Elements

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February 2013
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One Hundred Years of Geochronology

DANIEL J. CONDON and MARK D. SCHMITZ, Guest Editors

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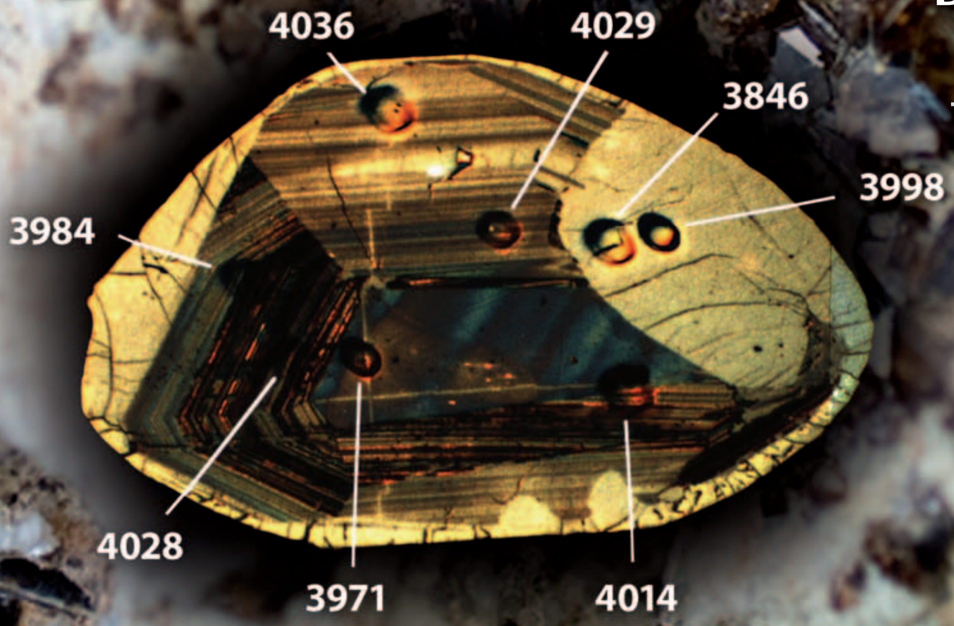

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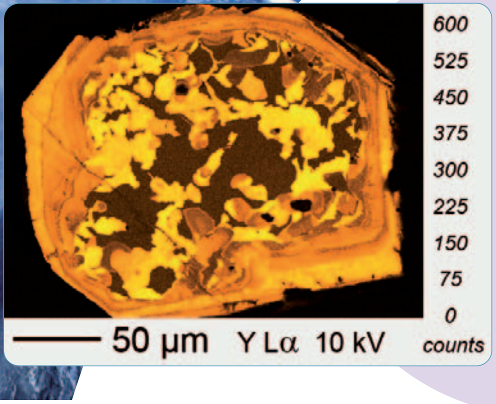

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Distribution of Y in a grain from granite of Cournols, France. Dated at 343±20 m.y by measuring Th, U, Pb and Y along a 20 points linescan across the grain.

Sample courtesy of Dr Guillaume Wille, BRGM, Orléans France.

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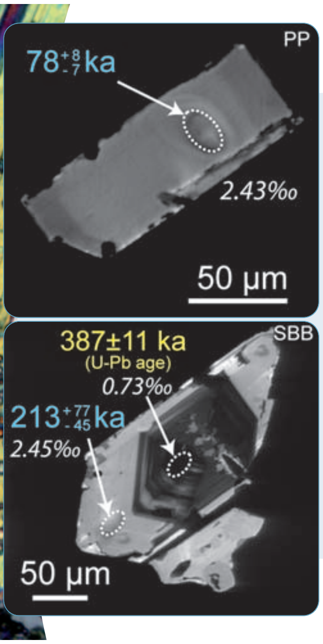

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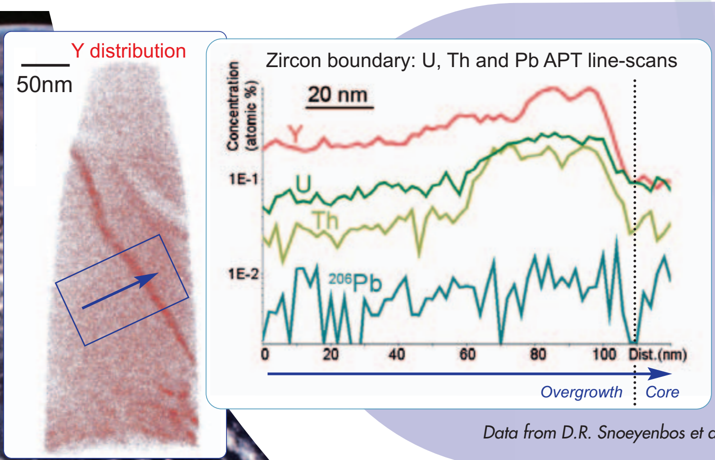
Magmatic dating and isotope study of individual crystals from the Yellowstone supervolcano: CL images of zircons dated for U-Th ages (blue) and U–Pb ages (yellow), and analyzed for oxygen isotope compositions (white). Analyzed spots are bounded by dashed ellipses.

