploration, Geological Survey of Canada) - Frank Brenker (mineralogy, University of Frankfurt) -
Paolo Nimis (petrology, University of Padova) - George Read (diamond exploration, Shore Gold) -
Matteo Alvaro (mineral physics, University of Padova)

International organizing committee:
Fabrizio Nestola (University of Padova, Italy)
Steven Shirey (Carnegie Institution, Washington DC, USA)
Graham Pearson (University of Alberta, Canada)

For more information:
www.indimedea.eu/diamond_school_2015.htm



The Clay Minerals Society

www.clays.org

THE PRESIDENT'S CORNER



Michael Velbel

In my previous (and last solo) President's Corner, I prepared to bid farewell. By the time you read this, my successor will have taken office. Crawford Elliott's first President's Corner follows. Thank you all for helping CMS thrive.

Best wishes,

Michael Velbel (velbel@msu.edu)

Past President, The Clay Minerals Society



W. Crawford Elliott

nanocomposites and three field trips visiting local soils, lignite mines, and Ca bentonites. We are fortunate to have a dedicated and committed membership contributing to improve our knowledge of these fine-grained minerals. This new knowledge reaches throughout the *Elements* family and to the broader scientific community. At this meeting, we thanked Michael Velbel for serving as president for the past year. As I start my term as president, to last until July 2015, I would like to thank Michael again on behalf of the CMS.

The CMS values being part of the *Elements* family. *Elements* and our journal *Clays and Clay Minerals* are our scientific voices to the larger scientific communities. We look forward to contributing to *Elements* and being part of the *Elements* family.

Best wishes,

W. Crawford Elliott (wcelliott@gsu.edu)

President, The Clay Minerals Society

STUDENT RESEARCH SPOTLIGHT



Erik Oerter

Congratulations to **Erik Oerter** (University of California at Berkeley) for winning a CMS Student Research Grant and to **Anke Hertam** (Freiberg University of Mining and Technology), **Florence Ling** (Pennsylvania State University), and **Austin Boles** (University of Michigan) for winning a CMS Student Travel Award!

Erik Oerter's research aims to elucidate the **role of clay minerals in influencing the isotopic composition of soil water**. Erik's research has shown that the exchangeable cations (Mg, Ca, K, Na) adsorbed on smectite clay minerals can significantly influence the isotopic composition of soil water. For example, in montmorillonite

with 5% water content, adsorbed Mg and Ca cations deplete the $\delta^{18}\text{O}$ value of water by up to 1.55‰ relative to pure water, K ions enrich $\delta^{18}\text{O}$ by up to 0.86‰, and Na ions exert no effect. This adsorbed cation isotope effect has implications in studies of pedogenic carbonate, plant-soil water use, and soil-atmosphere interaction. Erik's Student Research Grant was accompanied by the Robert C. Reynolds, Jr. award for the best proposal received by CMS in 2013.



Anke Hertam

Anke Hertam is examining the **utility of lithium-bearing mica for the recovery of battery-grade lithium carbonate**.

In particular, Anke is investigating correlations between the structural features and leachability of zinnwaldite, a Li-bearing mica from a deposit near the municipality of Zinnwald, Germany. Anke is applying a range of analytical methods (vibrational spectroscopy, MAS-NMR, powder XRD, SEM-EDX, and Mössbauer measurements) to characterize the effects of fluoride concentration and Fe(II) oxidation during dry thermal and hydrothermal treatments of zinnwaldite with various aqueous electrolyte solutions. Anke's presentation of her work at the 50th Annual Meeting of the CMS in 2013, for which she won the award for the best student poster presentation, was a highlight of her year and led to new connections with many clay scientists.



Florence Ling

Florence Ling's research aims to characterize the **uptake of lead by manganese oxides**. The cycling of lead in air, soil, and groundwater is an important societal concern because of its long-term neurological impact on children and the large number of sites contaminated by lead. Birnessite and other Mn oxides are known to exhibit a strong affinity for Pb, but the adsorption mechanism is not fully understood. Florence is using time-resolved X-ray diffraction in a series of flow-through experiments to characterize Pb uptake by hexagonal H-birnessite and triclinic Na-birnessite. Her results indicate that lead, in addition to adsorbing on the external surfaces, also enters the birnessite interlayers. This interlayer uptake takes place on time-scales of days to weeks and is slower for hexagonal than for triclinic birnessite.



Austin Boles

Austin Boles' research includes the investigation of **neomineralized clays in continental fault zones**. Stable isotope analysis of clay minerals from gouge rocks of the San Andreas Fault (California, USA), the North Anatolian Fault (Turkey), and the Alpine Fault (New Zealand) is underway and promises to yield interesting data that may help identify mineralizing-fluid sources. Another project currently underway involves a test of the orogenic fluid-flow hypothesis, whereby hot basinal brines are extruded laterally from deep basins in response to mountain building. Again, the neomineralized clay phases are proposed to act as tracers of the orogenic fluid composition. These avenues of inquiry promise to lead to a better understanding of the fluid architecture of the upper crust.



Meteoritical Society

<http://meteoritalsociety.org>

METEORITE NOMENCLATURE COMMITTEE REPORT



Chris Herd

The purpose of the Nomenclature Committee (NomCom) is to approve new meteorite names, and to establish guidelines and make decisions regarding the naming of meteorites. We are also charged with keeping the community apprised of new meteorites through the *Meteoritical Bulletin* and the Meteoritical Bulletin Database (www.lpi.usra.edu/meteor/metbull.php). The issue of how best to publish the *Meteoritical Bulletin* is close to resolution. In the meantime, you should be aware that all new meteorites are automatically added to the next issue of the *Bulletin*

by the database editor, and the issues are now yearly (e.g. MB102 = 2013, MB103 = 2014). The contents of a particular *Bulletin* are accessible using the "Publication" dropdown window in the database. MB102 will contain 3141 meteorites (1433 non-Antarctic), and MB103 currently has 904 meteorites (358 non-Antarctic). The need for a regularly updated database has never been greater!

As of January 1, we welcome Carl Agee as the new editor of the *Bulletin*. Carl is the director of the Institute of Meteoritics at the University of New Mexico. New NomCom members include Tasha Dunn, Jérôme Gattaccea, and Audrey Bouvier. Special thanks to Michael Weisberg, Laurence Garvie, and Pierre Rochette, who have completed their terms on the committee. Laurence was a dedicated editor, and his service was outstanding. Michael also served as editor, and his insights have been invaluable.

Please do not hesitate to contact me (herd@ualberta.ca) with questions or concerns about NomCom and especially with suggestions for improvement. Essential information on meteorite nomenclature, instructions and the template for reporting new meteorites, and NomCom membership may be found on our homepage: http://meteoritalsociety.org/?page_id=106.

Chris Herd, NomCom Chair



ASTEROIDS, COMETS, METEORS MEETING 2014

JUNE 30–JULY 4, 2014

Helsinki, Finland

The Asteroids, Comets, Meteors meeting focuses on the research of small Solar System bodies. Small bodies are the key to understanding the formation and evolution of the Solar System, as they carry signals from presolar times. Understanding the evolution of the Solar System helps unveil the evolution of extrasolar planetary systems. Societally, small bodies will be important future resources of minerals. The near-Earth population of small bodies continues to pose an impact hazard, whether it is from small pieces of falling meteorites or from larger asteroids or cometary nuclei capable of causing global environmental effects.

Asteroids, Comets, Meteors (ACM) is the leading international conference series in the field of small Solar System bodies. The first three conferences took place in Uppsala, Sweden, in 1983, 1985, and 1989. The conference is now returning to a Nordic country after a quarter of a century. After the Uppsala conferences, meetings took place in Flagstaff, Arizona, USA, in 1991; Belgirate, Italy, in 1993; Paris, France, in 1996; Ithaca, New York, USA, in 1999; Berlin, Germany, in 2002; Rio de Janeiro, Brazil, in 2005; Baltimore, Maryland, USA, in 2008; and Niigata, Japan, in 2012. ACM in Helsinki, Finland, in 2014 will be the 12th conference in the series (www.helsinki.fi/acm2014; e-mail: acm-2014@helsinki.fi).

Looking forward to seeing you in Helsinki!

Karri Muinonen

Chair, ACM2014 Scientific Organizing Committee
Department of Physics, University of Helsinki and
Finnish Geodetic Institute

METSOC ANNUAL MEETING SCHEDULE

2014	September 8–12, Casablanca, Morocco
2015	July 27–31, Berkeley, California, USA
2016	August 7–12, Berlin, Germany
2017	Dates to be announced, Albuquerque or Santa Fe, New Mexico, USA



Mineralogical Society of Great Britain and Ireland

www.minersoc.org

NOTES FROM LONDON

New Society Award, in Honour of Prof. R. A. Howie: The Mineralogical Society Best Paper Award

The R. A. Howie Memorial Lecture Award is named in honour of Prof. R. A. Howie (1923–2012), who was a distinguished professor of mineralogy at Kings College London and Royal Holloway University, London. The award will be made annually to “the lead author of the ‘best paper’ published (in English) in a mineralogical journal (*sensu lato*) within three years of award of his/her PhD”. The nomination process is outlined below.



The award will take the form of a bursary (£1000) to attend an international conference (to be agreed with the Society) to present a paper which will be entitled the R. A. Howie Memorial Lecture. The money will be paid on receipt of an official confirmation of registration for the conference.

Nominations

Nominations can be made by any scientist (including a co-author) but not the nominee him/herself and must be supported by a fellow scientist familiar with the nominee’s work.

Nominations will be received by the Executive Director before the closing date of September 1 each year. The Society’s Awards Committee will consider the nominations and rank them. This ranking will then be passed to the Society’s Council (by mid-October) for a formal decision at the November meeting of that committee. Council will make a decision and inform the winner.

Nominations should consist of a letter of nomination together with at least one letter of support along with a copy of the paper being nominated and a copy of the nominee’s CV. The letter(s) should address the criteria outlined below and how any or all of them are met by the paper in question. Each nomination package should be submitted in electronic form (a single PDF file) and sent to the Society’s executive director, Kevin Murphy (kevin@minersoc.org).

Award Criteria

The Awards Committee will take into consideration the following points:

- Novelty
- Inter-disciplinarity
- Applicability
- How the science is advanced by the new work

Timing

The nominated paper must have been published in the calendar year before the nomination and within three years of the award of the candidate’s PhD and will remain on the slate for up to two years.



Some of the Society’s current Council at its March 2014 meeting: (back row, left to right) David Alderton, John Adams, Martin Lee, Russell Rajendra, Caroline Peacock, Geoff Bromiley; (front row, left to right) Frances Wall, Mike Widdowson, Brian O’Driscoll, Martin Hughes and Claire Corkhill (PHOTO BY K. MURPHY)

Society Council for 2014

The Society’s Council for 2014 is as follows:

President: F. Wall; General Secretary: K. Goodenough; Treasurer: J. Adams; Publications Manager: currently vacant; Principal Editors of *Mineralogical Magazine*: P. Williams; R. Mitchell; Principal Editor of *Clay Minerals*: G. E. Christidis; Public Relations Officer: A. Kerr;

Elements representative: M. E. Hodson; Editor of the Landmark Series: D. J. Vaughan; Ordinary Members of Council: J. Lloyd, M. Lee, B. O’Driscoll, C. Corkhill, C. Greenwell and M. Tyrer (co-opted);

Special Interest Group Chairs: D. Alderton, M. Anand, G. Bromiley, C. Greenwell, N. Harris, J. Lloyd, C. Peacock and A. Saunders.

