From Cosmic Scarcity to 300 Minerals
Evolution of Early Solar System
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Origin of RNA and Precursors to Life

Boron: Light and Lively

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Boron: Light and Lively

Guest Editor: Edward S. Grew

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The Clay Minerals Society (CMS) was 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, including new annual meetings, workshops, and field trips, and publishes papers and books through the CMS Workshop Lectures series. Membership benefits include reduced registration fees to the annual meeting, discounted CMS Workshop Lectures, and Elements.

The Clay Minerals Society of Great Britain and Ireland (CMS) is an international society for all those working in the field of clay science. The society aims to advance the knowledge and use of the scientific knowledge of the formation, application, and interpretation of clay minerals and to host a meeting in 2022. The Clay Mineralogy members are dedicated to promoting clay mineralogy internationally. The society is an active and dynamic organization of over 240 members, 30% of whom are Goldschmidt conference organization publications. The society is a platform for the advancement of knowledge in clay mineralogy.

The Clay Minerals Journal (CMJ) is a member of the Clay Minerals Society. Membership benefits include a digital subscription to Elements, a reduced registration fee for annual meetings, and access to the Clay Minerals Journal.

The Clay Minerals Society (CMS) is for individuals interested in mineralogy, crystallography, petrology, and geochemistry. Founded in 1919, the CMS is dedicated to promoting knowledge of mineralogy and its application to other subject areas, including crystallography, geochronology, environment, environmental science and economic geology. The society is the national body representing the interests of exploration geochemists, facilitating the acquisition and distribution of scientific knowledge, promoting the exchange of information, and encouraging research and development. Membership includes the AGG Journal, Geochemistry, Exploration, Environmental Geology, the AGG newsletter, EXPLOR, and Elements.
In 2004, I assumed an administrative role in my university, thus joining what is commonly referred to as the “Dark Side” of academia. I have only just returned to my position as a faculty member. Some pursue administration as a career path and expect to move up the academic ladder, progressing from department head, to dean, to provost, and, perhaps, even to president. Others, like myself, view administration as an intriguing experiment: I certainly didn’t anticipate staying away from a faculty role for so long (almost 13 years). Like many faculty, I had little experience with organizational leadership when I joined the Dark Side. I was like a Padawan apprentice (another reference from Star Wars) aspiring to be a Jedi and greatly in need of master Yoda’s training.

I share below what I have learned from my experience, not only for those considering a position in academic administration but also for others to gain an appreciation of this important role:

- Administrators create an atmosphere that allows faculty members to exercise their dreams and accomplish their goals. This is accomplished by taking care of the day-to-day administrative tasks that ensure the smooth running of a department. As a former Dean told me, it is like “making sure there is toilet paper in the bathroom.”

- The pace and workload that an administrator handles is unrelenting. E-mails, reports, budgets, and phone calls come in steadily. You will always have an internal list of things that must be done right away, projects to start, and projects that you should start. To be successful, an administrator needs to prioritize and to balance output versus perfection.

- Administrators operate within an organizational unit. Life will no longer be as flexible as when you were a faculty member. You will have a supervisor to whom you will report on a regular basis. You, in turn, will supervise administrative and/or technical staff. You are held accountable for both the good and the bad of your unit.

- As an administrator, you will develop a new network of relationships. This network will be invaluable when you are troubleshooting an unfamiliar problem, but it may also mean that you may have to work with people who drive you crazy. As Yoda would advise, “Patience you must have, my young Padawan.”

- Administrators have to make decisions in a timely manner. You will need to address issues before they become emergencies by being in close touch with your faculty and staff. Results need to be communicated to all involved.

- Administrators need to think “outside-of-the-box.” Just when you think you have seen it all, a new and strange problem appears that demands a unique solution. Being a troubleshooter and producing practical solutions is the most creative part of an administrative assignment.

- Administrators are often expected to get deeply involved in conflict... not by instigating it (!) but by helping to resolve it.
The authors of this issue make a compelling argument that we shouldn’t undervalue boron. As an essential constituent of nearly 300 minerals such as tourmaline and colemanite in the Earth’s crust and even one in the Earth’s mantle (qingsongite), boron provides a unique indicator for deciphering Earth’s 4.6 billion-year evolution from a molten mass in the proto Solar System to a vibrant planet that can sustain life. Boron also allows us to peer into the complex dynamics of subduction zones, to trace paleoclimatic conditions and atmospheric CO₂, and to understand how the essential building blocks of life (e.g. RNA) could form in the hostile environments of the early Earth. But, boron isn’t just valuable for scientific pursuits, it also finds practical applications in glass and ceramics, detergents, fertilizers, and nuclear reactors among others.

Boron is literally “one-in-a-million.” The rarest and purest of diamonds, such as the Hope diamond, are blue because of boron. It rarely takes more than 1 boron atom per million carbon atoms to produce that rarest and most sought-after blue color. Registering on average ~11 ppm in soils, boron is critical to many plant functions. A plant can have all the carbon, nitrogen, and phosphorus it needs, but without boron, plants can’t thrive. Without boron, there would be no such thing as a cell wall and no processes such as cell division, metabolism, or moving sugars through a plant. To put it bluntly, without boron there would be no such thing as plants.

So, before anyone dismisses boron as not deserving our attention… think again. The articles in this issue give a fascinating glimpse into the many and varied roles played by this light but important element.

For another summary of the importance of boron, check out Ed Grew’s article published in the June 2015 issue of Elements. You can find it online at http://elementsjournal.org/2015/06/01/boron-the-crustal-element/

2016 IMPACT FACTOR = 4.0

The Thomson Reuters “InCites™ Journal Citation Reports” for 2016 were released in June 2017. Elements’ impact factor was 4.0 in 2016, which ranks 1st among the journals in the mineralogy category and 8th in the geochemistry/geophysics category.

Elements continues to generate significant interest and attention.

In 2016, the 455 articles published in Elements from 2005 to 2016 received 2,317 citations. That’s an average of 5.1 citations per article per year. Over 500 different journals cited Elements articles in 2016, with the most citations found in the journals Lithos (132), American Mineralogist (97), Chemical Geology (83), Geochimica et Cosmochimica Acta (61), Ore Geology Reviews (59), and Environmental Science and Technology (45). Perhaps even more interesting is the fact that these 455 Elements articles have been cited over 13,000 times in the last 12 years.

Unlike many other journals, each Elements issue is a collection of 5–7 related articles. The editors and authors work hard to have articles that don’t overlap in content but that together present a coherent picture of a topic. It’s a team effort. So, it is perhaps more important to glimpse not so much at an individual contribution but at the impact of the collective thematic whole. As of July 2017, the most highly cited issues since the time of publication are as follows:

- v3n1 – “Zircon, Tiny but Timely” (1,000 citations)
- v2n2 – “Arsenic” (567)
- v4n5 – “CO₂ Sequestration” (554)
- v1n5 – “Large Igneous Provinces” (442)
- v2n6 – “The Nuclear Fuel Cycle” (424)
- v3n3 – “The Critical Zone” (410)

These 6 issues were published between 2005 and 2008. Each continues to receive ~40–50 new citations a year. More recent issues are also being actively cited. For example, the issue “Rare Earth Elements” (v8n5) has had 364 citations over the last 6 years; “Ophiolites” (v10n2) has had 238 citations over the last 3 years. In fact, approximately one third of the 71 Elements issues to date have had over 200 citations each.

What do all these numbers mean? We can say that Elements issues continue to be used and cited well past their publication dates. Elements, although meant to be a magazine for general consumption, is proving that its thematic articles can compete with well-respected scientific journals. But, even more importantly, though Elements readers have access to excellent articles on fascinating geoscience topics, readers can also use the magazine to stay in touch with the activities of many scientific societies, see at a glance upcoming meetings and conferences, read relevant book reviews, search for job postings, learn about geoscience equipment and services, and so much more.

It is the continued commitment of the 17 participating societies that produce this magazine, the high quality of the articles themselves, the first-rate products and services advertised in our issues, and the over 16,000 members who read the magazine that are the key reasons why Elements continues to have such a positive impact on our scientific community.