Data from K. E. Watts, I. N. Bindeman, A.K. Schmitt, Contrib Mineral Petrol (2012).

APT



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Left: *2D projection of 70 million atom 3D dataset from a metamorphic zircon. Only Y atoms are displayed for clarity.*
Right: *the compositional structure of the boundary is revealed with greater than 50% atomic sensitivity & sub-nanometer three-dimensional resolution.*

Data from D.R. Snoeyenbos et al., Atomic Scale Imaging of U, Th and Radiogenic Pb in Zircon, Goldschmidt 2012.

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Elements

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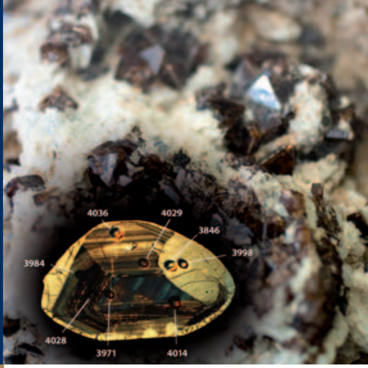

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About the Cover: Zircon is among the premier geochronometers described in this issue. Illustrated is a Nomarski contrast image of an acid-etched zircon from a 4.03 Ga tonalite of the Acasta gneiss complex, Canada, with ion probe analysis craters labeled in millions of years (Image courtesy of Samuel A. Bowring and Ian S. Williams). The background image shows zircon crystals on matrix from the Kola Peninsula (© Morgenstjerne | Dreamstime.com).

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

Elements is published six times a year. Individuals are encouraged to join any one of the participating societies to receive *Elements*. Institutional subscribers to any of the following journals—*American Mineralogist*, *Clay Minerals*, *Clays and Clay Minerals*, *Mineralogical Magazine*, and *The Canadian Mineralogist*—also receive one copy of *Elements* as part of their 2013 subscription. Institutional subscriptions are available for US$160 (US$175 non-US addresses) a year in 2013. Contact the managing editor (tremblpi@ete.inrs.ca) for information.

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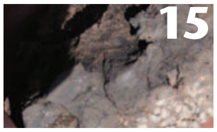
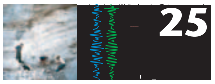
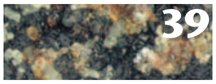
One Hundred Years of Geochronology

Guest Editors: **Daniel J. Condon and Mark D. Schmitz**







DEPARTMENTS

The Mineralogical Society of America is composed of individuals interested in mineralogy, crystallography, petrology, and geochemistry. Founded in 1919, the Society promotes, through education and research, the understanding and application of mineralogy by industry, universities, government, and the public. Membership benefits include special subscription rates for *American Mineralogist* as well as other journals, a 25% discount on Reviews in Mineralogy & Geochemistry series and Monographs, *Elements*, reduced registration fees for MSA meetings and short courses, and participation in a society that supports the many facets of mineralogy.

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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*.

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

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The Clay Minerals Society (CMS) began as the Clay Minerals Committee of the US National Academy of Sciences – National Research Council in 1952. In 1962, the CMS was incorporated with the primary purpose of stimulating research and disseminating information relating to all aspects of clay science and technology. The CMS holds annual meetings, workshops, and field trips, and publishes *Clays and Clay Minerals* and the CMS Workshop Lectures series. Membership benefits include reduced registration fees to the annual meeting, discounts on the CMS Workshop Lectures, and *Elements*.

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

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The European Association of Geochemistry was founded in 1985 to promote geochemical research and study in Europe. It is now recognized as the premiere geochemical organization in Europe, encouraging interaction between geochemists and researchers in associated fields and promoting research and teaching in the public and private sectors.

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

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The Société Française de Minéralogie et de Cristallographie, the French Mineralogy and Crystallography Society, was founded on March 21, 1878. The purpose of the Society is to promote mineralogy and crystallography. Membership benefits include the *European Journal of Mineralogy*, *Elements*, and reduced registration fees for SFMC meetings.

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The Association of Applied Geochemists is an international organization founded in 1970 that specializes in the field of applied geochemistry. It aims to advance the science of geochemistry as it relates to exploration and the environment, further the common 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 the AAG journal, *Geochemistry: Exploration, Environment, Analysis*; the AAG newsletter, *EXPLORE*; and *Elements*.

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The Deutsche Mineralogische Gesellschaft (German Mineralogical Society) was founded in 1908 to "promote mineralogy and all its subdisciplines in teaching and research as well as the personal relationships among all members." Its great tradition is reflected in the list of honorary fellows, who include M. v. Laue, G. v. 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*, *GMit*, and *Elements*.

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

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The International Association of Geoanalysts is a worldwide organization supporting the professional interests of those involved in the analysis of geological and environmental materials. Activities include the management of proficiency-testing programmes for bulk-rock and micro-analytical methods, the production and certification of reference materials and the publication of the Association's journal, *Geostandards and Geoanalytical Research*.