The Council meets three times per year (March, June and November) and a subset consisting of Officers, or the Executive Committee, meets in February, May and September.

Bursary Awards for 2014

Senior Bursary Awards for 2014 were made to the following: J. Harvey, G. Pesce and E. Versteegh.

Student Bursary Awards for 2014 were made to the following:

M. Allen, A. Band, J. Bedford, M. Berg, S. Broom-Fendley, U. O. Chukwura, M. M. Daswani, L. Faggetter, E. Fallon, H. Haggi, H. Hughes, E. Hunt, A. Jeffery, X. Ke, A. Keatley, S. Martin, C. McLean, L. Newsome, C. Spencer and D. P. W. Tsang.

Congratulations to you all! We look forward to publishing reports of your travels on the Society site (www.minersoc.org/bursary-report.html) in due course.

Membership Survey

Our thanks to the many of you who completed the recent membership survey. We have compiled the responses and discussed them at council. All of the points raised will be borne in mind as we go forward. An executive summary of the report considered by Council follows.

■ Members seem happy with the services offered by the Society and are glad, in most cases, to recommend membership to their students and colleagues. Responses about Chartered Status seem to suggest that many in academia have either not yet considered applying for CSci status or they have decided it is not relevant to an academic career or that we have not demonstrated clearly that it is relevant.

■ The journals are probably the most valued aspect of what we offer. About half of all who responded said they use library-provided e-access to the journals, but 40% still use their personal paper copy for access. Only 30% of those responding have published a paper in *Mineralogical Magazine* and only 8% in *Clay Minerals*. Interestingly, the most popular method of finding which content to read in our journals is by Google Scholar (67%), followed by Web of Science (56%). Between a quarter and a half of those who responded said they were aware of initiatives undertaken to improve the journals. Upwards of 80% of those who responded said they buy one or more books per year. Most purchase the books themselves and claim that the best way to improve sales to libraries is to send ads to the academics rather than librarians (though most claim to have no influence over library purchases). £30 seems to be the average upper price for books for students.

■ About a third of respondents appear to have attended a Society meeting in the last three years. The vast majority of people who attend Society meetings value them highly. The reasons for not attending are cost, travel, theme, etc. The most popular of the large international conferences are Goldschmidt Europe and EGU.

■ The Special Interest Groups (SIGs) vary in terms of the numbers of members they can claim from among the respondents, from 7% (MPG) to 44% (VMSG). There appears to be a reasonable level of satisfaction with group meetings and networking activities, with some suggestions that communication about events and initiatives could be improved. Many have offered to serve on SIG committees but some feel that they are too far away to be of use or have insufficient experience.

■ Two-thirds of respondents would like to attend a Society- or SIG-run course, with a wide range of topics suggested. Two-thirds also suggest that it is better to run these in association with a major conference.

■ There was a healthy level of response from amongst Society award winners. Many who responded suggested that they were not aware of how to go about making a nomination or felt under-qualified to do so.

■ All of the respondents feel that the Society is well run. There are some helpful suggestions about increasing the amount of interaction with members, and improving the appearance, content and timeliness of the website. Most believe the Society to be in a reasonable state of health. Respondents were very generous in terms of their offers to support the Society (though some clearly already do so) through serving on a group or Council, writing a (review) paper or being a lecturer.

A full copy of the report will be posted on the Society website in due course.

Kevin Murphy (kevin@minersoc.org), Executive Director

SPECIAL ISSUE OF MINERALOGICAL MAGAZINE IN HONOUR OF THE INTERNATIONAL YEAR OF CRYSTALLOGRAPHY, APRIL 2014

On the occasion of the 2014 International Year of Crystallography, the Editorial Board of the *Mineralogical Magazine* has dedicated a special issue to commemorating the role crystallography plays within mineralogy and the mineral sciences. A set of papers by members of the Board, as well as by special invitees, will showcase the different crystallographic techniques used to characterize minerals. Several review articles will also explore the crystallography of several important mineral groups. We hope that this special issue will serve as a lasting tribute to the impact that crystallography has had on mineralogy.

Dr. Stuart J. Mills

Associate Editor, *Mineralogical Magazine*,
and coordinator of the special issue



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J. D. Grice and R. Rowe

A review of crystal chemistry of natural silicates of alkaline elements in the light of new structural data

N. V. Zubkova, I. V. Pekov and D. Yu. Pushcharovsky

Zeolites at high pressure: A review

G. D. Gatta and Y. Lee

Crystal-chemistry and short-range order of fluoro-edenite and fluoropargasite: a combined X-ray diffraction and FTIR spectroscopic approach

G. Della Ventura, F. Bellatreccia, F. Cámaras and R. Oberti

Thermal expansion in C2/c pyroxenes: a review and new high-temperature structural data on a pyroxene of composition (Na_{0.53}Ca_{0.47})(Al_{0.53}Fe_{0.47})Si₂O₆ (Jd₅₃Hd₄₇)

M. Tribaudino and L. Mantovani

The influence of stereochemically active lone-pair electrons on crystal symmetry and twist angles in lead apatite-2H type structures

T. Baikie, M. Schreyer, F. Wei, J. S. Herrin, C. Ferraris, F. Brink, J. Topolska, R. Piltz, J. Price and T. J. White

The crystal structure of sarmientite, Fe₂³⁺(AsO₄)(SO₄)(OH)·5H₂O, solved *ab initio* from laboratory powder diffraction data

F. Colombo, J. Rius, O. Vallcorba and E. V. Pannunzio Miner

Synthesis and recovery of bulk Fe₄O₅ from magnetite, Fe₃O₄. A member of a self-similar series of structures for the lower mantle and transition zone

J. Guignard and W. A. Crichton

Local order in wüstite using a pair distribution function (PDF) approach

T. R. Welberry, D. J. Goossens and A. P. Heerdegen

Lillianites and andorites: new life for the oldest homologous series of sulfosalts

E. Makovicky and D. Topa

On the algorithmic complexity of crystals

S. V. Krivovichev

Deep Earth mineralogy revealed by ultrahigh-pressure experiments

K. Hirose

Mössbauerite, Fe₆³⁺O₄(OH)₈[CO₃]·3H₂O, the fully oxidized 'green rust' mineral from Mont Saint-Michel Bay, France

J.-M. R. Genin, S. J. Mills, A. G. Christy, O. Guerin, A. J. Herbillon, E. Kuzmann, G. Ona-Nguema, C. Ruby and C. Upadhyay

The quest for forbidden crystals

L. Bindri and P. J. Steinhardt

Details of other IYCr events are given at www.iycl2014.org.

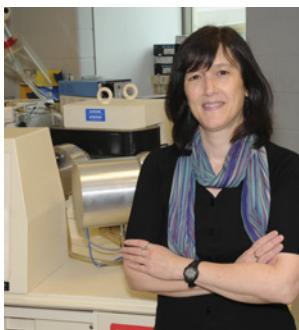


Geochemical Society

www.geochemsoc.org

PRESIDENT'S CORNER

Community Building: Highlights of Goldschmidt 2014



Barbara Sherwood Lollar

Earlier this summer, we celebrated the 24th Goldschmidt Conference in Sacramento, California. The meeting was jointly sponsored by the Geochemical Society and the European Association of Geochemistry, while the Geochemical Society of Japan was a principal cosponsor. We extend thanks and congratulations to Science Cochairs Adina Paytan and Dominique Weis; to the Local Organizing Committee composed of Paul Renne (chair), Charles Alpers, Lisa Hammersley, and Isabel Montanez; and to Paul Beattie, Jacquie Storey, and the whole team at Cambridge Publications.

A special focus of the California Goldschmidt was community building, with a particular emphasis on the group that is the foundation and future of geochemistry: students and early-career scientists. A total of \$61,000 was committed to subsidizing the registration and/or travel for students and international attendees from low-income countries. In addition to the traditional field trips and workshops, the local organizing and science program committees developed an unparalleled program of free events for students and early-career scientists (where “free” means paid for by 16 sponsors, including platinum sponsor Nu Instruments). The free-event program focused on themes as diverse as innovations in teaching; publishing and reviewing manuscripts; fellowship and grant writing; employment and career options (including academic and nonacademic careers, and the dual-career challenge); and research workshops on emerging themes in integrative topics, such as microbiology, geochemistry, geochronology, and Critical Zone Observatories. A very special thank-you goes out to those who volunteered their time, expertise, and insights to develop and run these workshops.

A student lounge and career center, as well as social events such as the student wine tasting, not only provided opportunities for informal and formal networking for our youngest attendees but highlighted the unique California location. The inaugural Goldschmidt Mentoring Program was a huge success, reaching almost 200 student attendees thanks to the dedication of 115 volunteer mentors. Sincere thanks are extended to the academic partners and organizations who donated their time, energy, and funding to support these initiatives. They are too numerous to list here, but I draw your attention to the conference website and program volume and ask you to extend your personal thanks. An initiative of this magnitude and diversity could not be carried off without these partners. The success of these events is a credit to the creativity and enthusiasm of the entire Goldschmidt community.

In addition to the world-class science and discovery that was the hallmark of the California Goldschmidt, this nurturing of the next generation of young scientists was a major achievement of the meeting, which we hope will set the standard for future Goldschmidt conferences. The remarkable young scientists we welcomed to Sacramento will no doubt be among the organizers, theme chairs, and attendees who will lead the Goldschmidt community for the next 25 years of its history.

Barbara Sherwood Lollar (bslollar@chem.utoronto.ca)
President, Geochemical Society



The historical Westminster Presbyterian Church, near the Sacramento Convention Center.
PHOTO: D. WEIS

THANK YOU VOLUNTEERS!

What we do at GS day after day to deliver on our mission to impact the direction of geochemistry at a global level is only possible through the Herculean efforts of our volunteers. Thank you! The following volunteers complete their term at the end of June 2014; an asterisk denotes committee chair. For full committee rosters visit www.geochemsoc.org/society/committeesandpersonnel/.

2014 PROGRAM COMMITTEE

*LESLEY WARREN (McMaster University, **Canada**)
HELEN WILLIAMS (Durham University, **UK**)

2014 AWARD NOMINATION COMMITTEE

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*JOHN VOLKMAN (CSIRO, **Australia**)
CINDY LEE (Stonybrook University, **USA**)

CALL FOR 2015 DIRECTOR NOMINATIONS

The Geochemical Society Nominations Committee is seeking potential nominees for two director positions. These are three-year terms beginning January 1, 2015, and concluding December 31, 2017. The new board members will succeed Directors Richard Walker (University of Maryland) and Edward Young (UCLA) who are completing their terms this December. The potential nominees should have established reputations of leadership in geochemistry and be willing to devote considerable time and effort to the work of the Society. Suggestions may be communicated, by **August 15, 2014**, to **bodnominations@geochemsoc.org**. More information regarding the duties and responsibilities of a director can be found on the Geochemical Society website: <http://www.geochemsoc.org/society/governance/>.