Bernard J. Wood, Friedhelm von Blanckenburg, Nancy L. Ross, and Jodi J. Rosso

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Meet the Authors

Penelope J. Brothers is a New Zealander educated at the University of Auckland (New Zealand) and Stanford University (California, USA). She has been a professor in the School of Chemical Sciences at the University of Auckland since 1988 and has been a visiting professor at several institutions, including both the Davis and Berkeley campuses of the University of California (USA), the University of Heidelberg (Germany), the University of Münster (Germany), the University of Burgundy (France), the Peking University (China), and the Arctic University of Norway. Penelope was a Fulbright Senior Scholar at Los Alamos National Laboratory (New Mexico, USA) and is an Associate Editor of Chemical Communications. She is currently investigating the chemistry of boron coordinated to porphyrin and corrole ligands, boron dipyrrin (BODIPY) fluorophores for sugar recognition, and surface patterning using molecular pentagons.

Yoshihiro Furukawa is an assistant professor in the Department of Earth Science at Tohoku University (Japan). He received his PhD from Tohoku University in 1995. He was one of the first to recognize the origin of such minerals, backed up by mineralogical, sedimentological, volcanic rocks, and related industrial raw materials. His research focuses on the prebiotic formation of life's building blocks, such as sugars, amino acids, and nucleobases. In particular, he has investigated the interactions between ribose and borate. He is also working on abiotic molecular organization and polymerization to form bio-important polymers. In 2014, as a visiting international scholar, he investigated abiotic RNA formation at the Foundation for Applied Molecular Evolution (Florida, USA).

Edward S. Grew is a research professor at the University of New England (Australia) and a Humboldt Fellow at the Ruhr University (Bochum, Germany). He has studied granulite-facies borosilicate assemblages in East Antarctica, Adirondack Mountains (New York, USA), South India, and the Aldan Shield (Siberia, Russia), as well as boron isotopes in Antarctic borosilicates and Eoarchean tourmaline from Greenland. He edited the Mineralogical Society of America’s Reviews in Mineralogy & Geochemistry volumes on boron (v33) and beryllium (v50) and has collaborated with Robert M. Hazen on the mineral evolution of these elements. In 2015, he was awarded the Collins Medal by the Mineralogical Society of Great Britain and Ireland.

Cahit Helvaci received his PhD in geology from the University of Nottingham (UK) in 1977. He was a member of Ege University (Turkey) from September 1977 to 1982, and since then has been at Dokuz Eylul University (Turkey). His primary research interests are on recent and ancient evaporites, the role of evaporites in the formation of large-scale ore deposits, hydrothermal systems, sedimentary and related industrial raw materials. Helvaci’s life-long study of borate minerals has resulted in a better understanding of the origin if such minerals, backed up by mineralogical, sedimentological, petrographic, and isotopic studies.

N. Gary Hemming is a geochemist working on the development and application of boron isotopes in marine carbonates as a proxy for the paleo-pH of the oceans and applying this method to paleoclimate studies. He developed an improved method for boron isotope analyses as a student at the Department of Earth and Space Sciences at Stony Brook University (New York, USA), where he received his PhD in 1995. He was one of the first to recognize the potential for using the offset in boron isotopes between minerals and fluids as a paleo-pH probe. He went on to the Lamont-Doherty Earth Observatory of Columbia University (New York, USA) as a post-doc in 1995 and continues there as an adjunct research scientist. He has been a professor at Queens College CUNY (USA) since 1999, and is also a visiting professor at Stony Brook University.

Takeshi Kakegawa is Professor of Geochemistry at Tohoku University (Japan). He received his BS in mineralogy, petrology, and economic geology from Tohoku University and his PhD in geochemistry from Pennsylvania State University (USA). His research interests include experimental studies on the origin of life, Precambrian geology, tracing life in early Archean rocks, biological elemental cycles on the early Earth, biogeochemistry and biomaterialization in terrestrial and submarine hydrothermal systems, petroleum genesis in diatomite, and submarine hydrothermal processes on ancient and modern ocean floors.

Martin R. Palmer has been Professor of Geochemistry at the University of Southampton (UK) since 1994. After studying for a BSc in chemistry at the University of East Anglia (UK), he received his PhD in geochemistry from the University of Leeds (UK) in 1985. He first started working on boron isotopes as a tracer of geological processes while a post-doc at the Massachusetts Institute of Technology (USA) in 1987. Since that time, he has applied this tracer to a wide variety of processes, including paleoceanography, non-marine evaporites, tourmalines from granites and ore deposits, and island arc petrogenesis. His present boron isotope project involves working with Yağıcın Ersoy and Cahit Helvaci from Dokuz Eylül University (Turkey) to use boron isotopes in volcanic rocks from western Anatolia (Turkey) to gain insight into crustal formation and recycling processes during continental collision.

E. Troy Rasbury received his PhD in geosciences from Stony Brook University (SBU) (New York, USA) in 1998. He was on the faculty at Queens College CUNY (USA) from 1998 to 1999 before returning to Stony Brook University as a faculty member in 1999. She is also a member of the Interdepartmental Doctoral Program in Anthropological Sciences at SBU. She specializes in isotope and trace element analyses of carbonates. Much of her work has focused on U–Pb dating of carbonates, but she has become increasingly interested in secular evolution of seawater chemistry, particularly how a high-resolution record of boron isotopes might help deconvolve climate and tectonic questions during the Paleozoic.

Charles “Chip” Shearer is an igneous petrologist–geochemist–mineralogist with a focus on the formation and evolution of the terrestrial planets. Chip is a senior research scientist and research professor in the Institute of Meteoritics and Department of Earth and Planetary Sciences at the University of New Mexico (USA). He is currently the deputy principle investigator for NASA’s MoonRise mission. The goal of this mission is to reconstruct the timing and planetary-scale effects of the late heavy bombardment of the inner Solar System by returning samples from the South Pole–Aitken Basin on the southern far side of the Moon.

Steven B. Simon received his PhD in geology from the South Dakota School of Mines & Technology (USA) in 1988. He is currently a senior research scientist in the Institute of Meteoritics at the University of New Mexico (USA), having recently relocated there after 28 years at the University of Chicago (Illinois, USA). He investigates the early history of the Solar System through petrologic studies of chondritic meteorites, concentrating on chondrules and refractory inclusions. He is also interested in redox (reduction–oxidation) conditions in the early Solar System and the Moon as recorded by the valences of Ti, Cr, and V in lunar rocks and chondrules.
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Boron: From Cosmic Scarcity to 300 Minerals

Edward S. Grew

INTRODUCTION: IN THE BEGINNING

Boron, like lithium and beryllium, is rare in the cosmos because its nucleus is “fragile.” So, how does one get from the interstellar medium, where boron was first produced, to Earth’s upper continental crust where boron is concentrated in deposits containing remarkably diverse suites of boron minerals? Processes that led to the formation of continental crust also concentrated boron, which is preferentially incorporated into melts and aqueous fluids. Deposits with high boron-mineral diversity include granitic pegmatites, peralkaline intrusions, boron-enriched skarns, and evaporite deposits. Despite the loss of boron minerals from the geologic record due to their ready solubility in water and breakdown at low temperatures, the increase in boron-mineral diversity with time is real, and is accelerated during supercontinent assembly.

Keywords: boron concentration, mineral diversity, continental crust, supercontinent assembly, boron cycling

THE EARLIEST BORON CONCENTRATIONS

Starting with 0.19 µg/g B in the primitive mantle (Marschall et al. 2017), how can boron be concentrated to reach the enrichments in Earth's crust today? The current estimated average boron concentration for the upper continental crust is 17 µg/g B (Rudnick and Gao 2014). This figure includes values for several enriched crustal reservoirs, such as boron in terrigenous detritus in pelagic sediments (30–150 µg/g B) (Leeman and Sisson 1996) and granitic pegmatites (e.g. 213–287 µg/g B) (Stilling et al. 2006; Simmons et al. 2016). White and Klein (2014) calculated the bulk boron content of oceanic crust to be 0.8 µg/g from the composition of lavas erupted at the surface plus that of cumulate minerals in the lower crust and upper mantle. These authors gave 1.8 µg/g B as the global average of mid-ocean ridge basalts (MORB), both of which are but modest enrichments from the mantle. It appears unlikely that magmatic processes would, by themselves, lead to the present average of 17 µg/g B in the upper continental crust.