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The Polskie Towarzystwo Mineralogiczne (Mineralogical Society of Poland), founded in 1969, draws together professionals and amateurs interested in mineralogy, crystallography, petrology, geochemistry, and economic geology. The Society promotes links between mineralogical science and education and technology through annual conferences, field trips, invited lectures, and publishing. Membership benefits include subscriptions to *Mineralogia* and *Elements*.

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The Sociedad Española de Mineralogía (Spanish Mineralogical Society) was founded in 1975 to promote research in mineralogy, petrology, and geochemistry. The Society organizes annual conferences and furthers the training of young researchers via seminars and special publications. The *SEM Bulletin* published scientific papers from 1978 to 2003, the year the Society joined the *European Journal of Mineralogy* and launched *Macla*, a new journal containing scientific news, abstracts, and reviews. Membership benefits include receiving the *European Journal of Mineralogy*, *Macla*, and *Elements*.

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

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

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

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THE AGE OF THE EARTH


John Valley

The “Age of the Earth” is one of the most common titles in the geological literature, and with good reason. The scientific and philosophical implications are immense. This issue of *Elements* is devoted to measuring geologic time on the 100th anniversary of a book with this title (Holmes 1913). The book is a good read—a clear historical account, with groundbreaking science that still stirs controversy today. It’s available free online.

Arthur Holmes was the first to use radioactivity to date a range of rocks, and before Dempster discovered ^{235}U in 1935, Holmes estimated Earth’s age at 1600–3000 million years (Ma) (Holmes 1927). This estimate was not improved on until 1953, when Clair Patterson, using a more advanced mass spectrometer, published the age of 4510–4560 Ma, soon refined to 4550 ± 70 Ma (Patterson 1953, 1956), in perfect agreement with modern estimates (this issue). In detail, geochronometers using extinct, short-lived isotopes have now shown that Earth accreted over an interval of time, which is within the uncertainty of Patterson’s age (e.g. Halliday 2006). There are many excellent accounts of this history (Burchfield 1975; Dalrymple 1991; Lewis 2000; Lewis and Knell 2001).

> “It is perhaps a little indelicate to ask of our Mother Earth her age.”
> —Arthur Holmes (1913)

While most readers of *Elements* understand that geochronology is based on observable data, refutable hypotheses, and repeatable tests, the age of the Earth, like evolution, continues to be challenged. Creationist beliefs, which morphed into Intelligent Design, are common. Questions of faith address issues that are outside the realm of science, which deals with what we can observe and test. Nevertheless, some politicians publicly proclaim that no one knows the age of the Earth, with the implication that modern science is wrong, and demands are made to include “scientific creationism” in science courses.

The age of the Earth is not controversial among scientists. Clear rebuttals to young-Earth advocates include those by Dalrymple (1991) and Wiens (2002). The academies of science in 67 nations have formally concluded that “within science courses taught in certain public systems of education, scientific evidence, data, and testable theories about the origins and evolution of life on Earth are being concealed, denied, or confused with theories not testable by science” and that no scientific evidence contradicts the age of 4500 Ma for Earth or the theory of evolution (IAP 2006). If we all agree, why do we need to talk about it?

The question is: how best to explain the age of the Earth to nonscientists? We confront this in many venues, including education at all levels. Each year, at the University of Wisconsin, I ask classes of 200 students, “Have you had a discussion with someone who thinks the Earth is much younger than 4500 million years?”, and about 50% say “yes.” I then have 50 minutes to talk about how rocks are dated and to compare 4500 Ma with earlier estimates. I explain that geochronology is based on observable data and that the hypotheses are testable, and I encourage students to at least look through the windows of clean-labs to see people running mass spectrometers. The serious students may read this issue of *Elements* and get an appreciation for the depth and complexity of determining age, but no first-year student, and certainly no younger student, is in the position to make these observations themselves. The data are observable to specialists running mass spectrometers, but not to most others. The scientific method is less interesting, and far less compelling, when someone can’t make the observations themselves.

Thus we also need to explain why the Earth cannot be 6000 years old using evidence that is more easily observed and understood by a layperson, such as tree rings, varves, layers in glacial ice, and rates of weathering, erosion, sediment deposition, and cooling of plutons, just to name a few. If the Pyramids are still standing after 5000 years, how can the Grand Canyon form in 6000? Many arguments made by Hutton and Lyell two centuries ago apply today. This brings me back to Holmes’s book, which reviews earlier estimates and was written at the end of the remarkable period before the First World War.