2015 AWARD NOMINATIONS

Geochemists want and need recognition for their work. Awards help to inspire individuals to do their best. Awards set the bar for others to match or exceed. Your participation in the awards program by being a nominator or writing a supporting letter of recommendation not only benefits the nominee, it benefits the geochemical community. Please take the time to highlight the accomplishments of your valued colleagues by nominating them. With your help, we can ensure that the award committees have a diverse and deserving pool of candidates.

	The V. M. Goldschmidt Medal is awarded for major achievements in geochemistry or cosmochemistry, consisting of either a single outstanding contribution or a series of publications that have had great influence in these fields.
	The F. W. Clarke Medal is awarded to an early-career scientist for a single outstanding contribution in geochemistry or cosmochemistry, published either as a single paper or a series of papers on a single topic.
	The C. C. Patterson Medal is awarded for a recent innovative breakthrough of fundamental significance in environmental geochemistry, published in a peer-reviewed journal.
	The Alfred Treibs Medal is awarded by the Organic Geochemistry Division for major achievements in organic geochemistry over a period of years.
	The GS/EAG Geochemical Fellows Award is bestowed upon outstanding scientists who have, over some years, made a major contribution in the field of geochemistry.
<p>Make a nomination at www.geochemsoc.org/awards/makeanomination.htm.</p> <p>Nomination Deadline: October 15, 2014</p>	

GEOCHEMICAL SOCIETY BUSINESS OFFICE

Seth Davis, Chief Operating Officer
 Kathryn Hall, Administrative Assistant

Washington University in St. Louis
 Earth and Planetary Sciences, CB 1169
 One Brookings Drive
 Saint Louis, MO 63130-4899, USA

E-mail: gsoffice@geochemsoc.org

Phone: 314-935-4131

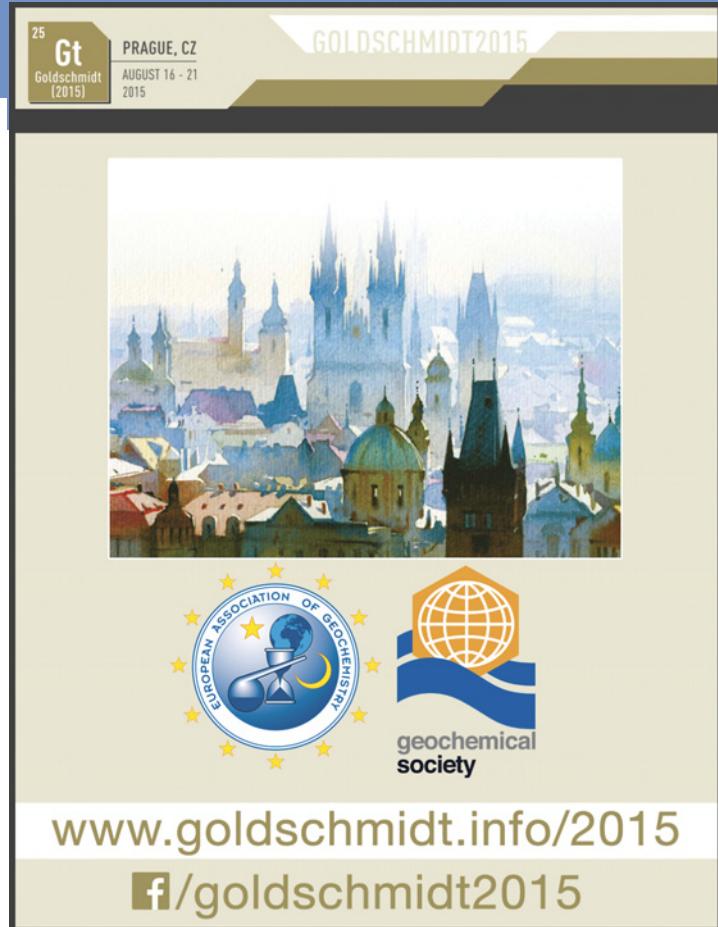
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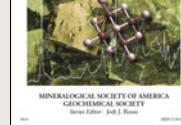
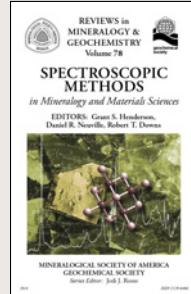


www.goldschmidt.info/2015
[f/goldschmidt2015](https://www.facebook.com/goldschmidt2015)

NEW TITLE

Reviews in Mineralogy and Geochemistry

Mineralogical Society of America and The Geochemical Society



MINERALOGICAL SOCIETY OF AMERICA
GEOCHEMICAL SOCIETY
Second Editor: Jack I. Evans
ISBN 978-0-939950-93-5

Spectroscopy is the study of the interaction between matter and radiation, and spectroscopic methods measure this interaction by measuring the radiative energy of the interaction in terms of frequency or wavelength or their changes. In 1988 a *Reviews in Mineralogy* volume (volume 18), *Spectroscopic Methods in Mineralogy*, was published by Frank Hawthorne (ed). Since then, there have been many significant advances in both the technological aspects of these techniques and their application to problems in Earth sciences in general, while the range and breadth of the techniques currently employed have greatly expanded since those formative years. The current volume complements the original volume and updates many of the techniques. In addition, new methods such as X-ray Raman and Brillouin spectroscopy have been added, as well as nonspectroscopic chapters such as transmission electron microscopy (TEM) and atomic force microscopy (AFM) for completeness.

For a description of the book and ordering online, go to www.minsocam.org or contact the Mineralogical Society of America, 3635 Concorde Pkwy, Ste 500, Chantilly, VA 20151-1110, USA; phone: +1 (703) 9950; fax: +1 (703) 652-9951; e-mail: business@minsocam.org. The cost is \$50 (\$37.50 for members of the MSA, GS, and CMS).



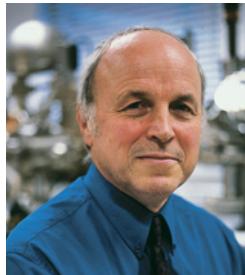
Mineralogical Society of America



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PRESIDENT'S LETTER

Onwards and Upwards



David Vaughan

At this stage in my role as your president, I am conscious of how little time is left for me to influence the directions taken by our Society. As my Letter title implies, I hope and believe that we are making progress and that our trajectory is 'upwards', although there are times when a more appropriate phrase might be 'soldiering on'. I am reminded that Churchill used to sign off his wartime telephone exchanges with President Roosevelt by saying 'KBO' – letters best left untranslated in a respectable magazine such as this one. In previous Letters, I have spoken about

both ongoing developments and new initiatives that we are taking in the MSA. So let me briefly update you.

First, I should like to tell you that the first of our new events, to which we have given the name 'workshops', has been programmed to coincide with the MSA's involvement in the 2014 GSA Annual Meeting in Vancouver. This will be on the 'hot topic' of "Deep Carbon through Deep Time" and is made possible by the generosity of former MSA President Bob Hazen, who has been the driving force behind organising this event. It will be held Saturday, October 18, from 8 am to 5 pm. Full details will be available shortly.

Second, the respective presidents and executive directors of MSA and of two British learned societies, namely the Mineralogical Society of Great Britain and Ireland and the Geological Society of London (UK equivalent of GSA), have now signed memoranda of understanding. The objectives of these documents are to foster understanding and collaboration between MSA and these two internationally respected British organisations. In the coming weeks, we will be exploring how best to improve the exchange of information among our societies and how to encourage joint meetings, joint publications and other forms of outreach. Our societies face similar challenges in the rapidly changing world of publishing and of organising meetings and events.

Third, thanks to sterling efforts on the part of MSA webmaster Gordon Nord and Executive Director Alex Speer, the MSA website has a new look. We believe that the new website is appropriate to the needs of both MSA members and the public and is a fitting 'shop window' for our internationally important organisation.

The subject of our flagship publication, *American Mineralogist*, was the focus of my last Letter so I will not say more on that topic. Possible new publications addressing the archiving of large bodies of data and the development of software for the 'mining' of large data sets are likely to feature as important activities for the future. More immediately, the appointment of Jodi Rosso as the new executive editor of *Elements* magazine is excellent news for the future of this most successful of publications.

David J. Vaughan (david.vaughan@manchester.ac.uk)
2014 MSA President

VOTE
2014 MSA ELECTIONS

NOTES FROM CHANTILLY

- Balloting for the 2014 election of MSA officers and councilors is underway. The slate of candidates is as follows. President: Steven B. Shirey, Carnegie Institution of Washington; vice president (one to be selected): Carol D. Frost, University of Wyoming and Rebecca A. Lange, University of Michigan; treasurer: Howard W. Day, University of California–Davis; councilors (two to be selected): Barry R. Bickmore, Brigham Young University; Abby Kavner, University of California–Los Angeles; Matthew J. Kohn, Boise State University; and Donna L. Whitney, University of Minnesota. Andrea Koziol continues in office as secretary. Continuing councilors are Isabelle Daniel, Kirsten P. Nicolaysen, Edward S. Grew, and Wendy Panero.

MSA members should have received voting instructions sent to their current e-mail addresses. Those who do not wish to vote online can request a paper ballot from the MSA business office. As always, the voting deadline is August 1.

- MSA will have a booth at the GSA meeting in Vancouver, BC, Canada, on 19–22 October 2014. During that week, MSA will hold its Awards Lunch; the MSA Presidential Address; the Joint Reception for the MSA, GS, and GSA's MGVP (Mineralogy, Geochemistry, Petrology, and Volcanology) Division; its Annual Business Meeting; its Council Meeting; and breakfasts for the past presidents and associate editors. Exhibits will be open Sunday (2–7 pm), Monday and Tuesday (9 am–6:30 pm), and Wednesday (9 am–2 pm).

The MSA Awards Lunch will be Tuesday, 21 October. The Roebling Medal will be presented to Bernard J. Wood and the MSA Award to Fang-Zhen Teng. The 2013–2014 MSA Distinguished Lecturers will also be recognized: Linda T. Elkins-Tanton, Nita Sahai, and Richard Wirth. The MSA Awards lectures, annual business meeting, and presidential address will be held on Tuesday, 21 October, at the Convention Center. This is also where Bernard J. Wood will give the Roebling lecture; Fang-Zhen Teng will give the MSA Award lecture; and David Vaughan will give his MSA presidential address. The MSA/GS/MGVP Joint Reception will follow at 5:45 pm–7:30 pm.

Topical sessions have been proposed for the two MSA Award recipients: T118 "Frontiers in Non-Traditional Stable Isotopes: In Honor of Fang-Zhen Teng, Recipient of the 2014 MSA Award" was submitted to GSA by Roberta L. Rudnick of the University of Maryland, with coorganizers William F. McDonough and Nicolas Dauphas, and T183 "Theory and Experiment in Petrology and Geochemistry: A Session in Honor of Bernard J. Wood, 2014 Roebling Medalist" was submitted to GSA by Jon Blundy and Andrew Matzen.

- The 2015 Dana Medal will be presented to Marc Hirschmann at the AGU Fall Meeting, San Francisco, California, USA, on 15–19 December 2014. There will be a special session, proposed in his honor by David Kohlstedt, during which he will give the Dana Lecture. The medal presentation will be made during the VGP-MSA Joint Reception.