Earth’s boron story appears to be inextricably linked to water: the formation of Earth’s oceans would be a prerequisite for concentrating boron. There are two possible sources for the Earth’s oceans: first, volatiles released by degassing of “wet” planetary embryos accreted during the second half of Earth’s formation; or second, volatile-rich comets originating in the outer Solar System. Whatever the source of water, there is evidence that the ocean could have been present during the Hadean. Harrison et al. (2017) cited O and Li isotopic evidence in Hadean zircons from Jack Hills (Western Australia) for a “clement” Earth from at least 4.3 Ga. At this time, chemical weathering could have played a major role in the disaggregation and breakdown of the then-exposed rocks, Earth’s earliest crust. Harrison et al. (2017) concluded that the Jack Hills zircons crystallized from relatively cool, wet, felsic melts partially sourced from types that constituted the complex mix from which the Earth and the other terrestrial planets formed. Although estimates for the bulk silicate Moon give 0.0743 µg/g B (Hauri et al. 2015), which is even more depleted than Earth’s primitive mantle, the preliminary determination of 10–100 µg/g B in calcium sulfate veins in Mars’ Gale Crater by the NASA Curiosity rover (Gasda et al. 2016) is consistent with Mars having a bulk boron content comparable to Earth’s bulk boron content.

Cosmic scarcity of boron resulted in a low-boron concentration in the Solar System, where boron remains scarce. Boron is not produced by nucleosynthesis, except the small fraction coming from the radioactive decay of ¹⁰⁷Be (Liu and Chaussidon 2017). Solar System boron concentration can be approximated from type CI (carbonaceous IVuna type) carbonaceous chondrites, coming out at 0.775 ± 0.078 parts per million (µg/g) B (Shearer and Simon 2017 this issue). Earth’s primitive mantle is depleted in boron relative to CI chondrites, i.e. 0.19 µg/g (Marschall et al. 2017). There is no reason to suspect that the early Earth was significantly more enriched in boron than other terrestrial planets, because it is unlikely that boron contents would have varied significantly between the different chondrite

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sedimentary protoliths at a plate boundary. In contrast, Kemp et al. (2010) argued that the Hf–Pb systematics of the Jack Hills zircons are consistent with protracted reworking of a mafic protocrust formed from solidification of a magma ocean, but with no juvenile additions after extraction from the primordial mantle at 4.4–4.5 Ga. The protocrust envisaged by Kemp et al. (2010) would probably not contain more than 2–3 µg/g B. However, exposure to the atmosphere and hydrosphere of the protocrust, whether mafic or felsic, could begin the process of concentrating boron. Chemical weathering released boron present in the protocrust, freeing it to be incorporated in the Earth’s ocean(s).

There are no constraints on boron contents of Earth’s ocean and crust until 3.8 Ga. At this time, rocks start to contain sufficient boron to be expressed mineralogically. Sedimentary precursors to metachert, mica schist, tourmalinite, and amphibolite in the 3.7–3.8 Ga Isua supracrustal belt (Greenland) contain enough boron to form tourmaline during amphibolite-facies metamorphism at 3.55 Ga (Fig. 1) (Grew et al. 2015). No bulk boron data have been reported for the Isua rocks, but comparable amphibolite-facies metapelites in other areas reveal 7–80 µg/g B (Leeman and Sisson 1996). Isua tourmalinites that contain 30%–50% modal tourmaline (Grew et al. 2015) would have a bulk boron content of ~10,000–16,000 µg/g.

The 3.7–3.8 Ga Isua supracrustal belt is the oldest geologic entity containing minerals for which boron is an essential constituent. No convincing evidence has been reported for boron concentrations or boron minerals prior to 3.8 Ga. Nonetheless, the presence of significant boron in the Isua supracrustal belt presumes some prehistory of concentrating boron. Furukawa and Kakegawa (2017 this issue) infer that volcanoes were a source of boron in the proto-arc, which presumes boron had already been incorporated in the source rocks of erupting magmas, i.e. boron could have originated from preexisting crust or seawater. It is possible that there were concentrations of boron in proto-arcs before Isua, which are plausible at Hadean plate boundaries (Harrison et al. 2017). But no such boron concentrations have been preserved.

**CRUSTAL GROWTH AND INCREASING BORON MINERAL DIVERSITY**

**Continental Crust Growth**

Virtually all investigators agree that the volume of continental crust has increased with time, but opinions differ on the calculated rate of growth, the extent of crustal destruction, and the proportion of recycling. Most of the proposed growth curves lie in the area bounded by the curve for ‘crustal growth with some recycling’ and the curve for ‘present-day exposure’ (Hawkesworth et al. 2013) (Fig. 1A).

Chaussidon and Albarède (1992) proposed a simple model (Fig. 2A) that relates the growth of the crust to seawater $\delta^{11}$B, which is the boron isotope composition expressed as per mil deviation from the standard NIST SRM 951 boric acid (Palmer 2017 this issue). The model assumes that the mass of the continental crust is the only reservoir that changes in size over time and that amount of boron recycled back into the mantle is negligible compared to the amount extracted. The $\delta^{11}$B of each reservoir varies with isotopic fractionation between two reservoirs, given as $\Delta^{11}B = \delta^{11}B_1 - \delta^{11}B_2$ in Figure 2A. Assuming values for $\Delta^{11}B$, boron concentration [B], and the mass (M) given in Figure 2A, Chaussidon and Alberède’s (1992) equations give $\delta^{11}B = -22.6‰$ for seawater at 4.3 Ga, which is a plausible age for the ocean (see above), and give $\delta^{11}B = -9.4‰$ for the continental crust today. Compare these values to the

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**Figure 1** Growth of continental crust versus boron mineral diversity. (A) Crustal growth, preserved juvenile crust and preserved continental crust plotted as a function of geologic time. Modified from Hawkesworth et al. (2013). (B) Cumulative increase in the number of boron minerals as a function of geologic time and the occurrence of five supercontinents (Kenorland incorporating Scavia and Superior), Nuna, Rodinia, Gondwana, Pangea) based on the oldest reported occurrences in the geological record of 274 boron minerals for which the requisite age data are available. Precursors to tourmaline-bearing metamorphic rocks in the Isua (Greenland) supracrustal belt are the oldest to contain sufficient boron for a boron mineral to form. Age data from Grew et al. (2016). Locations, oldest first, are as follows: Tanco (Manitoba, Canada) and Fort Hope (Ontario, Canada); Tayozhnoye (Russia); Långban (Sweden); Pitkäaranta (Karelia, Russia); Kalahari (South Africa); Angara (Siberia, Russia); Moncton (New Brunswick, Canada); Mont Saint-Hilaire (Quebec, Canada); Death Valley (California, USA), LCT = lithium, cesium, tantalum. (C) Histogram showing estimates of the number of boron minerals that had formed in a given 50 My interval, in relation to the five supercontinents, based on the reported earliest, intermediate, and latest occurrences in the geological record of 285 boron minerals for which the requisite age data are available. Modified from Grew et al. (2016) and Cawood and Hawkesworth (2013).
measured value of $-9.1\%$ by Marschall et al. (2017). By analyzing Isua tourmalines, Grew et al. (2015) estimated an Archean seawater composition of $\delta^{11}B = +14 \pm 15\%$ at 3.7–3.8 Ga, whereas the above model gives a seawater composition of $\delta^{11}B = -27\%$, which assumes that the mass of continental crust at 3.7–3.8 Ga was about 13% of the present-day mass. That the results are even this close could be fortuitous because the model is sensitive to the many assumptions made, particularly the constancy of seawater boron concentration with time and the starting isotope composition, i.e. $-7.1\%$ for depleted mantle and the bulk silicate Earth (Marschall et al. 2017). However oversimplified, the model does suggest a mechanism whereby increases in seawater $\delta^{11}B$ can be related to the growth of the continental crust, which appears to retain much of the boron extracted from the mantle. Because the mass of present-day continental crust is about 30 times that of the ocean, increases in seawater boron concentration would have an order-of-magnitude less impact on its $\delta^{11}B$ than growth of continental crust. This would justify the assumption of constancy of seawater boron content as a first-order approximation.