At the end of the 19th century, Lord Kelvin famously concluded that Earth formed 20–40 million years ago based on a simple thermal model (Kelvin 1895, 1899). This was disputed by geologists, who maintained that more time was needed to explain the evolution of Earth or life. Kelvin’s (1899) final estimate of 24 Ma old. elicited a strong response from T. C. Chamberlin (1899). The discussion at that time was far-reaching, and included Laplace’s solar nebula hypothesis as opposed to the newer idea of planetesimals, hot versus cold accretion of Earth, advective heat transfer in the mantle, the source of heat in the Sun, and the first habitats for life on Earth. Kelvin was confident in his position because the age of the Sun was estimated to be less than 20 Ma, based on the assumption that its energy derived from chemical reactions or gravitational energy during compression. At a time when radioactivity was unknown, it was a stretch to conceive of a hot Sun more than 20 Ma old. Chamberlin questioned nearly all of Kelvin’s assumptions, prophetically enquiring:

“Is the present knowledge relative to the behavior of matter under such extraordinary conditions as obtained in the interior of the sun sufficiently

Cont’d on page 4

THIS ISSUE

This issue takes us on a voyage in time, starting with the discovery of radioactivity and carrying us forward to today. We meet the giants the field of geochronology is indebted to. We see the challenges that have been met and those that lie ahead. We are reminded that for a mineral date to have meaning, the context of the mineral analyzed and the rock of which it is a constituent must be thoroughly documented. And this is an overarching theme of all papers in this issue.

It took me a while to understand the "crisis" mentioned in the Schmitz and Kuiper article. After all, 251.2 ±3.4 Ma and 249.98 ±0.2 Ma seemed like dates in pretty good agreement. But as geochronology matures and instruments allow higher precision, scientists set out to answer ever more complex questions.

While checking facts on the Web, I learned that Rutherford did most of the research that led to his Nobel Prize at McGill University in Montréal, and that his collaboration with Soddy also started at McGill—it began as a debate "where we hope to demolish the Chemists," said Rutherford. Read an account of this fascinating encounter at http://publications.mcgill.ca/headway/magazine/turning-points-a-look-back-at-how-a-great-debate-led-to-mcgills-first-nobel-prize.

And if you have only a few minutes to explain the dating of minerals in a Geology 101 class, I suggest you download a video produced by the EARTHTIME community. Noah McLean, a coauthor in this issue, explains his geochronology research in this 4 m 42 s long video, which you can access at http://www.youtube.com/watch?v=k9RbnRDx9ts.

Pierrette Tremblay, Managing Editor

INTRODUCING PATRICIA DOVE, PRINCIPAL EDITOR 2013–2015

With the start of 2013, Patricia M. (Trish) Dove joins the *Elements* team as a principal editor. Trish is the C. P. Miles Professor of Science in the Department of Geosciences at Virginia Tech. She earned her bachelor's and master's degrees at Virginia Tech, then her PhD at Princeton, and she completed a postdoctoral fellowship at Stanford. Trish is one of the outstanding geochemists of her generation. She has made wide-ranging contributions in the biogeochemistry of Earth processes, which includes mineral surface processes at the molecular scale, the kinetics of geochemical processes, mineral–microbe interactions, and biomineralization.

Honors she has received include the Clarke Medal of the Geochemical Society, the US Department of Energy's Best University Research Award (twice), Geochemical Fellow status jointly from the Geochemical Society and the European Association of Geochemistry, and membership in the National Academy of Sciences. She will be awarded the Mineralogical Society of America's Dana Medal in 2014. She has served on the Board of Directors of the Geochemical Society and has a strong interest in education and communication as well as research. We are delighted to have her as a member of the editorial team.

James I. Drever, Principal Editor 2010–2012

EDITORIAL *Cont'd from page 3*

exhaustive to warrant the assertion that no unrecognized sources of heat reside there? What the internal constitution of atoms may be is yet an open question." (Chamberlin 1899, p 12)

One wonders how much Chamberlin, a geologist in Chicago, knew of the implications of Henri Becquerel's physics experiments in Paris that began with a chance observation just three years earlier.

The decade before Holmes's book saw extraordinary advances that overturned Kelvin's age of the Earth. Important milestones were Becquerel rays (Becquerel 1896), the theory of radioactive decay (Rutherford and Soddy 1902), the discovery that radium decay produces heat (Curie and Laborde 1903), and the hypothesis of radioactive heating of the Sun (Rutherford and Soddy 1903). The discovery of radioactivity provided an explanation for an old Sun and is generally credited for the rejection of Kelvin's age. More importantly, however, mantle convection is also at odds with Kelvin's conductive model (Perry 1895; Chamberlin 1899; Richter 1986; England et al. 2007). The real importance of radioactivity, as laid out by Holmes (1913), was to provide better and well-founded techniques of geochronology. This issue of *Elements* describes impressive new capabilities that deserve the attention of Earth scientists, but the earlier writings may help you explain them to others.

John Valley* (valley@geology.wisc.edu)
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* Principal editor in charge of this issue

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Robert A. Berner, Emeritus Professor at Yale University, won the 2013 Benjamin Franklin Medal in Earth and Environmental Science of the Franklin Institute "for deepening our understanding of the Earth system through studies of the chemistry of geologic processes and their influence on the atmosphere and oceans." In his 55 years of research, Robert Berner has tried to show how chemical principles can be applied to a wide variety of geological problems. This includes the mineralogy and thermodynamic stability of iron sulfides and iron oxides, the processes of sedimentary pyrite formation, the electrochemistry of modern sediments, calcium carbonate chemistry in the oceans, silicate mineral surface chemistry during weathering, modeling of biogeochemical changes during early diagenesis, the effect of land plants on chemical weathering, and the geochemical cycles of carbon, sulfur, and phosphorus. His work has led to the development and refinement of models for the evolution of atmospheric oxygen and carbon dioxide over Phanerozoic time.