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

IN MEMORIAM

JAMES A. FERRAIOLI – Member, 1982

50- AND 25-YEAR MSA MEMBERS

The following individuals will reach 50 or 25 years of continuous membership in the Mineralogical Society of America during 2014. Their long support of the Society is appreciated and is recognized by this list and by 25- or 50-year pins mailed in early January. If you should be on this list and are not, or have not received your pin, please contact the MSA business office.

50-Year Members

Harvey E. Belkin
Richard S. Braithwaite
John B. Callen
William A. Crawford
M. Charles Gilbert
John E. Grover
Richard B. Hatheway
Paul B. Moore
Dennis Radcliffe
John Rucklidge

25-Year Members

John P. Brodholt
Richard M. Conrey

Masaki Enami
James Farquhar
Tanya Furman
Patrick J. Jenks
Gi-Young Jeong
Masayuki Kawasaki
Hans Keppler
Marguerite J. Kingston
John H. Lake
Andrew J. Locock
Craig S. Schwandt
Adejardo Francisco da Silva Filho
Piet H. M. Thijssen
Lance Tuckruskye
Pier Francesco Zanazzi

2014–2015 MSA DISTINGUISHED LECTURERS

The Mineralogical Society of America is pleased to announce its Distinguished Lecturers and their lecture titles for 2014–2015:

- **Betheny Ehlmann**, Department of Geological and Planetary Science, California Institute for Technology, and the Jet Propulsion Laboratory, Pasadena, California, USA, who will offer lectures entitled “Aqueous Environments during Mars’ First Billion Years: Mineralogic Clues from Orbiting Infrared Spectrometers” and “Roving Mars with Curiosity: Geochemistry and Mineralogy at Gale Crater.”
- **Colleen Hansel**, Department of Marine Chemistry and Geochemistry, Woods Hole Oceanographic Institution, Woods Hole, Massachusetts, USA, who will offer lectures entitled “Making and Breaking Minerals: Microbes as Single-Celled Geochemists” and “Microbial and Geochemical Synergy in the Biomineratization of Manganese.”
- **Lutz Nasdala**, Institute of Mineralogy and Crystallography, University of Vienna, Vienna, Austria, who will speak on the subjects “Micro-Spectroscopy: New Opportunities to Explore Non-Destructively Minerals and Their Internal Textures” and “Natural Radiation Damage in Minerals: What Can We Learn?”

The schedule of the Lecturers’ tours will be posted on the MSA website (www.minsocam.org). Check to see if they will be at a location near you. MSA expresses its appreciation to these individuals for undertaking such a service to our science.

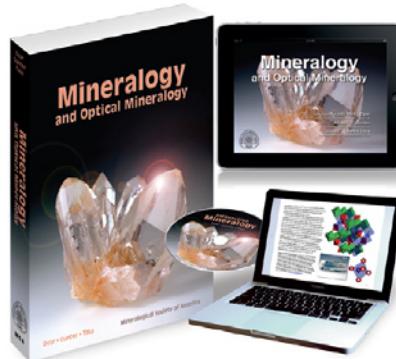
MINERALOGICAL SOCIETY OF AMERICA UNDERGRADUATE PRIZE FOR OUTSTANDING STUDENTS

The Society welcomes the following exceptional students to the program’s honor roll and wishes to thank the sponsors for enabling the Mineralogical Society of America to recognize them. MSA’s Undergraduate Prize (MSA-UP) is for students who have shown an outstanding interest and ability in mineralogy, petrology, crystallography, and geochemistry. Each student is presented a certificate at an awards ceremony at his or her university or college and receives an MSA student membership, which includes a subscription to *Elements*, and a Reviews in Mineralogy or Monograph volume chosen by the sponsor, student, or both.

Past MSA-UP awardees are listed on the MSA website, as well as instructions on how MSA members can nominate their students for the award.

- Eloise C. Andry, Williams College, sponsored by Prof. Reinhard Wobus
- Keri Belcher, University of Texas at Austin, sponsored by Dr. Jung-Fu Lin
- Samantha Blanchett, Smith College, sponsored by Dr. John Brady
- Travis C. Dawson, University of Vermont, sponsored by Dr. John Hughes
- Anthony M. Frushour, Appalachian State University, sponsored by Dr. Sarah Carmichael
- Brian James Gallagher, University of Oklahoma, sponsored by Dr. David London
- William Junkin, University of Maryland, sponsored by Dr. Sarah Penniston-Dorland
- Alicia Koshman, University of British Columbia, sponsored by Dr. James Scoates
- Madeline Lewis, Indiana University, sponsored by Prof. David Bish
- Michael Ream, University of Maryland, sponsored by Dr. Sarah Penniston-Dorland
- Heather J. Saburova, George Mason University, sponsored by Dr. Giuseppina Mattiotti

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Now you and your students can choose this dynamic mineralogy textbook either as a printed book with DVD-ROM or as an exciting new digital series of chapters available on iBooks for the iPad and Mac.

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Go to the **Mineralogical Society of America** website at www.minsocam.org for more information about the textbook, or to purchase the **printed version**, as well as find a link to purchase the individual chapters in the **digital version**.

The “Mineral Database” app is also available on the App Store.



International Association of GeoChemistry

www.iagc-society.org

2014 IAGC AWARDS

The International Association of GeoChemistry is pleased to announce its society awards for 2014. Congratulations to all the recipients, and thank you for your service to the IAGC and the geochemical community!

Vernadsky Medal

The Vernadsky Medal is awarded biennially to honor a distinguished record of scientific accomplishment in geochemistry over the course of a career.

Ian Hutcheon, University of Calgary, Canada

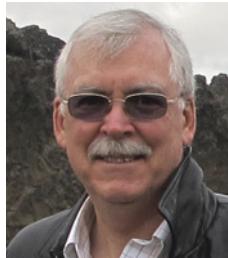


Professor Ian Hutcheon is a professor emeritus at the University of Calgary, Canada. Ian graduated with a PhD from Carleton University in 1977 following an MS in 1972 and a BS from the University of British Columbia in 1969. He subsequently worked at the Geological Survey of Canada before commencing at the University of Calgary in 1978. Ian has contributed much world-class and internationally recognized research in the broad fields of petrology and geochemistry, including significant contributions to processes in high-grade metamorphic terrains, water–rock–gas interactions in sedimentary basins, diagenesis, and CO₂ sequestration. This work has been founded on a base of careful and meticulous observations combined with the rigorous application of fundamental thermodynamics and kinetic principles. Ian has also served on committees for many national and international scientific, government, and industrial bodies, and has delivered well-received short courses across the globe. Through the supervision of PhD and MS students and his extensive undergraduate teaching, Ian has helped inform and train many geoscientists. For this lifetime of application and achievement, Ian is a very worthy recipient of the Vernadsky Medal for 2014.

Distinguished Service Award

The Distinguished Service Award recognizes outstanding service by an IAGC member to the Association or to the geochemical community that greatly exceeds the normal expectations of voluntary service.

Russell Harmon, U.S. Army Corps of Engineers



Dr. Russell Harmon received a BA from the University of Texas, an MS from the Pennsylvania State University, and a PhD from McMaster University. Russ is currently the director of the International Research Office of the U.S. Army Engineer Research and Development Center, where he conducts international science and technology engagement. Previously, Russ was a program manager at the RDECOM-ARL U.S. Army Research Office, where he managed the extramural basic research program in terrestrial sciences. Russ is an internationally renowned isotope geochemist who has worked at NASA, the Scottish Universities Research and Reactor Centre (UK), and the Natural Environment Research Council Isotope Geosciences Laboratory (UK). Russ has also held faculty positions at Michigan State University and Southern Methodist University and is an adjunct faculty member at North Carolina State University. He has edited or coedited more than 30 books and journal special issues, authored or coauthored more than 220 peer-reviewed publications, and worked tirelessly for the IAGC over

many years. He 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 to 2010 and past-president from 2010 to 2012. He has helped the organization in many other ways as well, including as chair of the Publications Committee, and 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 as chair of the Strategic Planning Committee. For this lifetime of achievement and dedication to the IAGC, Russell Harmon is awarded the IAGC Distinguished Service Award.

Ebelmen Award

The IAGC's Ebelmen Award is given biennially to a geochemist of particular merit and outstanding promise less than 35 years old at the time of nomination.

Sophie Opfergelt, Université catholique de Louvain, Belgium



Dr. Sophie Opfergelt is currently a research scientist at the Université catholique de Louvain, Belgium. Sophie completed her PhD at the Université catholique de Louvain in 2008 and was a postdoctoral researcher at the University of Oxford, UK. Sophie's research interests involve the application of novel stable isotope systems, such as silicon isotopes, to the understanding of biogeochemical processes, particularly the interactions between rocks, soils, and plants during weathering. She has refined techniques for the use of silicon isotopes to distinguish biological and inorganic processes and the role of plants in the Si cycle. Sophie is at the forefront of this research and has become a globally recognized expert in this field. For undertaking this original and challenging research, Sophie is awarded the Ebelmen Award for 2014.

IAGC Fellows

The honorary title of IAGC Fellow is bestowed annually on scientists who have made significant contributions to the field of geochemistry.

Karen Johannesson, Tulane University, USA



Professor Karen Johannesson is currently a professor at Tulane University, USA. Karen graduated with a BS from the University of New Hampshire in 1985 and obtained an MS from Boston College in 1988 and a PhD from the University of Nevada in 1993. Karen is a recognized international authority on the behavior of the rare earth elements in the hydrosphere. She was one of the first to estimate rare earth element speciation in terrestrial waters, and she illustrated the importance of complexation and pH as controls on their behavior. Her more recent work has included the investigation of the behavior of oxyanion-forming trace metals, such as arsenic, selenium, and tungsten, in groundwater systems and how their concentrations and speciation change along a flow path due to pH and redox changes. She has combined field, analytical, and experimental approaches in order to develop geochemical models that have improved the understanding of the biogeochemical process controlling trace element speciation and element cycles in the near-surface environment. Karen is also actively

involved in graduate student supervision and undergraduate teaching. For carrying out this important research in the aquatic biogeochemistry of trace elements over many years, Karen is named an IAGC Fellow for 2014.

Jérôme Gaillardet, Institut de Physique du Globe de Paris



Jérôme Gaillardet is a professor at the Institut de Physique du Globe de Paris. Jérôme completed his PhD at the Université Paris 7 in 1996. He was also a researcher at Université Paris-Diderot between 1996 and 2001, before joining the Institut de Physique du Globe de Paris in 2001. Jérôme is internationally recognized for his pioneering research in river geochemistry, in particular for the innovative use of element and isotope geochemistry to estimate global weathering rates and the role of continental weathering in CO₂ sequestration. He is currently involved in international research collaborations via the Critical Zone Exploration Network and also in the application of novel isotopic tracers (such as B, Li, and Zn) in waters to understand both natural and polluted systems. Jérôme has served on a range of national and international committees involved with research and teaching. For this important and novel research, Jérôme is named an IAGC Fellow for 2014.