![Boron exchanges between reservoirs](image)

**Figure 2** Cycling of boron. (A) Schematic box model of boron exchanges between major reservoirs. Present-day size of the reservoir given in grams (M); boron concentration ([B]) in μg/g; isotopic compositions of $\delta^{11}B$ in per mil: these are present-day values for the reservoirs and have not been used to calculate the fractionation between reservoirs used in the modeling of $\Delta^{11}B$. Modified from CHaussidon and ALBAREDE (1992) with additional data from PALMER (2017 this issue) and MARschall et al. (2017). (B) Schematic cross section through a subduction zone showing boron concentrations. Larger arrows indicate transfer directions of boron, including newer values for boron concentrations of primitive mantle and fresh MORB. Modified from WUNDER et al. (2005) with additions from PALMER (2017 this issue), FURukAWA and KAKegAWA (2017 this issue), and BOSCHI et al. (2008).
The boron cycle can be recast into a geologic framework for the period following the onset of modern plate tectonics (Fig. 2B). Extrusion of MORB could be accompanied by the release of boron into seawater, MORB being subsequently altered by reaction with seawater to form altered oceanic crust; extruded mantle is serpentinized. Both the altered MORB and mantle rocks can contain over 100 µg/g B (e.g. Wunder et al. 2005; Boschi et al. 2008; Palmer 2017 this issue). Boron is then cycled through the subduction zone and arc volcanoes, followed much later by incorporation in illite or dissolved in rain water after weathering of crustal rocks and is eventually transported by rivers back to the ocean to end up in pelagic sediments or oceanic crust to enter another cycle. Whether boron is recycled in the subducted slab back into the mantle remains an open question (queried in Fig. 2); modelling suggests that only small amounts of boron remain in dry subducted rocks, but some could survive in phengite (e.g. Konrad-Schmolke and Halama 2014; Palmer 2017 this issue). Evidence that crustal boron could be recycled back into the mantle is from the occurrence of qingsongite (natural cubic BN) in crustal rocks subducted to ~400 km depth (Dobrzhinetskaya et al. 2014).

Mineralogical Diversity

With the growth of the continental crust, the possibility for boron to be concentrated to levels well above the upper crustal average of 17 µg/g B (Rudnick and Gao 2014) also increases. Such an increase would result in more opportunities for mineralogical diversity. Figure 1 quantitatively relates crustal growth to increasing diversity of boron minerals, which can be expressed in one of two ways. First, by showing the cumulative increase in the total number of boron mineral species inferred to have formed by a given time in Earth’s history, as based on the reported first occurrences in the geological record and for which the requisite age data are available. This applies to 274 boron minerals (Fig. 1B). Second, by showing boron minerals that existed at a given time in Earth’s history, specifically, the number of species inferred to have been present during a given 50 My interval for which the requisite age data are available. This applies to 285 minerals (Fig. 1C). Comparing the proportion of exposed continental crust at a given geologic period (Fig. 1A) with cumulative diversity (Fig. 1B) might suggest that species diversity is simply a matter of exposed area—low species diversity in older rocks is due to their limited exposure. However, for the period between 1,825 Ma and 550 Ma the increase in the number of species inferred to have been present during a given 50 My interval is modest compared to the marked increase in present-day exposure of continental crust. Instead, existing boron mineral diversity somewhat better matches the curve for increase in crust with recycling.

There is another factor involved in the diversity of boron minerals. Eighty-eight (or about 30%) of boron minerals are soluble in water or are broken down at relatively low temperatures (Grew et al. 2016, 2017). An example of this is sassolite (natural boric acid) (Fig. 3). The greatest diversity of ephemeral minerals is found in evaporite deposits (Helvacı et al. 2012), including those from marine settings (e.g. the Angara basin near Irkutsk, in Siberia, Russia, and the Moncton Basin of New Brunswick, Canada) and nonmarine settings (e.g. Death Valley in California, USA). Such ephemeral minerals are largely restricted to the Phanerozoic, during which they contribute significantly to the steep increase in both cumulative (Fig. 1B) and existing diversity (Fig. 1C). Their scarcity in the Precambrian could be more a matter of preservation, e.g. by armoring (Fig. 3A), than of areal exposure.

Nonetheless, if discussion were restricted to the refractory minerals, there would still be an increase in diversity of boron minerals, even during the Phanerozoic (Figs. 1B, 1C). This increase is punctuated by steps in cumulative diversity and both steps and spikes in existing diversity. The three oldest steps and spikes in cumulative and existing diversity correspond not only to the collisional phases of the supercontinent cycles of Kenorland, Nuna, and Rodinia (Cawood and Hawkesworth 2013), but also, albeit more approximately, to the humps in the curve for preservation of juvenile crust at ~2,500 Ma, ~1,700 Ma, and ~1,100 Ma (Fig. 1A). For example, pegmatites of the lithium–cesium–tantalum (LCT) family, such as the pegmatites in southeastern Manitoba (at Tanco) and neighboring Ontario (the Fort Hope pegmatite field) that contributed significantly to the step at 2,640–2,650 Ma (Kenorland), are typical for settings of crustal thickening associated with horizontal tectonic processes of subduction and continental collision (Cerný et al. 2012). Localities contributing to steps at 1,825–1,950 Ma (Nuna) and at 1,010 Ma (Rodinia) include localities with diverse suites of boron minerals: the
Two steep increases in diversity between 2,700 Ma and 1,850 Ma are followed by a near leveling off between 40 and 50 boron mineral species from 1,850 Ma to 550 Ma (Fig. 1C). This implies that many of the minerals first reported in the geologic record prior to 1,850 Ma have been forming ever since, in part because the geologic environments for these minerals, such as those of the LCT pegmatites, have formed throughout geologic time, and that, in part, these minerals can occur in more than one environment. In contrast, spikes at 1,825 Ma, 1,525 Ma, 1,025 Ma, 925 Ma, and 925 Ma can largely be attributed to localities of high diversity that feature boron minerals occurring at no more than 4–5 localities worldwide (in many cases, just one, e.g., Långban). During the Phanerozoic, diversity in refractory boron minerals again increases markedly. There are several major spikes due to the development of boron-rich skarns and peralkaline intrusions, including Mont Saint-Hilaire. These latter types of deposits show greater boron mineral diversity than their Precambrian analogues (Grew et al. 2016). With an estimated ~200 boron minerals remaining to be discovered in Earth's crust (Grew et al. 2017), further increases in the diversity shown in Figure 1B and 1C can be expected.

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Boron Behavior During the Evolution of the Early Solar System: The First 180 Million Years

Charles K. Shearer and Steven B. Simon

INTRODUCTION

The behavior of boron during the early evolution of the Solar System provides the foundation for how boron reservoirs become established in terrestrial planets. The abundance of boron in the Sun is depleted relative to adjacent light elements, a result of thermal nuclear reactions that destroy boron atoms. Extant boron was primarily generated by spallation reactions. In the initial materials condensing from the solar nebula, boron was predominantly incorporated into plagioclase. Boron abundances in the terrestrial planets exhibit variability, as illustrated by B/Be. During planetary formation and differentiation, boron is redistributed by fluids at low temperature and during crystallization of magma oceans at high temperature.

KEYWORDS: solar nebula, condensation, accretion, magma ocean, moderately volatile elements

NEBULAR PROCESSES DURING SOLAR SYSTEM FORMATION

Boron provides a unique perspective on Solar System processes. This is because of the unusual nuclear synthesis reactions involved in its production; its valence and size characteristics, which are distinctly different from those of many other moderately volatile elements (e.g. K, Na); its mobility during fluid/rock interactions; its significant partitioning into a vapor phase; and its isotope systematics, which are sensitive to a variety of processes and conditions (e.g. pH, temperature). The access to numerous planetary environments through meteorites and returned samples and the development of new analytical techniques (e.g. secondary ion mass spectrometry, laser ablation inductively coupled plasma mass spectrometry) have given us the ability to look at boron behavior backward in time and upward beyond Earth. Here, we examine the behavior of boron and its stable isotopes during the first 180 million years of our Solar System, from the formation of the first particles to the primordial differentiation of large and small rocky planetary bodies.