Founded in 1824, along with the Franklin Institute, the Franklin Institute's awards program has long been recognized as bestowing the oldest and most comprehensive science and technology honor in the United States and around the world. Dr. Berner will receive his award in April at the Franklin Institute.

J. William Schopf, Distinguished Professor of Paleobiology at the University of California, Los Angeles, is the recipient of the U.S. National Academy of Sciences Award in Early Earth and Life Sciences, presented this year with the Charles Doolittle Walcott Medal. Schopf is being honored for his studies of the microscopic fossils that represent the earliest forms of life on Earth and for his generous and inspirational leadership of large, collaborative research groups. These "Precambrian Paleobiology Research Groups" have brought together scientists from multiple scientific disciplines and focused their efforts to yield new ideas and information. Their work has stimulated countless further studies of the earliest history of life on Earth. The Walcott Medal is presented every five years with a $10,000 prize and recognizes contributions to research on Cambrian or Precambrian life. Schopf contributed to the Early Earth issue of *Elements* with an article titled "The First Billion Years: When Did Life Emerge?" He will be among the 18 individuals recognized by the National Academy of Sciences for their outstanding scientific achievements in a wide range of fields spanning the physical, biological, and social sciences. The National Academy of Sciences is a private, nonprofit institution that was established under a congressional charter signed by President Abraham Lincoln in 1863. The year 2013 marks the 150th anniversary of its creation.

2012 AGU FELLOWS

Among the 61 individuals who were elected as 2012 Fellows of the American Geophysical Union, we highlight those who are members of one of *Elements'* participating societies. Fellowship is awarded to AGU members who have made exceptional scientific contributions and attained eminence in the fields of Earth and space sciences. The 2102 Fellows were recognized during an honors ceremony at the 2012 AGU Fall Meeting in San Francisco.

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1 **Joel D. Blum**, for innovative and important contributions in trace metal and isotopic geochemistry that have significantly advanced understanding of Earth processes

2 **Janne Blichert-Toft**, for being the world's leading geochemist in the application of hafnium isotopes to the evolution of the Earth and the early Solar System

3 **Robert H. Byrne**, for his groundbreaking research and scientific leadership in the physical chemistry of seawater and the global carbon cycle

4 **John M. Ferry**, for his contributions to metamorphic geology and fluid-mediated processes in Earth's crust

5 **Andrew J. W. Gleadow**, for pioneering contributions to fission-track analysis as a tool for geological dating and thermotectonic investigations

6 **Nicolas Gruber**, for his extraordinary scientific accomplishments and visionary leadership in ocean biogeochemistry research and education

7 **George W. Luther III**, for his pioneering research in redox reactions, trace element speciation, and the development of novel in situ electrochemical methods

8 **Kenneth H. Nealson**, for his pioneering work and leadership in the fields of geomicrobiology and geobiology and for his qualities as an inspirational mentor and creative scientist

9 **Yuji Sano**, for his studies of volatile isotopes of volcanic and environmental systems, and for his invention and application of ion microprobe U–Pb dating of apatite

10 **Jane Selverstone**, for elucidating the relationships among metamorphism, fluid composition, and fluid flow, and the mechanisms of deformation in the crust

11 **Stephen Self**, for his fundamental work in understanding the mechanisms and consequences of explosive and effusive eruptions

FIELD-PORTABLE XRF: A GEOCHEMIST'S DREAM?

Recalling back several decades to my undergraduate field training, high-tech involved a Brunton compass, black-and-white air photos, and perhaps dragging a theodolite over the mountains of northwestern Wyoming. Well, technology has certainly brought much change in the methods geologists use for collecting and interpreting data in the field. GPS location determinations, GIS software run on "ruggedized" tablet computers, and easy access to satellite images represent some of the more obvious advances in the field geologist's toolkit. One technology that many readers might not be so familiar with is the field-portable X-ray fluorescence (pXRF) device, an analytical tool that has experienced rapid uptake in recent years. Such devices weigh only a couple of kilograms, can rapidly quantify most elements heavier than aluminum, and often provide limits of detection reaching the low micrograms/gram range (Fig. 1).

Figure 1 Example of a pXRF instrument being used to investigate the chemical composition of a soil profile. The quantitative results are reported on the instrument's display. Image courtesy of Gwendy Hall, Geological Survey of Canada

A few years back, my interest in pXRF technology was piqued by stories of hordes of workers being dispatched to survey entire tropical river basins. The strategy was to systematically survey the entire length of each and every tributary, with the hope of finding a geochemical anomaly in the river sediments that might reveal some previously unknown natural treasure. Often anomalies will be on the scale of a few tens of micrograms/gram of some high-value element, whereas readings from elsewhere remain "below the detection limit." This strategy obviously leads to concerns about the robustness of the data from such handheld devices. Could a false positive result in large expenditures for acquiring prospecting claims where no economic resource exists? Could a false negative lead to a valuable resource being overlooked?