Certificates of Recognition

IAGC Certificates of Recognition are awarded to IAGC members for outstanding scientific accomplishment in a particular area of geochemistry, for excellence in teaching or public service, or for meritorious service to the Association or the international geochemistry community.

Prof. Pierpaolo Zuddas, of the Institute of Earth Sciences, Université Pierre et Marie Curie, Paris, France, receives the IAGC Certificate of Recognition for his leadership role in the 14th International Symposium on Water–Rock Interaction (WRI-14). This highly successful IAGC working group meeting was held in Avignon, France, in June 2013. Conference proceedings were published in the open access Elsevier journal *Procedia Earth and Planetary Science*, ensuring wide readership.

Prof. Halldór Ármannsson, of the Division of Geology & Environmental Sciences, Iceland GeoSurvey, Reykjavik, Iceland, receives the IAGC Certificate of Recognition for his involvement as a member of the WRI Working Group leadership over many years and the guidance he provided to the organizers of WRI-14 in Avignon.

Dr. Attila Demény and **Dr. István Fórizs**, of the Institute of Geological & Geochemical Research, Hungarian Academy of Sciences, Budapest, Hungary, receive the IAGC Certificate of Recognition for their leadership roles in organizing and running the 10th International Symposium on Applied Isotope Geochemistry (AIG-10). This very successful IAGC working group meeting was held in Budapest, Hungary, in September 2013. The proceedings of extended abstracts were published for the first time as a special issue of the *Central European Journal of Geosciences*.

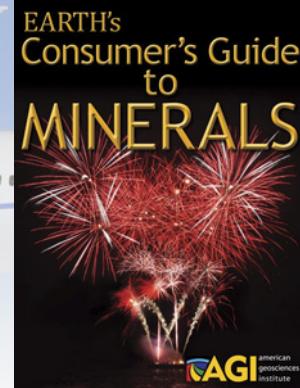
THE CONSUMER'S GUIDE TO MINERALS

Edited by Christopher Keane and Megan Sever

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The *Consumer's Guide to Minerals* is a compilation of monthly articles from EARTH Magazine. The *Guide* is a collaborative effort between EARTH Magazine and the U.S. Geological Survey.

Background: top: ©2010 Boeing; bottom: Digital Vision



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MESSAGE FROM THE PRESIDENT



I became the president of the Mineralogical Association of Canada (MAC) at the annual general meeting. As I see how the Association works, I am impressed by its commitment to education. Each year, MAC distributes \$25,000 in scholarships to help students conduct research or travel to present their work at conferences. This year, in Fredericton, the Association offered a short course on cathodoluminescence (see photo). This was the 45th course in the popular series; for most courses, the course notes live on and can be purchased from the MAC website. I have found these course notes to be an excellent teaching resource. The Association also offers Berry Schools, and a three-day school in optical mineralogy was held recently at the University of Ottawa (see next page).

The Canadian Mineralogist continues to move forward with several new initiatives. Color figures are now available at no additional cost to authors, and online manuscript submission and tracking is fully established. We are pleased to report that submission-to-publication times have come down substantially, and continue to decline. Over the next months the journal will transition to a digital-first publication model, while retaining our print volumes; we are doing this in order to further improve our ability to disseminate information on advances in our field quickly. Finally, beginning in 2015, the publication schedule of *The Canadian Mineralogist* will move ahead one month, such that the first issue will appear in January.

Ron Peterson (Peterson@queensu.ca)
MAC President

2014 MEDALS AND AWARDS

The Mineralogical Association of Canada presented its 2014 awards during its annual luncheon at the GAC-MAC annual meeting in May.

2014 Peacock Medal Awarded to Don R. Baker



The Peacock Medal for 2014 was awarded to Dr. Don Baker of McGill University for his outstanding contributions to experimental and igneous petrology. Dr. Baker has made substantial advances in our understanding of the character, origin, and behavior of a diversity of silicate melts and the processes that dictate their evolution.

Don Baker was born in southern Illinois, USA. When he was 11, he learned the story of Volcán de Parícutin and fell in love with geology and the idea of a volcano growing in nearby corn fields. Don received his AB in geophysical sciences in 1979 from the University of Chicago, where he did research with A. T. Anderson Jr. and P. J. Wyllie. At the Pennsylvania State University, he experimentally investigated island arc petrogenesis under David Egger and received his PhD in geochemistry and mineralogy in 1985. After working at the Smithsonian for one year with Bill Melson investigating plagioclase zoning in Mt. St. Helens dacites, Don moved on to a second postdoc, with Bruce Watson at Rensselaer Polytechnic Institute. There he applied kinetics to the study of diffusion in silicate melts and its influence on the rates of igneous processes. He took up a faculty position at McGill in 1990. Since that time he has been using high-temperature geochemistry to study the equilibrium and kinetic



A short course, organised by Ian Coulson and Michael Robertson, on cathodoluminescence (CL) took place prior to the annual meeting in Fredericton, New Brunswick, this past May. The course, attended by 38 students and professionals, included aspects of theory and the causes of CL in minerals and their host rocks, practical demonstrations, applications to the various fields of geology, recent advances in CL instrumentation, and the interpretation of CL imagery/spectroscopy data. The accompanying Short Course Volume 45 (*Cathodoluminescence and Its Application to Geoscience*) will be published in June.

processes responsible for the origin and evolution of igneous rocks and their minerals with his excellent students and collaborators. He has sat on the Mineralogical Association of Canada's council, is an associate editor of *American Mineralogist*, and is currently the secretary of the VGP section of AGU.

Hawley Medal Awarded to Felix V. Kaminsky, Richard Wirth, and Anja Schreiber

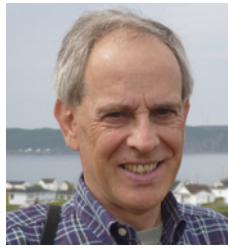
The Hawley Medal is awarded to the best paper published in *The Canadian Mineralogist* in 2013: "CARBONATITIC INCLUSIONS IN DEEP MANTLE DIAMOND FROM JUINA, BRAZIL: NEW MINERALS IN THE CARBONATE-HALIDE ASSOCIATION," *Canadian Mineralogist* 51: 669-688

Recent studies of mineral inclusions in diamond have provided us with unprecedented information about the mineralogy of the lower mantle and the nature and role of fluids in the deep Earth. The study by Kaminsky, Wirth, and Schreiber (2013) represents a significant advance in this field. The authors carefully used transmission electron microscopy, electron diffraction, analytical electron microscopy, and other methods to document the associations, textures, and compositions of micro- and nanomineral inclusions in lower-mantle diamond. Their results demonstrate that the diamond formed in a lower-mantle, carbonatitic, carbonate–halide–phosphate–fluoride medium that was enriched in rare earth elements and volatiles. Future studies will focus further on the origin of this primary, deep-seated carbonatitic magma and its significance in models of the accretion and differentiation of the Earth.



Felix V. Kaminsky graduated from the Lomonosov Moscow University in 1959 with an MSc degree in geology and from the Gubkin Moscow Oil Institute in 1966 with an MSc degree in geophysics. He received a PhD degree from the Russian Academy of Sciences in 1969. From 1970 to 1994, he worked at TsNIGRI, Moscow, as a chief research scientist in the diamond department. He found eleven new diamond localities, including nonkimberlitic diamonds in polar Siberia, Mongolia, Koryakia, Kamchatka, and Armenia. On this basis, he obtained a DSc degree in mineralogy and petrology from the Institute of Mineral Resources, Moscow, and published a monograph entitled *Diamond Potential of*

Non-Kimberlitic Rocks. In the 1980s he discovered the first diamonds in the Archangelsk area, which subsequently led to the discovery of the world-class Lomonosov diamond deposit. In 1991, he was elected as a member of the Russian Academy of Earth Sciences and established the Institute of Diamonds. In 1994, he left Russia and created KM Diamond Exploration Ltd. in Vancouver, Canada. He has since consulted for numerous Canadian companies and prospected for diamond deposits in Canada, Brazil, Venezuela, Ghana, Mali, Mauritania, Madagascar, and Saudi Arabia. At the same time as exploring for diamond deposits, he continues to work as a research scientist. His main fields of interest are the petrology of kimberlites and the mineralogy of diamond.



Richard Wirth is the supervisor of the electron microscopy laboratory at the GFZ German Research Centre for Geosciences, Potsdam, Germany. After receiving his PhD in 1978 at the University of Würzburg, Germany, he spent three years as a postdoctoral fellow at the Institute of Metals Physics at the University of Saarbruecken. Then he held research scientist positions at the University of Cologne and was the head of administration at the Institute of Advanced Materials, Saarbruecken and

Ruhr-University-Bochum. In 1994 he established the TEM laboratory at GFZ Potsdam. His main research areas are micro- and nano-inclusions in minerals, the structure and behavior of grain boundaries, and meteorites. He was awarded the GFZ Research Award in 2003 and was appointed as the W. F. James Chair in Science at St. Francis Xavier University in Antigonish, Nova Scotia, Canada, in 2005. In 2009 he became a fellow of the Mineralogical Society of America and in 2010 a fellow of the Geological Society of America. He was nominated as a distinguished lecturer of the Mineralogical Society of America for 2013–2014.



Anja Schreiber is the laboratory manager of the TEM sample preparation laboratory at GFZ Potsdam. She earned a degree as technician in chemistry at Schering AG (now Bayer AG) in Berlin. She began preparing foils for TEM use at GFZ Potsdam using the focused ion beam technique in 2008. Since that time she has produced approximately 3000 foils from different materials, such as silicates, carbonates, sulfides, metals, alloys, ceramics, diamonds, and fossils. In 2011 Anja Schreiber was awarded the GFZ Prize for Technicians.

2014 Young Scientist Award to J. Gregory Shellnutt



Dr. J. Gregory Shellnutt of the National Taiwan Normal University was awarded the 2014 Young Scientist Award for his achievements in igneous petrology and the geochemistry of magmatic mineral deposits. Gregory Shellnutt completed his BSc (honors) in geology at Saint Mary's University in 1998 and his MSc degree at the University of Western Ontario in 2000. After a successful internship at the Instituto de Geología, Universidad Nacional Autónoma de México, he obtained his PhD from the University of Hong Kong in 2007. He then moved to the Institute of Earth Sciences, Academia Sinica, in Taipei, Taiwan, where he received a distinguished postdoctoral fellowship. After three years at Academia Sinica he was hired by the National Taiwan Normal University as an assistant professor in the Department of Earth Sciences, where he

established a new WD-XRF laboratory. Greg has published extensively on the formation of magmatic Fe-Ti oxide deposits and their association with A-type granites, the large igneous provinces of China (Emeishan) and India (Panjal Traps), the mafic dike swarms of the Canadian Shield, granite petrogenesis, silicic rocks on Venus, silicate-liquid immiscibility in volcanic rocks, and the India-Eurasia collision. Greg is an editorial board member of *Lithos* and has edited two special journal issues appearing in *Lithos* and the *American Journal of Science*.