BEHAVIOR OF BORON DURING NEBULAR PROCESSES

Bulk Boron Content of the Solar System

Abundances of elements in the Solar System are obtained by spectral analysis of the photosphere of the Sun—the Sun contains >99% of the mass of the Solar System—and from the compositions of CI chondrites, which contain solar abundances of the condensable elements. Abundances are typically reported in wt% element or in atoms per 10^6 silicon atoms. Zhai and Shaw (2009) assumed that the boron content of carbonaceous chondrite matrices is representative of the Solar System abundance and reported the average for seven samples: 0.69 ± 0.09 ppm and 16.9 ± 2.2 atoms per 10^6 Si. More recently, Lodders et al. (2009) reported an average CI content of 0.775 ± 0.078 ppm and a bulk Solar System content of 18.8 atoms per 10^6 Si, in agreement with Zhai and Shaw (1994). The abundance of boron (and Be and Li) in the Solar System is substantially depleted relative to adjacent light elements (e.g. H, He, C, O) and is the result of thermal nuclear reactions that destroy boron isotopes during hydrogen burning. Boron was primarily generated by spallation reactions between high-energy particles in galactic cosmic rays and C, N, and O nuclei in the interstellar medium (Reeves et al. 1970), rather than thermal-nuclear reactions. Subtleties of boron formation processes and boron behavior in the solar nebula are revealed by the examination of primitive Solar System materials.

Behavior of Boron During Condensation

It is thought that the inner Solar System was once completely vaporized and that the solid materials we see today condensed from that vapor. At high temperatures, the dominant boron-bearing gas species in this vapor are BO, HBO, and HBO2 (Lauretta and Lodders 1997). Given the bulk composition of the Solar System and the thermodynamic properties of the elements, the equilibrium condensation sequence can be calculated, starting with the highly refractory platinum-group elements and continuing with the refractory lithophile elements, the major elements, the moderately volatile elements, and the volatile elements (Fig. 1). Different mineral phases become
stable with decreasing temperature, which affects the condensation temperatures of the elements in addition to their volatility. In a solar gas at a total pressure of $10^{-3}$ atm, the first major phase to condense is corundum ($\text{Al}_2\text{O}_3$) at 1,730 K. It starts to react with Ca in the gas to form hibonite ($\text{CaAl}_2\text{O}_4$) at 1,700 K, followed by grossite ($\text{CaAl}_4\text{O}_7$) at 1,660 K, clinoxyroxene [($\text{Ca}$($\text{Mg}$,$\text{Ti}$,$\text{Al}$)($\text{Si}$,$\text{Al}$)$_2\text{O}_6$)] (Grossman 2010).

Calculations by Lauretta and Lodders (1997) showed that boron should initially condense into feldspar as danburite ($\text{CaB}_2\text{Si}_2\text{O}_8$) and then as reedmergnerite ($\text{NaBSi}_3\text{O}_8$). In both components, boron is substituting for Al in tetrahedral coordination. Condensation temperatures of elements are typically reported as the temperature at which the element is halfway to complete condensation. The 50% condensation temperature for boron was estimated to be ~910 K by Zhai (1995), essentially identical to the value of 908 K given by Lodders et al. (2009). Chaussidon and Jambon (1994) proposed that the condensation temperature of boron could be ~700 K if it condensed mainly as borides and borates. For comparison, refractory Ca–Al-rich inclusions (CAIs), which are some of the oldest materials in the Solar System (Fig. 1), condensed at temperatures between 1,300 K and 1,700 K (Fig. 1). The ancient ages of CAIs are reflected in their preservation of extinct radionuclide systems ($^{10}\text{Be}$, $^{26}\text{Al}$, $^{53}\text{Mn}$, and $^{129}\text{I}$), even if they were reheated and became partially molten. Note that although the inclusion is not a primary gas–solid condensate, it consists of phases predicted to condense at high temperatures from a gas of solar composition.

**Behavior of Boron During Ca–Al-rich inclusion (CAI) Remelting**

As a moderately volatile element, boron is depleted in CAIs. Based on modal mineralogy and the average boron contents of the phases (assuming the boron content of spinel to be negligible) in Allende Type B1 inclusion 3529-41 (Fig. 2), Chaussidon et al. (2006) calculated a bulk boron content of 0.125 ppm (~0.18 times the content of CI chondrites). Chaussidon et al. (2006) noted that the volatility of boron is similar to that of sodium and suggested that, like sodium, boron could have been introduced to CAIs during low-temperature alteration in the nebula prior to remelting and then redistributed during fractional crystallization. Therefore, the bulk boron content of the CAIs represents an upper limit for primary boron concentrations.

Boron has two stable isotopes, $^{10}\text{B}$ and $^{11}\text{B}$, with $^{11}\text{B}/^{10}\text{B} \approx 4$. Throughout this paper, boron isotope ratios will be referred to in terms of their $\delta^{11}\text{B}$ values in ‰, such that,

$$\delta^{11}\text{B} = \left( \frac{^{11}\text{B} / ^{10}\text{B}}{^{11}\text{B}_{\text{standard}} / ^{10}\text{B}_{\text{standard}}} - 1 \right) \times 10^4.$$  

The standard commonly used is NIST SRM 951 boric acid. Refractory inclusions have negative $\delta^{11}\text{B}$ values (negative $\delta^{11}\text{B}$ reflects enrichment in the light isotope ($^{10}\text{B}$) relative to the standard), a feature that is not consistent with Rayleigh isotopic fractionation that would accompany evaporation from a melt. Instead, refractory inclusions exhibit $^{10}\text{B}$ excesses correlated with Be/B ratios. The daughter product of $^{10}\text{Be}$ decay is $^{10}\text{B}$ (half-life = 1.5 My), so these excesses in $^{10}\text{B}$ are interpreted as evidence that CAIs incorporated live $^{10}\text{Be}$ that decayed in situ to $^{10}\text{B}$ (McKeegan et al. 2000; MacPherson et al. 2003). The short-lived $^{10}\text{Be}$ radionuclide is produced by spallation reactions, not stellar nucleosynthesis. Also important are the $^{10}\text{Be}/^{9}\text{Be}$ ratios that are derived from analyses of CAIs. If these ratios were uniform, that would indicate that the $^{10}\text{Be}$ excesses were inherited from the dense interstellar cloud that became the solar nebula. They are not uniform, however, and are not correlated with $^{26}\text{Al}/^{27}\text{Al}$ ratios (MacPherson et al. 2003). This suggests that $^{10}\text{Be}$ formed by local irradiation processes within the nebula (Srinivasan and Chaussidon 2013).
Boron During Chondrule Formation

Chondrules are a major component of many chondritic meteorites, ranging in abundance from 0% to 80%. The majority of chondrules are submillimeter igneous spheres that mainly consist of ferromagnesian silicates and glass. An image of a glass-rich chondrule from the Murchison meteorite, with a texture that strongly indicates that it was once a molten droplet, is shown in Figure 1. The mineral assemblages in chondrules have been re-equilibrated to varying degrees within the solar nebula or on their parent bodies after accretion. Therefore, they provide another window to nebular and parent body behavior of boron. The behavior of boron and δ11B in these products of nebular processes has been explored using secondary ion mass spectrometry (Brearley and Layne 1998) (Fig. 1). The mineral assemblages in chondrules have been re-equilibrated to varying degrees within the solar nebula or on their parent bodies after accretion. Therefore, they provide another window to nebular and parent body behavior of boron. The behavior of boron and δ11B in these products of nebular processes has been explored using secondary ion mass spectrometry (Brearley and Layne 1998; Chaussidon and Robert 1998; Shearer 2002). Chondrules in unequilibrated assemblages in chondrules have been re-equilibrated to varying degrees within the solar nebula or on their parent bodies after accretion. Therefore, they provide another window to nebular and parent body behavior of boron. The behavior of boron and δ11B in these products of nebular processes has been explored using secondary ion mass spectrometry (Brearley and Layne 1998; Chaussidon and Robert 1998; Shearer 2002). Chondrules in unaquilibrated chondrites (e.g. the Semarkona meteorite) that experienced minimal degrees of parent-body alteration probably provide the best view of nebular processes and boron reservoirs. The B/Be ratio of moderately volatile/refractory element in the least metamorphosed chondrules are generally less than solar (Brearley and Layne 1996). The strong inverse correlation between beryllium and boron and the limited correlation between chondrule surface area and boron contents suggests that volatile loss during chondrule formation was not a major control (Brearley and Layne 1996). In this case, the sub-solar B/Be in the precursor material may reflect fractionation of boron from beryllium during condensation from the solar nebula at T > 900 °C (Lauretta and Lodders 1997). Melbom et al. (2001) observed that in a metal-rich chondrite, the B/Be in chondrules varied over two orders of magnitude and was negatively correlated with the Ca/Si ratio (Melbom et al. 2001). These observations indicate that the B/Be in chondrules represents both the precursor material of the chondrules and their temperature of formation.