Portable XRF devices have existed for well over a decade—early reviews by Potts et al. (1995) and Argyraki et al. (1997) are worth consulting. Such field-portable devices work on the same, well-established principles as larger, laboratory-size instruments. Basically, a sample is excited by primary X-rays, which cause it to fluoresce at characteristic wavelengths, the intensity of a given spectral line being roughly proportional to the concentration of the corresponding element in the target. In the case of portable devices, data are acquired using an energy-dispersive detector, and it is not uncommon that low-intensity lines are significantly overlapped by high-intensity spectral peaks with similar wavelengths. Obviously such overlaps must be corrected for. The pXRF approach differs from lab-based hardware not only in the size of the apparatus but also by the fact that the analysis of geochemical samples in the field generally involves little sample preparation beyond the removal of a weathered surface or the digging of a trench to reach a target soil horizon. There are some obvious advantages associated with such portable technology:

- Data are obtained in real time within a period of a minute or two (no need to collect samples, submit them for analysis, and wait for results).
- Data are collected in situ (effectively eliminating laboratory blank problems).
- The method is by its very nature nondestructive (of critical importance for rare samples, such as cultural heritage objects).

For an in-depth review of pXRF technology, I point the reader to a tome edited by Potts and West (2008) on this subject.

Technological advances both in the generation of the excitation X-rays as well as the quantification of the resulting fluorescence spectra have greatly encouraged the uptake of pXRF technology. Miniaturized X-ray tubes, providing adequate brightness while remaining compatible with battery-derived power, have supplanted earlier radioactive X-ray sources. Perhaps more important has been the development of Si(PIN) detectors, now commonly supplanted by silicon drift detectors, these having obviated the need for cumbersome cryostats, which were required in the early years. New features, including touch-screen color displays, wireless data transfer, advanced factory software for spectral deconvolution, and automated integration of Bluetooth-delivered GPS data, have all contributed to the interest in this technology. Instrument manufacturers have developed both handheld and portable benchtop models to satisfy diverse user demands (Fig. 2a, b). Such rapid developments in both analytical capabilities and user friendliness point towards pXRF becoming a fundamental tool in a very broad range of fields, including:

- mineral prospecting by field geologists
- ore-grade evaluation at processing plants
- site contamination and remediation surveys
- art and cultural heritage fingerprinting
- metal recycling, scrap sorting, and precious metal assaying

Regardless of the rapid growth in utilization, a nagging question remains: how well do pXRF data fit the real-world needs of the geoscience community? A recent study addressing this issue was published by Kenna et al. (2011), who compared pXRF data to the "true" concentration values for a suite of sediment and soil reference materials (RMs). Although they did report examples of significant drift in instrument

Figure 2 (**A**) Portable XRF instrument mounted under a table for on-site chemical analysis of drill core samples. Image courtesy of Gwendy Hall (**B**) Handheld device being used to survey soil contamination at a former industrial site. Image courtesy of M. H. Ramsey, University of Sussex

sensitivity as a function of time, these authors found reasonably good agreement between the pXRF data for 31 elements and the established values for the 10 RMs they studied.

A good understanding of the performance parameters of pXRF instrumentation is of crucial importance to the mining industry. For this reason, the Canadian Mining Industry Research Organization (CAMIRO) sponsored a study, funded by 31 companies involved in the mining sector, with the goal of establishing empirical performance parameters for pXRF technology (Hall et al. 2011). With its 171-page report and equally voluminous material in the five appendices, the CAMIRO Phase I study provides an amazingly detailed picture of what one can expect from pXRF instrumentation. Hall et al. (2011) looked at five devices that had been provided by instrument manufacturers, including three handheld instruments and two portable benchtop models. Each of these units was used to analyze 41 well-characterized RMs spanning a spectrum of compositions as diverse as soils, stream sediments, gabbros, and even pitchblende ore. Concentration data were recorded for all elements that a given instrument reported (typically around 45 or 50 elements per analysis), and this exercise was conducted using both the "soil" and the "ore" factory-set calibrations provided by each of the instruments. The pXRF data sets were plotted against the "assigned" concentration values for the given material, and each of these plots was evaluated for slope, intercept, and the r^2-defined scatter of the data from the best-fit regression (Fig. 3a, b).