A BERRY SUMMER SCHOOL ON OPTICAL MINERALOGY



(Front row, from left) Nancy Normore, Rhea Mitchell, Susan Kingdon, Heidi Tomes, Annemarie Pickersgill, Arianne Petley-Ragan; (second row) Andy McDonald (co-convenor), Sarah Jackson-Brown, Jim Nicholls (co-convenor), Victoria Maneta, Jacques Desmarais, Timothy Mount, John Weirich, Wladyslaw Betkowski; (back row) Doug Tinkham (lecturer), David Diekrup, Andrew Olejarz, Claude Gagnier, Fergus Tweedale, Bill Nesse (lecture), Cole Kingsbury, Chris Pelow, Anna Chanou, Neil Ball. Absent: Tony Fowler (lecturer)

A Berry Summer School (BSS) on optical mineralogy, sponsored by the MAC and the MSA, with gracious financial support from the Goodman School of Mines and Olympus, Inc., along with logistical support from the universities of Calgary, Northern Colorado, Ottawa, and Idaho and Laurentian University, was held on 25–28 May 2014. The BSS was able to make use of the superlative polarized-light microscopy lab at the University of Ottawa. Lectures were presented covering the basics of transmitted-light microscopy (Nesse); the quantitative use of birefringence and crystal orientation, and the optical properties of olivines, pyroxenes, and amphiboles (Nicholls); the role of optical mineralogy in discovering the history of metamorphic rocks (Tinkham); “nonequilibrium” crystallization of minerals in igneous systems (Fowler); and reflected-light microscopy (McDonald). The BSS was completely booked, with 15 senior undergraduate and graduate students from across Canada, along with five professionals. All were provided with a complimentary copy of the text *Mineralogy and Optical Mineralogy* (Dyar and Gunter), graciously provided by the MSA. Initial feedback indicates the BSS was hugely successful, with all involved, from registrants to presenters, garnering novel 21st-century ideas and applications for this “vintage” technique.



Société Française de Minéralogie et de Cristallographie

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SOCIETY NEWS

IYCR2014

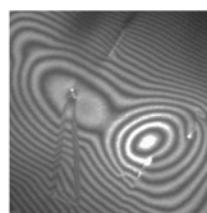
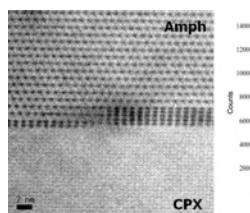
The International Year of Crystallography (IYCr2014) was inaugurated in an official opening ceremony, held by UNESCO and IUCr, at the UNESCO head office in Paris on 20–21 January 2014. For this occasion, the steering committee of Année Internationale de la Cristallographie en France, AICr2014, of which the SFMC is an active member, organized two satellite events:

- A “Festival de la Cristallographie,” held in Paris on 18–19 January 2014 to celebrate the diversity of crystallography. The general public could visit mineral exhibitions, grow and build crystals using candy, and listen to talks telling the story of diamonds, quasicrystals and synchrotron radiation centers.
- A satellite meeting entitled “Cristallographie, une clé de la connaissance – Crystallography, a key for knowledge,” held on 22 January 2014 at UNESCO headquarters. At this meeting, all the current challenges of crystallography were introduced, and the possibilities opened by this science in the domains of biology, chemistry, physics and Earth sciences were highlighted. The oral presentations are now available on the website www.aicr2014.fr, along with information about all other events scheduled in France during IYCr2014.



TEM IN MINERALOGY: GRADUATE AND PHD COURSE, MINTEM 2014

The third MINTEM school on the theme “Transmission Electron Microscopy in Mineralogy,” organized by the SFMC and the SFµ (French Microscopy Society), will be held at Lille University on 3–7 November 2014. The main aspects of TEM techniques (conventional and high-resolution imaging, diffraction, spectroscopy and chemical analysis) will be covered by the course, which will feature practical sessions, simulations and worked examples. Short courses will add theoretical support to the experiments, analysis and interpretation. The number of participants is limited to 12. The school will interest graduate students, postdocs and researchers. For more information and registration, go to <http://umet.univ-lille1.fr/Animation/MinTem.php>.



Sociedad Española de Mineralogía

www.ehu.es/sem

SEM 2014 ANNUAL MEETING IN GRANADA

The 34th Annual Meeting of the Spanish Mineralogical Society (SEM) will take place in Granada on 1–4 July 2014. It will be organized by the University of Granada and coordinated by Salvador Morales, Fernando Gervilla, and José Torres.

The program for the SEM 2014 meeting includes:

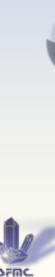
- A one-day workshop seminar entitled “Active Mining.” The seminar will take place on July 1, and the speakers will be scientists and professionals of international prestige. The aim of the seminar is to present and discuss new perspectives and ideas about this topic, particularly for young scientists.
- Scientific sessions. The scientific sessions will take place on July 2–3 and will feature invited scientists who will deliver plenary lectures on topics of general interest. Oral and poster presentations in the fields of clays, mineralogy, petrology, and geochemistry may be submitted. The main objective is to hold high-quality scientific sessions that become a platform for debate, the exchange of ideas, and the establishment of new scientific collaborations.
- A geological excursion. It will be held on July 4 and will visit the iron deposits of the Guadix Basin.

For updated information, go to <http://congresomineralogia.com/>.



MÉTHODES D'ANALYSE DES MINÉRAUX ET MATERIAUX

20 et 21 novembre 2014



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- Spectroscopies
- Expérimentation
- Diffraction
- Microsondes
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<http://www.sfmc-fr.org>
contact : methodesdanalyse@sfmc-fr.org
Comité d'organisation : Anne-Line Auzende, Étienne Balan, Marc Blanchard (IMPMC)

TRAINING DAYS – MÉTHODES D'ANALYSE DES MINÉRAUX ET DES MATERIAUX

The Society will hold two training days at Pierre & Marie Curie University in Paris, France, on November 20–21, 2014. These days will be devoted to a review of a wide range of technical tools, in the spirit of the previous sessions held in 2000, 2002, 2004 and 2010. This meeting is intended for a wide audience, from PhD students to engineers and researchers. Each invited speaker will present one or two analytical methods suitable for the study of minerals and/or fluids. Applications of the techniques will be related to open questions in Earth and planetary sciences, and speakers will show how parameters determined at a molecular or nanometre scale can provide important constraints on our understanding of global processes.

Organizing committee: A.-L. Auzende, E. Balan and M. Blanchard (contact: methodesdanalyse@sfmc-fr.org). Early registration will be possible from September 8, 2014.

Further information is available at <http://sfmc-fr.org/>.

DEVELOPING A TALENT FOR SCIENCE*

In the last couple of years, several “how to” books pertaining to a successful career in science have landed on my desk. I set out to read some of them to evaluate if they might be useful to my daughter-in-law who is contemplating graduate studies in biology.

I was pleasantly surprised by *Developing a Talent for Science*. Written by Ritsert C. Jansen, a professor of bioinformatics at the University of Groningen, this slim book packs a lot into its 178 pages. It was written for students of science, postdocs, and young researchers, and for “anyone interested about developing their talent or others’ talents.” The mixture of short chapters, real-life stories, questionnaires, and exercises for self-reflection makes it entertaining to read, and it can be read for a quick overview in one sitting of a couple of hours. But to get the most out of it, one would need to go back and do the exercises in each chapter. In fact if you had only one book to recommend to a student, I would suggest this one. It is all there: the tips that, if applied, will make you a good presenter, an inspiring communicator, a sought-after collaborator, and more. I would also suggest that anyone nurturing students should read it—there are many tips on how to inspire and support students.

Each section presents techniques you need—to develop your talent (section 1), use other people’s talent (section 2), develop other people’s talent (section 3), and make it happen (section 4). For each section, six habits to gain are introduced, and the reader is asked to rate intuitively and with the help of a questionnaire how he or she fares for



each of these habits. Plotting the result on a web-like graph gives an interesting visual presentation that highlights strengths and weaknesses. Going through the exercises will help the reader develop concrete objectives for the short, middle, and long terms. After going through all sections, the reader is ready to develop a SMARTI action plan (specific, measurable, acceptable, realistic, time-dependent, and inspiring). All graphs and forms can be downloaded from the website <http://talent4science.wordpress.com>.

The author encourages students to dream their greatest future. He recommends that they prepare a sales pitch about their research under 5 minutes in length so that they are prepared to seize any opportunity that presents itself.

And yes, the book passed the test: it has been sent to my daughter-in-law with my love.

Pierrette Tremblay, Executive Editor, *Elements*

* Jansen RC (2013) *Developing a Talent for Science*. Cambridge University Press, Cambridge, ISBN 9780521149617, 180 pp, \$29.95

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A VISIT TO HADJER EL HAMIS, WEST-CENTRAL CHAD

J. Gregory Shellnutt*

In late January of 2013, my colleagues and I visited Chad (République du Tchad) for a week as part of an ongoing research project focusing on the Central Africa Shear Zone and the basement rocks of oil-producing basins. The intent of the new project is to characterize the plutonic and volcanic basement rocks of west-central Chad. The general geology of Chad is documented by regional-scale maps; however, the detailed geological history, in particular the geochronology, is poorly constrained and a number of geological problems need to be resolved, not just for resource exploration but also to fully understand the tectonomagmatic history of north-central Africa.

The exposure of bedrock in west-central Chad is limited due to the fact that 7000 years ago the region around N'Djamena was submerged beneath a ~400 000 km² inland sea, the precursor to modern Lake Chad (~1350 km²). Consequently much of the region is now mostly a featureless, arid transition zone between the Sahel (dry grassland) and Sudanese savanna (semiarid grassland). The adverb *mostly* is used because the region is not entirely featureless: rising out of the Sahel, just to the east of Lake Chad, is a spectacular, semicircular arrangement of five variably sized, columnar-jointed buttes collectively known as Hadjer el Hamis (Figs. 1, 2).

The buttes tower over the flat landscape and are reminiscent of Devils Tower, Wyoming, USA. The 40-million-year-old Devils Tower, known as Mathó Thípila (Bear Lodge) by the Lakota people, is one of the finest examples of a protruding, columnar-jointed, phonolitic, hypabyssal stock. In addition to the sanctity of Devils Tower to the Lakota, it became the first national monument in the United States, dedicated in 1906. The hexagonal, columnar structures at both Hadjer el Hamis and Devil's Tower are due to cooling of subaerial volcanic and hypabyssal magmatic rocks.

* National Taiwan Normal University
88 Tingzhou Road, Section 4
Taipei 11677, Taiwan



FIGURE 2 The five buttes of Hadjer el Hamis (the western butte is on the left and the four eastern buttes are on the right).



FIGURE 1 Location of Hadjer el Hamis, Chad

The impressive appearance of columnar-jointed structures is recognized around the world as they are often preserved as heritage sites or geoparks.

The geological relationships of the five buttes at Hadjer el Hamis indicate they are remnants of at least two separate volcanic structures within the same caldera and may be tectonically linked to regional magmatic activity associated with the Cameroon Line during the Late Cretaceous. The buttes are composed of peralkaline pantellerites (silicic volcanic rocks) and are separated into two main groups. The four smaller buttes to the east are actually part of the same stock, whereas the larger butte (more of a hill) to the west is a structurally different stock. The eastern grouping contains the famous "Le rocher des éléphants," in which the jointed rocks resemble two elephants, and "La roche du lion,"

which resembles the mouth of a yawning lion (Figs. 3, 4, and 5). In the past, when Lake Chad was larger, the buttes would have been a group of small islands.