The δ11B values of chondrules from several chondrites range from −50‰ to +44‰ (i.e. 11B/10B between 3.86 and 4.23) and are correlated with B/Si ratios (e.g. Chaussidon and Robert 1998). This heterogeneity of δ11B observed in individual chondrules has not been reported in bulk meteorite analyses (Zhai et al. 1996). Further, this heterogeneity contrasts with measurements by Hoppe et al. (2001) that exhibited a much more limited variation in δ11B. Liu and Chaussidon (2017) concluded that to resolve these contrasting results required further analytical effort.

Although the results of Zhai et al. (1996), Chaussidon and Robert (1998), and Hoppe et al. (2001) contrast with regard to the variability of δ11B, they are all consistent with a 11B/10B ratio for chondrules of ~4. However, this value is not consistent with boron being solely produced by galactic cosmic ray spallation, which yields a 11B/10B value of 2.5. Chaussidon and Robert (1998) and Liu and Chaussidon (2017) concluded that boron in the Solar System was a product of mixing of the boron produced by galactic cosmic ray spallation (δ11B = -400‰) and the boron produced by a low-energy spallation process that favors the production of 11B over 10B (δ11B = +110‰).

Boron During Parent-Body Metamorphism

Both chondrules and chondrites have experienced parent-body processes involving interaction with fluid phases and reheating (e.g. Brearley and Jones 1998). Brearley and Layne (1998) illustrated that chondrules modified by low-temperature alteration have B/Be ratios that are greater than solar. This fractionation above the solar ratio reflects the relative mobility of boron compared to beryllium. The mobility of boron on the parent body is further suggested by the enrichment of boron in carbonaceous chondrite matrix (0.69 ppm) relative to chondrules (0.23 ppm) and the positive correlation of boron with another fluid-mobile element, sulfur (Zhai and Shaw 1994). Krot et al. (1995) proposed that an iron–alkali–halogen vapor/fluid phase was responsible for asteroidal parent-body alteration and that this phase would have been responsible for the transport of boron. The characteristics of this fluid phase (e.g. pH, temperature) would systematically fractionate boron isotopes, but such fractionation associated with aqueous alteration of chondrites has yet to be examined in detail.

BEHAVIOR OF BORON DURING THE ACCRETION OF THE TERRESTRIAL PLANETS

According to the solar nebula theory, planetary development initiated with the condensation and formation of primitive aggregates of undifferentiated solar nebular material followed by accretion and differentiation of this primitive material (Fig. 1). As discussed above, the memory of this primitive material is preserved in undifferentiated meteorites, such as chondrites. Contemporary models advocate that the planets are the end products of a hierarchical accretionary process that first assembles a large number of kilometer-sized planetesimals from an initial protoplanetary disk of gas and dust (e.g. Elkins-Tanton 2012; Chambers 2014). Growth during this stage was controlled by surface, electromagnetic, and electrostatic forces. These small bodies then coalesced into proto-planets—planets whose evolution was controlled primarily
by gravitational interactions. The formation of Mars-size embryos occurred in as little as $10^5$ years. The final stages of planetary accretion, which may have persisted for $10^6$ years, are characterized by large, discrete impact events, such as the impact that formed the Moon, and subsequent events recorded on the lunar surface (e.g. Elkins-Tanton 2012).

The relationship between the estimated composition of the protoplanet and the primordial Solar System composition provides clues to planetary formation processes. Boron for bulk planetary bodies provides some insights into how the volatile reservoirs of the solar nebula were incorporated into the mantles of planetary bodies. As the terrestrial planets have undergone substantial differentiation and evolution since their assembly, determining the composition of their precursors and understanding the processes that were instrumental in their formation is an important, but formidable, task.

Estimates of the moderately volatile element and bulk boron content of many of the terrestrial planets have been calculated based on the following: analyses of samples (collected samples, returned samples, meteorites); geophysical and geochemical measurements by spacecraft (in situ and from orbit); and cosmochemical models for planetary assembly. Although boron abundances have not been determined directly by many spacecraft observations, the combined observations have been used to calculate indices of a planet’s volatile element characteristics [e.g. K(moderately volatile element)/Th(refractory element)]. Using this index, McCubbin et al. (2012) proposed that the moderately volatile elements were depleted in the order $K/Th_{Mercury} = K/Th_{Mars} > K/Th_{Venus} = K/Th_{Earth} > K/Th_{Vesta} = K/Th_{Moon}$. How does this sequence in K/Th ratios compare to estimates of B/Be ratios and boron for planets that have not been sampled? Can the K/Th relationship be extended to planets that have not been sampled, for which only remotely sensed data are available?

The terrestrial planets for which the bulk boron concentrations, B/Be, and $\delta^{11}B$ are best known are the Earth and the Moon. Based on mantle-derived magmas and crust compositions, the bulk silicate Earth has approximately 0.25 ppm B (Chaussidon and Jambon 1994) with a B/Be of approximately 4.5 (Shearer 2002 and references within; Chaussidon and Jambon 1994). The $\delta^{11}B$ of oceanic basalts range from −7.40‰ to +0.65‰ (Chaussidon and Jambon 1994; Zhai et al. 1996). In individual glass suites, $\delta^{11}B$ is correlated with boron concentration, water content, and δD and is interpreted as the result of assimilation and fractionation processes (Chaussidon and Jambon 1994). This would imply that the bulk silicate Earth has a $\delta^{11}B$ at the lower end of this range (~7.40‰). Marshall et al. (2017) estimated a value of ~7.1‰ for the bulk silicate Earth. Estimates for the boron content of the bulk silicate Moon vary dramatically from 0.013 ppm to 0.54 ppm. Perhaps a better estimate is that based on the differences between the most common lunar basalts (very low- to low-Ti mare basalts) and uncluttered terrestrial oceanic basalts. Whereas the terrestrial basalts (corrected for fractional crystallization and alteration) range from 0.5 ppm to 1.3 ppm, the low-Ti primordial lunar volcanic glasses have boron concentrations in the range of 0.11 ppm to 0.40 ppm (Shearer 2002). These volcanic glasses also have B/Be values that are approximately 2. These comparisons indicate that, along with a lower moderate volatile element content implied by the K/Th ratio, the Moon has a lower bulk boron content and lower B/Be than the Earth. The reported $\delta^{11}B$ of the Moon ranges from −4.13‰ to −4.87‰.

Boron, B/Be and $\delta^{11}B$ data for other differentiated planetary bodies (e.g. 4 Vesta, Mars) from which we have samples are far more limited. Data from Zhai et al. (1996) (lunar and meteorite samples) and Shearer (2002) (only meteorites) reveal that eucrites exhibit boron content variations from 0.11 ppm to 0.92 ppm, B/Be ratios between 0.87 ppm and 2.4 ppm, and have $\delta^{11}B$ values from ~6.90‰ to ~1.60‰. Although the database for martian basalts is limited, a comparison can still be made with regard to Earth. Examination of clinopyroxenes shows that the B/Be ratios in martian magmas are significantly higher than in pyroxenes from terrestrial ocean island basalts (Lentz et al. 2001).