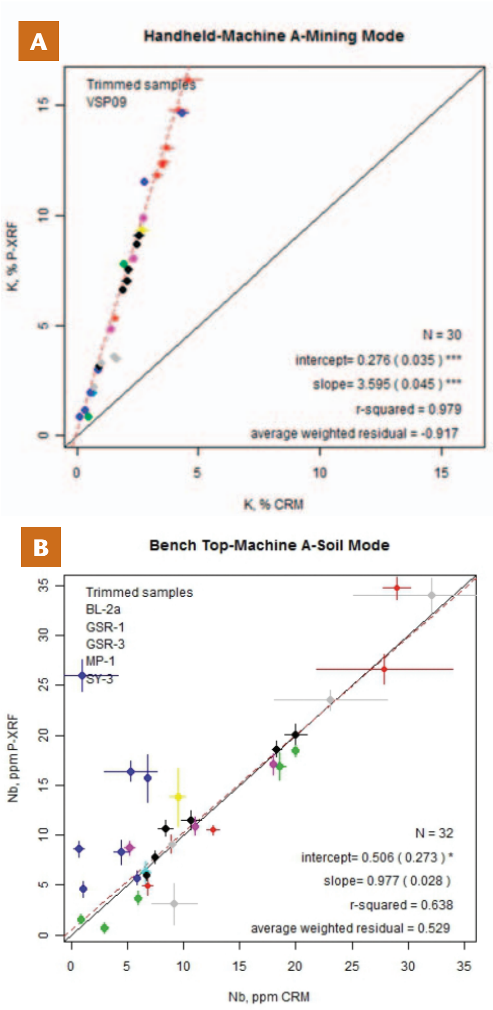

Figure 3 Examples of data plots from the CAMIRO Phase I study. (**A**) Potassium determined using "Handheld A" operating in mining mode. The data show very good correlation, but the slope indicates a systematic offset by a factor of 3.6. (**B**) Niobium determined by "Benchtop A" operated in soil mode. The data show reasonable correlation but there are major analytical uncertainties beyond what would be predicted by the observed repeatability of the measurement, as indicated by the vertical error bars. The colors identify different material types.

Not surprisingly, the instruments provided varying degrees of data quality. No single instrument was found to provide consistently superior data across the range of rock types and elements. The benchtop and handheld models were not found to systematically differ in their data quality. It was also shown that instrument drift and background issues need close attention, including the role of the thin foils often used to protect the samples. The most important conclusion was that relying on factory-set calibrations puts the user at risk of unreliable, or even systematically wrong data. The CAMIRO report recommended that users pay close attention to the need to recalibrate their pXRF instrument using well-characterized RMs. Such calibration sets are now becoming available from RM providers, and these need to be used if the user wants accurate data (Fig. 4); using them should lead to significantly improved data quality.

Figure 4 An example of a suite of reference materials for field calibration of pXRF devices. Each packet contains six plastic wells, each of which contains a pressed powder disk made from a certified reference material; each disk is covered by a thin plastic foil to make it suitable for rugged field conditions. Image courtesy of Mike McWha, African Mineral Standards

The CAMIRO Phase I report will soon appear at www.appliedgeochemists.org for public download. I strongly recommend this as essential reading to anyone interested in pXRF technology. The CAMIRO Phase II study is already completed—certainly, it too will provide much fascinating reading when it is released to the public in August 2013. ▪

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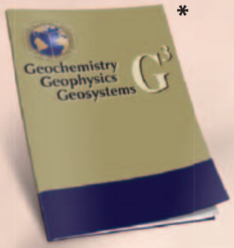

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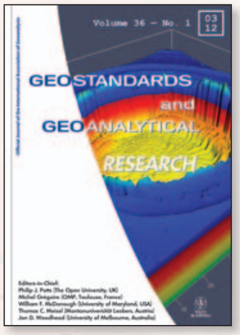

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Meet the Authors

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Morten B. Andersen is an isotope geochemist. After completing his PhD at ETH Zürich, Switzerland, he spent 6 years doing postdoctoral research in the School of Earth Sciences, University of Bristol, UK, before returning to ETH Zürich as a senior scientist. His research is focused on paleoclimatology using isotope proxies, with particular interest in the behavior of uranium and its daughter isotopes in Earth system processes and its application in high-precision U-series geochronology.

Daniel J. Condon is a research scientist at the NERC Isotope Geosciences Laboratory (British Geological Survey, UK). He received a PhD from the University of St Andrews (2002) and was a postdoctoral researcher at the Massachusetts Institute of Technology. His research interests are in geology and geochronology, with an emphasis on stratigraphic applications from the Quaternary to the Paleoproterozoic and on the U–Pb and U–Th dating methods.

Matthew S. A. Horstwood is the Plasma Mass Spectrometry Facility manager at the NERC Isotope Geosciences Laboratory (UK), where he has worked since 2000. After completing his BSc in geology at the University of Wales Aberystwyth (1994), he earned a PhD from Southampton University (1998). His research focuses on LA–ICP–MS U–Th–Pb geochronology, the development of LA and ICP–MS analytical science and its application to isotope geoscience, particularly with respect to appropriate data handling, uncertainty quantification, and their impact on interpretation. He is a fellow of the Geological Society, member of the Geochemical Society, and vice president of the International Association of Geoanalysts.

Trevor R. Ireland is a professor in Earth chemistry at the Research School of Earth Sciences, Australian National University (ANU). After a geology–physics undergraduate degree in New Zealand, he migrated to Canberra to carry out research on the recently installed SHRIMP ion microprobe, receiving his PhD in 1987. He is interested in the application of microscale analytical techniques to the analysis of natural materials. His research has ranged from cosmochemistry (notably chemical and isotope systematics of refractory inclusions in meteorites) to zircon U–Pb geochronology (particularly of Gondwana). He is currently head of the SHRIMP facility at ANU.