FIGURE 3 East-looking view of elephant rock (on the right)



FIGURE 4 Tony Lee (left) and the author appearing to be studious while visiting Hadjer el Hamis. The yawning lion is in the background.



FIGURE 5 A cave into the weathered columnar joints resembles the mouth of a yawning lion.

The outcrops are frequented by determined tourists, not only to see the unique formations and their beauty but to view a troop of Tantalus monkeys living among the rocks. The monkeys often become agitated if they see their taller, hairless relatives walking around, especially if one has a geological hammer (Figs. 4, 6). The rocks themselves have not been studied in detail, and the only age (69 ± 1.4 Ma) available was by the K-Ar method and published in the late 1960s. Unfortunately the area is one of the few places where one can find gravel suitable for construction, and so there is active quarrying between the western and eastern stocks. The stocks themselves are not being quarried, just the bedrock separating the western and eastern parts. It would be nice to see the entire area fully protected as a heritage site or geopark because of the beauty of the rock formations, but resource exploitation in the region often takes precedence.

Working in west-central Chad presents many challenges. The near-equatorial climate means that there is a rainy season from June to September and a dry season from October to May. The daily temperature during our trip typically peaked at around 42°C , which, in my opinion, is better than the hot and humid conditions of Southeast Asia. The population density of Chad is highest along the Chari River (i.e. N'Djamena) and in the south near Central African Republic, but the area to the north and east of N'Djamena is remote. The relative remoteness of Hadjer el Hamis and other areas we visited (Ngoura) reminded me of working in the southern Arctic of North America where great distances separate communities and services are limited. Logistical support for our project was provided by the Chinese Petroleum Corporation (Taiwan), which has been investing in Chad (along with other state and multinational oil companies) for nearly a decade. In cooperation with the World Bank, the government of Chad wishes to develop the petroleum industry so that much-needed infrastructure projects can be built, thus providing stable and gainful employ-

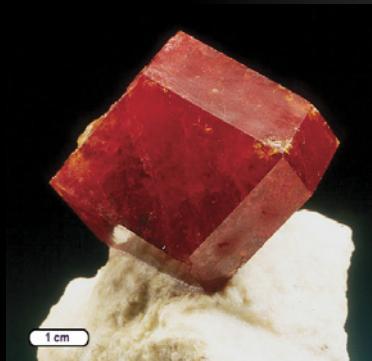
ment. There are already signs of infrastructure investment as power lines were being extended to communities surrounding N'Djamena and roads were being constructed. Perhaps in the near future geological field work will be a little easier. ■



FIGURE 6 An inhabitant (Tantalus monkey) of Hadjer el Hamis

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CALENDAR

2014

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

June 30–July 4 30th SEGH (Society of Environmental Geochemistry and Health) Conference, University of Northumbria, Newcastle, UK. Web page: www.segh.net/events/segh-conference

July 1–4 34th Annual Meeting of the Spanish Mineralogical Society, Granada, Spain. Website: http://congresomineralogia.com

July 13–17 BIOGEMON 2014 – 8th International Symposium on Ecosystem Behavior, Bayreuth, Germany. Web page: www.bayceer.uni-bayreuth.de/biogeomon2014

July 14–18 Eighth International Conference on Mars, Pasadena, CA, USA. Web page: www.hou.usra.edu/meetings/8thmars2014

July 28–August 1 Asia Oceania Geosciences Society 11th Annual Meeting, Sapporo, Japan. Web page: www.asiaoceania.org/society/index.asp

August 2–7 IUMAS-6 held in conjunction with Microscopy & Microanalysis 2014, Hartford, CT, USA. Web page: www.iumas6.org

August 3–7 Microscopy & Micro-analysis 2014, Hartford, CT, USA. Web page: www.microprobe.org/events/microscopy-microanalysis-2014

August 3–7 Tephra 2014 - Maximizing the potential of tephra for multidisciplinary science, Portland, OR, USA. Web page: www.geohazards.buffalo.edu/documents/Tephra2014.shtml

August 5–7 First Meeting of the IAGC Urban Geochemistry Working Group, Columbus, OH, USA. Web page: www.iagc-society.org/UG.html

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

August 10–14 248th ACS National Meeting & Exposition, San Francisco, CA, USA. Web page: www.acs.org

August 18–23 Geochemistry of the Earth's Surface (GES-10), Paris, France. Web page: www.ipgp.fr/GES10

August 19–22 14th Quadrennial IAGOD Symposium, Kunming, China. Website: www.14iagod.org

August 25–September 3 EMU School 2014: Planetary Mineralogy, Glasgow, Scotland. Web page: http://eurominunion.org

September 1–5 21st General Meeting of the International Mineralogical Association (IMA2014), Johannesburg, South Africa. E-mail: info@ima2014.co.za; web page: www.ima2014.co.za

September 1–6 31st International Conference on Ore Potential of Alkaline, Kimberlite and Carbonatite Magmatism, Antalya, Turkey. Website: http://alkaline2014.com

September 4–7 ERES – European Rare Earth Resources Meeting, Milos Island, Greece. Web page: http://eres2014.conferences.gr

September 7–14 Annual Meeting of the Meteoritical Society, Casablanca, Morocco. Web page: www.metsoc-2014casablanca.org

September 9–13 Cities on Volcanoes 8, Yogyakarta, Indonesia. E-mail: info@citiesonvolcanoes8.com; website: www.citiesonvolcanoes8.com

September 10–12 Joint SGI-SIMP Meeting, Milano, Italy. E-mail: info@geoscienze2014.it; web page: www.geoscienze2014.it

September 10–12 Planet Formation & Evolution 2014, Kiel, Germany. Web page: www1.astrophysik.uni-kiel.de/~kiel2014/main

September 15–16 Deep Earth Processes: Windows on the working of a planet, London, England. Web page: www.geolsoc.org.uk/deep-earth14

September 16–19 7th Mid-European Clay Conference (MECC2014), Dresden, Germany. Website: www.mecc2014.de

September 17–19 Japan Association of Mineralogical Sciences Annual Meeting, Kumamoto University, Japan. Web site: http://jams.la.coocan.jp/e-meeting.html

September 17–19 Topo-Europe 2014: Interplay between surface, lithospheric, and mantle processes, Barcelona, Spain. Web page: www.iplusdinnova.com/es/conference/topo-europe-2014-earth-top-down-bottom

September 21–24 The 92nd Annual Meeting of the German Mineralogical Society (DMG), Jena, Germany. Website: www.dmg2014.de

September 24–26 20th Congress of the Carpathian Balkan Geological Association (CBGA2014), Tirana, Albania. Website: www.cbga2014.org

September 27–30 Society of Economic Geologists (SEG) 2014 Conference: Building Exploration Capability for the 21st Century, Keystone, CO, USA. Web page: www.seg2014.org

October 12–16 MS&T'14: Materials Science & Technology Conference and Exhibition, Pittsburgh, PA, USA. Web page: www.matscitech.org/about/future-meetings/

October 16–19 XXI Petrology Session: From Magma Genesis to Ore Formation: Evidence from Macro- to Nanoscales, Boguszyn, Poland. Web page: www.geo.uw.edu.pl/21sesjaptmin/indexeng.html

October 19–22 Geological Society of America Annual Meeting, Vancouver, BC, Canada. E-mail: meetings@geosciency.org; web page: www.geosciency.org/meetings

October 20–24 Short Course "Introduction to Secondary Ion Mass Spectrometry in the Earth Sciences", Potsdam, Germany. Web page: www.gfz-potsdam.de/SIMS/

October 27–31 24^e Réunion des Sciences de la Terre, Pau, France. Web page: http://rst2014-pau.sciencesconf.org

November 3–5 Workshop on Volatiles in the Martian Interior, Houston, TX, USA. Web page: www.hou.usra.edu/meetings/volatiles2014

November 17–22 5th International Maar Conference, Queretaro, Mexico. Web page: http://maar2014.geociencias.unam.mx

November 21–22 12th Swiss Geoscience Meeting, Fribourg, Switzerland. Details forthcoming

November 24–28 Matériaux 2014, Montpellier, France. Web page: www.sifmc-fr.org/spip.php?article151

November 30–December 5 MRS Fall Meeting & Exhibit, Boston, MA, USA. Web page: www.mrs.org/fall2014

December 15–19 AGU Fall Meeting, San Francisco, CA, USA. Web page: http://sites.agu.org/meetings

2015

January 25–30 39th International Conference and Expo on Advanced Ceramics and Composites, Daytona Beach, FL, USA. Details forthcoming

January 27–31 International Diamond School, Bressanone-Brixen, Italy. Web page: www.indimedia.eu/diamond_school_2015.htm

March 16–20 46th Lunar and Planetary Science Conference, The Woodlands, TX, USA. Web page: www.hou.usra.edu/meetings/calendar

March 22–26 249th ACS National Meeting & Exposition, Denver, CO, USA. Web page: www.acs.org

April 20–24 27th International Applied Geochemistry Symposium (IAGS), Tucson, AZ, USA. Website: www.27iags.com

May 3–7 AGU-GAC-MAC-CGU Joint Assembly, Montreal, Canada. Web page: http://ja.agu.org/2015

May 31–June 3 AAPG 2015 Annual Convention & Exhibition, Denver, CO, USA. Web page: www.aapg.org/meetings

June 7–13 Applied Mineralogy & Advanced Materials - International Conference AMAM 2015, Castellaneta Marina, Taranto, Italy. Website: www.amam2015.org

June 22–29 Extensional Reactivation of Thrust Faults, Coseismic Surface Rupture, and Crustal Evolution in the Eastern Basin and Range Transition Zone, Evanston, WY, USA. Web page: www.geosociety.org/penrose

June 22–July 2 XXVI General Assembly of the International Union of Geodesy and Geophysics (IUGG), Prague, Czech Republic. Web page: www.iugg2015prague.com/.

July 5–10 Euroclay 2015, University of Edinburgh, UK. E-mail: stephen.hillier@hutton.ac.uk; web page: www.minersoc.org/euroclay.html

July 27–31 78th Annual Meeting of the Meteoritical Society, Berkeley, CA, USA. Web page: www.meteoriticalsociety.org

August 2–6 Microscopy & Micro-analysis 2015, Portland, OR, USA. Web page: www.microprobe.org/events/microscopy-microanalysis-2015

page: www.microprobe.org/events/microscopy-microanalysis-2015

August 8–14 Geoanalysis Conference, Leoben, Austria. Web page: www.geoanalysis.info

August 16–20 250th ACS National Meeting & Exposition, Boston, MA, USA. Web page: www.acs.org

August 16–21 2015 Goldschmidt Conference, Prague, Czech Republic. Web page: www.geochemsoc.org/programs/goldschmidtconference

August 23–28 29th Meeting of European Crystallographic Association (ECM29), Rovinj, Croatia. Web page: http://ecm29.ecanevents.org

August 24–27 SGA 13th Biennial Meeting, Nancy, France. E-mail: sga-2015@univ-lorraine.fr

September 9–11 8th European Conference on Mineralogy and Spectroscopy (ECMS 2015), Rome, Italy. Details forthcoming

September 20–25 8th Hutton Symposium on Granites and Related Rocks, Florianópolis, Brazil. Web page: www.hutton8.com.br

October 4–8 MS&T'15: Materials Science & Technology Conference and Exhibition, combined with ACers 11th Annual Meeting, Columbus, OH, USA. Details forthcoming

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

2016

June 26–July 1 Goldschmidt2016, Yokohama, Japan. http://goldschmidt.info/2016/

July 24–28 Microscopy & Micro-analysis 2016, Columbus OH USA. Web page: www.microprobe.org

August 7–12 79th Annual Meeting of the Meteoritical Society, Berlin, Germany. Web page: www.meteoriticalsociety.org

August 27–September 4 35th International Geological Congress, Cape Town, South Africa. Website: www.35igc.org

September 5–9 International Ni-Cu-PGE Symposium, Perth-Fremantle, Western Australia. E-mail: Steve.Barnes@csiro.au

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

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 <http://homepages.udayton.edu/~akoziol1/meetings.html>). To get meeting information listed, please contact her at Andrea.Koziol@udayton.edu.