Based upon boron abundances and B/Be for Earth, Moon, 4 Vesta, and Mars, it appears that the B/Be values correlate with the estimated K/Th. Extending this correlation to Venus and Mercury allows approximations of the relative bulk boron and B/Be of these planetary bodies. These comparisons suggest that B/Be$_{CI$ chondrite} $>$ B/Be$_{Mercury} = B/Be_{Mars} > B/Be_{Venus} = B/Be_{Earth} > B/Be_{Moon} > B/Be_{Vesta}$, and the order of the extent of boron depletion relative to CI chondrite is 4 Vesta > Moon > Earth = Venus > Mars = Mercury $>$ CI chondrite. These estimates of bulk planetary boron contents, B/Be ratios, and measurements of $\delta^{11}B$ provide valuable information concerning accretion of the rocky planets. All of the rocky planets are depleted in boron and have lower B/Be and B/Si relative to CI chondrites. The extent of the boron depletion factor is similar to those for elements with similar condensation temperatures, such as K, Rb, Cs, and Ge. Therefore, boron was a moderately volatile element during planetary accretion, and the degree of volatility observed reflects either the accreting material or the temperature of accretion. The degree of boron loss was not a function of heliocentric distance from the Sun. The $\delta^{11}B$ values for the Earth, Moon, and 4 Vesta are similar to each other and are distinctly different from the values predicted by the production of boron strictly from galactic cosmic rays.

**Behavior of Boron during Primordial Differentiation. A Lunar Perspective**

Primordial differentiation of planetary bodies perhaps started on small bodies as early as 2 My after CAI formation and may have extended to as late as 4.38 Ga for the Moon.
Since the return of samples from the Moon during NASA's Apollo Program, a fundamental concept for large-scale primordial differentiation has been developed and applied to many of the terrestrial planets, moons, and differentiated asteroids: the concept of 'magma oceans'. This planetary-scale process involved total or partial melting soon after accretion and occurred over a range of pressure–temperature regimes, enabling the formation of cores, mantles, and crusts (Elkins-Tanton 2012). Perhaps the best-recognized remnants of planetary magma oceans are those preserved on the Moon. The Moon is thought to have formed through accretion of materials generated by a collision between proto-Earth and a Mars-sized body (Theia), after which the Moon differentiated through internal melting followed by solidification of the lunar magma ocean (LMO) many hundreds of kilometers in depth (Warren and Taylor 2014 and references therein). In the LMO theory of lunar differentiation, the initial crystallization of the molten Moon resulted in a sequence of cumulates that included the following: (1) mafic cumulates, mainly containing olivine and pyroxene (with a crystallization sequence of olivine → orthopyroxene ± olivine → clinopyroxene + orthopyroxene ± olivine); (2) flotation cumulates that formed a plagioclase-rich, ferroan anorthositic crust; (3) ilmenite-rich cumulates; and finally (4) very late-stage lithologies characterized by high K, rare-earth element (REE), and P abundances, and therefore given the acronym “KREEP”. The interactions between these primary crystallization products of the LMO are believed to be responsible for the compositional diversity of lunar rocks (e.g. Warren and Taylor 2014). For example, lunar basalts are products of melting of the mafic cumulates that make up the Moon’s mantle. The compositions of these various LMO components provide insights into the behavior of boron during the primordial differentiation of the Moon. Lunar basalts are partial melts of these primordial LMO cumulates and, therefore, provide insights into the LMO process. Light lithophile element data for lunar volcanic glasses, lunar basalts, and crust have been documented by Shearer et al. (1994) and Zhai et al. (1996). A transmitted-light image of lunar high-Ti volcanic glasses is shown in Figure 4. Presumably, this glass represents a partial melt of a lunar mantle source with a significant ilmenite-rich LMO cumulate component.

Within the context of this simple LMO crystallization model, boron contents should increase from a bulk LMO composition of <0.25 ppm at the first mafic cumulate phase and rise to 25 ppm during the last KREEP stage of LMO crystallization (Warren and Taylor 2014). Boron (and Be) should be enriched to greater degrees than Li in the KREEP component of the LMO. This behavior is strictly the result of the contrasting behavior of boron (and Be) compared to Li in olivine. Boron is highly incompatible in basaltic melts, whereas Li is moderately incompatible (Shearer et al. 1994 and references therein). This resulted in the modification of Li/B signatures of the mantle cumulate sources. Based on the pyroclastic glass data from Shearer et al. (1994) and the assumption that the Li/B ratio does not fractionate during source melting, the early cumulate horizon of the LMO (olivine + pyroxene cumulates) had a higher Li/B (>25) than the late-stage products of LMO crystallization such as the ilmenite cumulates (Li/B = 5–20) and KREEP (Li/B = 1.6). Therefore, this ratio decreases with LMO crystallization and may reflect the preference of pyroxene for Li relative to B. The boron concentration and Li/B ratio are useful fingerprints for determining the cumulative horizon from which the basaltic magma originated and can be used to model the extent of LMO cumulate mixing.

Only a few boron isotopic compositions have been obtained for samples of lunar basalt and primordial crust (Zhai et al. 1996). The limited range of δ11B varies from −4.13‰ to −4.87‰ for all lithologies derived from mafic cumulates, flotation cumulates, and KREEP. These values overlap the range determined for terrestrial oceanic basalts (Chaussidon and Jambon 1994). The limited variation in δ11B in basalts derived from LMO cumulates contrasts with isotopic fractionations observed in other moderately volatile elements. For example, some KREEP basalts exhibit 37Cl enrichments of up to +50‰, which has been attributed to degassing of 37Cl during the last stages of LMO crystallization (Boyle et al. 2015).

**INTERPRETING THE FIRST 180 MILLION YEARS**

The story of boron during the first 180 million years of Solar System history can still be read through the subsequent evolutionary conditions experienced by a planet—planet size, oxygen fugacity, availability and state of H-species, stagnant-lid versus plate-tectonic thermal regimes, stability and composition of atmosphere. These evolutionary conditions influenced the nature of the boron reservoirs (from mineral- to planetary scales) and the planetary boron cycle itself. The initial processes of nebular, accretionary, and primordial differentiation shaped the starting points for boron contents and δ11B in the terrestrial planets (Fig. 1).
Spallation by galactic cosmic rays is an important boron-producing process, but on its own will not yield appropriate $^{10}$B/$^{11}$B for the Solar System. Low-energy spallation is a possible mechanism for producing more $^{11}$B-rich components. These processes still need to be further quantified with respect to the production of $^{11}$B. In addition, refractory inclusions show evidence of in situ decay of $^{11}$B. There is some variation of the initial $^{10}$Be/$^{9}$Be ratio in CAIs. The boron concentration and $^{10}$B/Be in chondrites and chondrules may suggest a high degree of heterogeneity of boron isotopes in the chondrite-forming portion of the Solar System. The mobility of boron in parent-body fluids at relatively low temperatures may have led to a heterogeneous distribution of boron and fractionation of boron isotopes. Still, there remain questions concerning the condensation temperature of boron and the real variability of $^{11}$B. The $^{10}$B/Be remains a potential future tool for better understanding the conditions of chondrite parent-body aqueous alteration. Boron isotope systematics are sensitive to pH and temperature changes and can fractionate during phase separation. During primordial differentiation in a magma ocean, boron will generally behave incompatibly and increase in concentration during crystallization. It provides an index for magma ocean cumulate horizons and potential cumulative mixing. Late-stage magma ocean volatile loss has been called upon to explain fractionation of isotopes of other moderately volatile elements on the Moon (e.g. $^{3}$He). However, boron shows limited degrees of isotopic fractionation during this magma ocean process.