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James M. Mattinson, professor emeritus in the Department of Earth Science at the University of California, Santa Barbara, received a BA (1966) and PhD (1970) in geology from UCSB, then was a postdoctoral fellow at the Geophysical Laboratory of the Carnegie Institution of Washington from 1970 to 1973. He returned to UCSB as a faculty member, where he specialized in U–Pb geochronology, dividing his time about equally between applying geochronology to geologic problems and developing improved techniques for U–Pb zircon analysis.

Noah McLean is a postdoctoral researcher at the NERC Isotope Geosciences Laboratory, British Geological Survey. He received a BS in geology from the University of North Carolina, Chapel Hill (2004) and a PhD in geochemistry from the Massachusetts Institute of Technology (2012). His research interests include geochemistry, geochronology, and thermochronology, with a special emphasis on acquiring and using statistics to confidently interpret data at the highest precision possible and applying these data to explore complex problems in the Earth sciences.

Leah Morgan is a Marie Curie postdoctoral fellow at the Scottish Universities Environmental Research Centre. She previously had studied at Carleton College (BA), the University of California at Berkeley (PhD), and the Vrije Universiteit Amsterdam (GTSnext postdoctoral position). She is an ^{40}Ar/^{39}Ar geochronologist with interests in various applications of the method, particularly those involving human origins. She is also leading an effort to recalibrate mineral standard ages via metrological ^{40}Ar and ^{40}K concentration measurements.

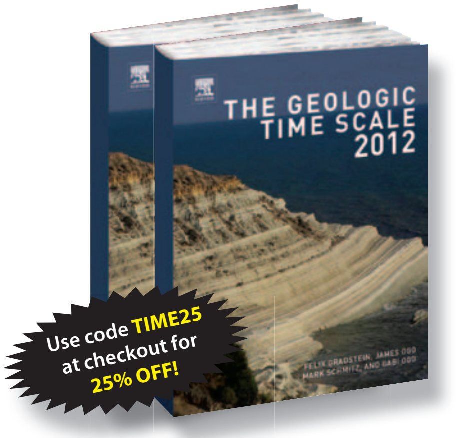
Alexander A. Nemchin is an associate professor at Curtin University in Perth, Western Australia. His research interests are in isotope geochemistry and the geochronology of Earth and planetary materials. After completing his PhD at Curtin University, he joined the Western Australian School of Mines in Kalgoorlie. In 2001 he moved back to Perth where he concentrated his research on the ancient zircon population from the Jack Hills metasedimentary belt; this work led to his interest in lunar chronology. Since 2005 he has worked extensively on the use of U–Pb isotope systems in accessory minerals to determine a chronological framework for lunar magmatic evolution and the impact history of the Moon, becoming an international investigator on NASA's Lunar Science Institute team.

David A. Richards is a senior lecturer in geographical sciences and a member of the Bristol Isotope Group at the University of Bristol. He also has postdoctoral experience working in isotope geochemistry laboratories at the universities of Minnesota and Leeds. He is interested in past sea levels, landscape evolution, human and faunal evolution, archeology and paleoclimate, using speleothems, in particular. He has focused on U–Th and U–Pb geochronology for the past 20 years and is the editor responsible for such applications for the journal *Quaternary Geochronology*.

Blair Schoene is an assistant professor in geosciences at Princeton University, where he runs the Princeton radiogenic isotope laboratory. He became interested in geochronology as a PhD student at the Massachusetts Institute of Technology, where he combined extensive fieldwork with U–Pb geo- and thermochronology to understand the evolution of Archean lithosphere. He has also been part of the EARTHTIME initiative, working with an international network of laboratories dedicated to increasing precision and accuracy in geochronology. His recent interests involve integrating accessory mineral geochronology with geochemistry and petrology to understand crustal evolution, and the application of U–Pb zircon chronostratigraphy to problems in Earth history.

Mark D. Schmitz is an associate professor of geochemistry and director of the Isotope Geology Laboratory in the Department of Geosciences at Boise State University, Idaho, USA. His research interests range from the evolution of continental lithosphere to the record of Earth–life–climate dynamics in the deep-time stratigraphic record. A consistent theme in these pursuits is the application of isotope geochronology to understanding the timing and tempo of geologic processes and events. His recent endeavors include work on Milankovitch forcing of climate, glacioeustasy, and sedimentation during the Late Paleozoic ice age and serving as geochronology coeditor for *The Geological Time Scale 2012*.

Martin J. Whitehouse is a senior research fellow and director of the Nordic ion microprobe consortium (Nordsim) at the Swedish Museum of Natural History in Stockholm. He applies isotope geochemistry and geochronology to problems of crustal evolution across nearly the entire geological age spectrum, from Hadean zircon to Miocene orogenic belts, and has special interest in early Earth processes. High-spatial-resolution investigations using the ion microprobe form a key component of many of his studies.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