FRIENDLY BRICK

I have been challenged by a distinguished ex-editor of *Elements* to write something interesting about brick. The prospects are not good. I've just entered 'brick firing' into Web of Science and been rewarded with a list of 7122 papers of which 6538 have never been cited! Ambitious younger readers take note.

The common English phrase 'you can't make bricks without straw', meaning that you cannot make something without the necessary materials, originates from the Bible. The pharaoh punishes the Israelites by stopping their supply of straw, essential for making mud bricks, while insisting they maintain productivity. Modern labour relations often run aground on such matters. It is certainly the case that you can't make bricks without clay, so brick is an appropriate topic for this *Elements* issue.

The simplest type of brick is simply air-dried mud, the adobe of the south-western USA. Adding straw can both strengthen the product and facilitate the drying process, even if the mud is subsequently fired, by providing porosity. The oldest-known shaped mud bricks are about 10,000 years old, from Tell Aswad near Damascus in Syria. Sadly this cradle of civilization is now immersed in a terrible civil war. Substantial permanent structures can be built from unfired mud. The great mud mosque in Agadez, Niger, was built in 1515, and rebuilt in the same style in 1844 (Fig. 1). Of course, the climate is favourable: 109 mm of rain a year, almost all in July and August when the average daily highest temperature is near 40°C, so drying out is very fast. Mud brick would be less successful where I live: 1883 mm of rain with average summer highs soaring to 18°C.

Bricks fired in kilns are much tougher. The oldest kilns, at Yarim Tepe in modern Iraq, are 8000 years old and could reach 900°C, not much less than the modern 1100°C. The simplest (called scoves) were piles of mud bricks with tunnels at the base through which the heat from fires could pass upward. The tops were closed off with a mix of wet sand and clay. In modern 'tunnel' kilns, 3000 bricks move on trolleys through a long kiln reaching progressively higher temperatures, are allowed to cool, and then automatically stacked, packed and dispatched.

Considering the importance of brick in our lives and history, there is remarkably little published work on what happens mineralogically when you heat natural mixtures of (mainly) quartz and clay minerals, with or without carbonates. It is encouraging that the most highly cited publication of the 7122 is from the *European Journal of Mineralogy*¹. It is essen-



FIGURE 1 The mud mosque in Agadez, Niger, January 1991

tially a process akin to very fast contact metamorphism, pyrometamorphism, a playground for both metastable melting and metastable crystallization. The presence of carbonate has a large effect on the beginning of melting and on the new phases that appear, which include mullite, gehlenite, wollastonite, diopside and anorthite. Above 1000°C the porosity is reduced when silicate liquid fills original pores.

There is something personal and friendly about brick. Each was individually laid, carefully, skilfully, by a bricklayer, or 'brickie' as we call them in the UK. The layers of red brick in the flint wall at Burgh Castle, shown in figure 2, were laid by a 3rd century Roman brickie who



FIGURE 2 A Roman flint and brick wall from Burgh Castle, eastern England

thought the grey flint needed brightening up with some of the characteristic Roman thin red bricks. He was building a shore fort 1800 years ago to keep marauding Saxons out. I spent my boyhood in the village of Eynsford, only 30 km south-east of the centre of London, riding my bike across the ford in companionable proximity to the work of Norman (11th century) and Elizabethan (16th century) brickies (Fig. 3). American brickies built some exquisite brick buildings in the 19th century, like my example from Denver (Fig. 4), but brick buildings are only practicable up to 18 floors, and steel and glass were needed as the skyscraper – hostile and remote – took over our cities. In the early 20th century enormous suburbs of mean houses of red brick were built in London, the red colour chosen to make them visible in the 'pea-soup' fogs of the time.



FIGURE 3 Bricks in a Norman bridge, largely built of flint, and an Elizabethan cottage, Eynsford, south-east England

¹ Cultrone G and 4 coauthors (2001) Carbonate and silicate phase reactions during ceramic firing. *European Journal of Mineralogy* 13: 621-634



FIGURE 4 Exquisite brickwork from 1889 – the Denver City Cable Railway Co building, Denver, Colorado, USA



Bricks are often embossed with the name of the manufacturer, giving some fascinating glimpses of times past. For an obscure reason, the depression created by the embossing tool is called a 'frog'. Tom Clark has sent me some pictures of bricks spotted on a recent holiday in Barbados. Two are from 19th century Scotland (FIG.5), Glenboig is near Glasgow, which by the mid 19th century was an industrial powerhouse, the 'second city of Empire' (after London) producing more steamships than anywhere else on Earth. Enormous amounts of brick were exported all over the

world from several hundred small brick companies, of which Glenboig was one of the largest. Bonnybridge is on the eastern side of Scotland. Its bricks were unusual in being made from finely crushed shale, which was mixed with water to make a stiff paste.

In the final picture (FIG. 6) the peacock and the lovely little girl are unaware they are standing on a pathway of 19th century English brick, from Canning Town in the docks area of East London. The word 'Scotch' is misleading. It refers to a style of brick, and can be made anywhere. In 1857, the great novelist and socialist Charles Dickens wrote: 'Canning Town is the child of the Victoria Docks. The condition of this place and of its neighbour prevents the steadier class of mechanics from residing in it ... Many select such a dwelling place because they are already debased below the point of enmity to filth; poorer labourers live there, because they cannot afford to go farther, and there become debased. The Dock Company is surely, to a very great extent, answerable for the condition of the town they are creating. Not a few of the houses in it are built by poor and ignorant men who have saved a few hundred pounds, and are deluded by the prospect of a fatally cheap building investment'. *Plus ça change...*



FIGURE 5 Spotted in Barbados, 19th century bricks from Scotland

FIGURE 6 Bricks in a pathway in Barbados that were made in Canning Town, a notorious mid-19th century slum district of East London. 'Scotch' is a style of brick.

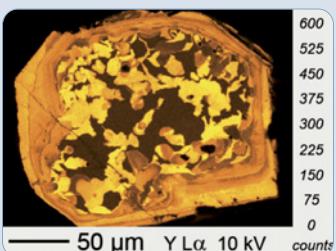
The days of the friendly brickie may be numbered. Construction Robotics, of Victor, New York, has several movies on YouTube showing SAM, their semi-automated mason, laying bricks. SAM is engaging to watch: pick up brick, rotate, slurp on some mortar, rotate, advance, gently but exactly lower into place, retreat, repeat. Unfortunately SAM does not seem to have the brickie's knack of deftly removing excess mortar with the tip of a trowel – it just dribbles down – so 'semi-' is perhaps a crucial word, particularly in the higgledy-piggledy context of a real building site. I think an autonomous robotic brickie is still some way in the future.

Ian Parsons
University of Edinburgh, UK
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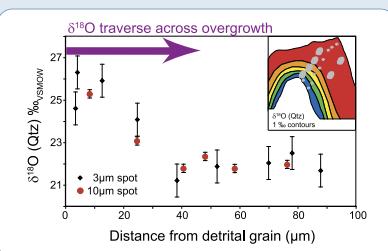
Distribution of Y in a grain from granite of Cournols, France. Dated at 343 ± 20 m.y by measuring Th, U, Pb and Y. Sample courtesy of Dr G. Wille, BRGM, France.



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

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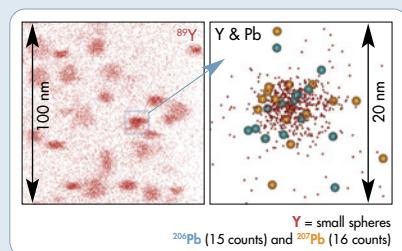
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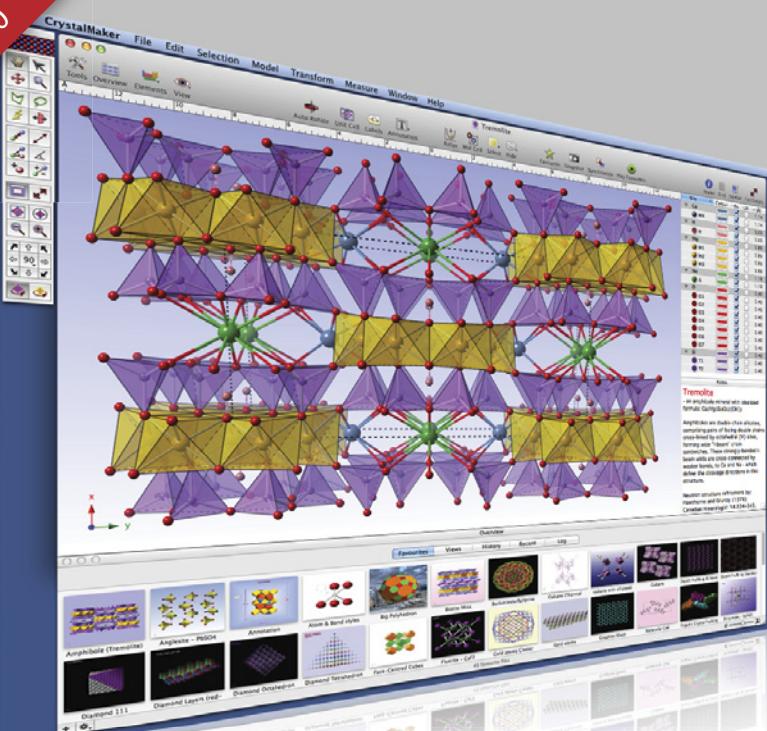
One of the hundreds of clusters analyzed from a zircon crystal from the Jack Hills of Western Australia showing the 3D distribution of ^{89}Y and radiogenic ^{206}Pb and ^{207}Pb atoms at the nanometer scale. Analysis of the data confirm the 4.4 Ga age and a heating event that occurred ~1 Ga after its formation.

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



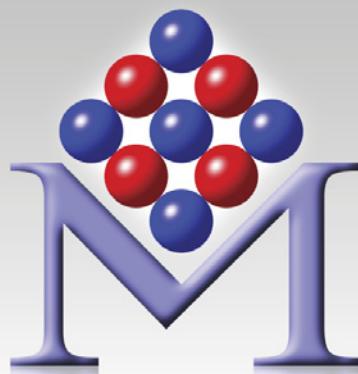
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