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Boron Cycling in Subduction Zones

Martin R. Palmer

INTRODUCTION

At subduction zones, oceanic crust and some of its sedimentary overburden descend into the mantle (Fig. 1). Water is carried down with the slab in sediment pore water and in hydrous minerals in the sediments and crust. As pressures and temperatures increase in the descending slab, the pore water rapidly returns to the oceans, while some mineral-associated water will be carried deeper. Eventually, the pressure and temperature will increase sufficiently to cause the hydrous mineral phases to release almost all of their remaining water, thus hydrating the overlying mantle wedge and forming serpentinites. These serpentinites may then rise as diapirs in the forearc or be dragged deeper into the subduction zone. At greater depths and temperatures, further release of hydrous fluids initiates partial melting in the overlying mantle wedge. This magma rises through the subarc mantle to form volcanoes and plutonic rocks. After it has lost almost all its water and other volatile components, the slab is subducted deep into the Earth’s mantle. It may then mingle with the deep mantle and be incorporated into the melts that form intraplate ocean island basalts (OIBs).

There are several attributes of boron that make it a sensitive tracer of these processes, especially in tracing the role of fluids. Compared to the mantle, boron is enriched in continental crust by several orders of magnitude. This enrichment is inherited by the terrestrial sediments that lie on the subducted crust. Boron is also very soluble, so it is one of the few elements to have a higher concentration in seawater (4.5 ppm) than in the mantle (<0.1 ppm). Thus, the pore waters that make up ~50% of the volume of the sediments on the subducted crust carry a substantial boron inventory, with some of this boron adsorbed on clay minerals. Prior to subduction, most oceanic crust has experienced millions of years of interaction with seawater circulating through the upper crust. During high temperature water–rock interaction at mid-ocean ridge crests, boron is leached from the rock. As the crust moves away from the ridge crest, the temperature of the circulating seawater drops and the behavior of boron reverses, with seawater boron taken up into secondary hydrous minerals. The extent of this reaction is such that the concentration of boron rises from values of <1 ppm in fresh oceanic crust to up to 100 ppm in the altered ocean crust that enters the subduction zone.

Boron possesses another property that enhances its utility in this setting – the ratio of its stable isotopes, $^{10}\text{B}$ and $^{11}\text{B}$, which is expressed as:

$$\delta^{11}\text{B} = \left( \frac{^{11}\text{B}/^{10}\text{B}}{^{11}\text{B}_{\text{standard}}/^{10}\text{B}_{\text{standard}}} \right) - 1 \times 10^3$$

where the standard is the NIST SRM 951 boric acid that is used in most studies (e.g. Palmer and Swihart 1996). The $\delta^{11}\text{B}$ values vary greatly between the various components of the subduction zone (Fig. 1). For example, the $\delta^{11}\text{B}$ of seawater is +40‰, as compared to −7‰ in the mantle that is the source of mid-ocean ridge basalt (MORB) (Marschall et al. 2017). These large differences allow the $\delta^{11}\text{B}$ of solid and fluid phases to be used to further constrain boron sources and pathways in subduction zones.

The objective here is to review our understanding of boron cycling in subduction zones, including the nature of boron-hosting phases in the subducted slab and whether their stability under the changing pressure–temperature–chemical conditions may allow crustal boron to be recycled into the mantle. The process is of particular interest because the high boron concentrations and distinct $\delta^{11}\text{B}$ in slab phases relative to the mantle make boron a potentially sensitive tracer of crustal recycling into the deep mantle.

Keywords: subduction zones, water, serpentinite, phengite, crustal recycling
Figure 1  (A) Schematic of an oceanic-crust subduction zone, with insets of specific areas that are shown in panels B and C. Arrows show directions of motion. Pressure and equivalent depths indicated. Boron isotope data (see legend) indicated in per mil (‰). (B) Detail of forearc setting, as boxed in 1A. Yellow = forearc basin mélangé; grey = serpentinite; green = accretionary prism and sediments; orange = altered oceanic crust. (C) Detail of magma (red) production zone of the subducting plate as boxed in 1A (after Stern 2002). Boron isotope data are from Palmer and Swihart (1996) and Marschall et al. (2017).
THE BORON INVENTORY OF THE SUBDUCTING SLAB

The major boron reservoir in marine sediments is clay minerals, within which boron is partitioned between a lattice-bound fraction and an adsorbed fraction derived from seawater. The boron concentration in the two fractions varies, but is typically 80–150 ppm in the lattice-bound fraction and 10–30 ppm in the adsorbed fraction. The δ11B value of the lattice-bound fraction largely reflects that of the crustal protolith (~5‰ to +5‰), whereas fractionation of seawater boron isotopes during adsorption onto clays yields typical δ11B values of +14‰ to +16‰ (Spivak et al. 1987; Ishikawa and Nakamura 1993; Palmer and Swihart 1996).

The boron concentration of fresh MORB is <1 ppm and has a δ11B value of ~7‰, but when circulating seawater interacts with ocean crust at ~100°C, then the boron is taken up into secondary minerals. Again, there is large variability in the boron content and δ11B of altered oceanic crust, but compilations of ocean cores and ophiolite sections give average boron contents of ~5 ppm and δ11B values of +3‰ for the upper oceanic crust (Smith et al. 1995). The lower, gabbroic part of the oceanic crust is less altered (Vils et al. 2009), but the upper mantle may be altered to serpentine by circulating seawater, particularly at slow-spread mid-ocean ridges. This geological setting leads to typical boron concentrations of 20–90 ppm and δ11B values of between +10‰ and +15‰ (Boschi et al. 2008).

SUBDUCTION ZONE PROCESSES

The Forearc Zone

The initial stages of subduction commonly involve the formation of an accretionary wedge of sediment and portions of oceanic crust being scraped off the subducting plate (Fig. 1B). At shallow depths, fluids are expelled along fractures and faults in the wedge (Martin et al. 1996). Boron concentrations in these fluids can reach >10 times seawater levels, with δ11B values similar to the adsorbed fraction of boron in clays (You et al. 1995).

Not all fluids in the forearc return boron directly to the oceans. Consider serpentinite: it is formed during the hydration of the overlying mantle wedge by water driven off the subducting slab. Because serpentinite is buoyant, it may ascend into the accretionary prism and the forearc mélangé to form boron-rich serpentinite seamounts and muds (Benton et al. 2001; Savov et al. 2007). However, some serpentinite generated in the forearc is dragged deeper into the mantle (Straub and Layne 2002). The δ11B of serpentinite minerals and the fluids from which they were derived are similar to the exchangeable component of sediments, but other chemical and isotopic signatures indicate that this adsorbed fraction cannot be the major boron source. Rather, much of the boron within serpentinites that have formed in the subduction zone (as distinct from serpentinites formed prior to slab subduction) is derived from boron that was structurally bound in sediments and in altered oceanic crust. This structurally bound boron is then extracted by the breakdown of hydrous minerals during increasing pressures and temperatures (Benton et al. 2001; Pabst et al. 2012). The δ11B of fluids released from the altered ocean crust shows a progressive change during subduction (Peacock and Hervig 1999) – a decrease from +25‰ at ~100°C to +5‰ at 500°C, with the δ11B of the slab restite showing a corresponding decrease from ~3‰ to ~10‰ (Pabst et al. 2012).

The Arc Magma Production Zone

Arc volcanic rocks contain elevated boron levels and distinct δ11B values relative to the mantle. These values reflect boron input from the subducted slab (Fig. 1C). For example, in the Izu arc (Western Pacific Ocean), the amount and isotopic composition of slab-derived boron varies according to the distance of the volcanic centre from the subduction front and the depth to the slab (Ishikawa and Nakamura 1994).

Thus, volcanoes closest to the slab have higher δ11B values and B/Nb ratios (+7‰ and ~40, respectively) than those that sit further back from the forearc and where the depth to the slab is greater (+18‰ and ~2, respectively).

Similar patterns are observed in other arcs, with a common feature that the δ11B of arc rocks extend to values (up to +18‰) that are too high to be derived from quantitative extraction of boron from sediments and/or altered oceanic crust. Instead, the likely source of boron with elevated δ11B is from serpentinite dehydration. There are two possible sources of serpentinite-derived boron. First, serpentinite that formed in the subduction zone and is then dragged down on top of the subducting slab; second, serpentinite that formed prior to subduction and that is located deeper in the subducting lithosphere (Fig. 1B). Three-dimensional modelling suggests that even in NE Japan, where 130 Ma oceanic crust is being subducted, the temperature at the top of the slab beneath the volcanic front is likely ~800°C (Morishige and van Keken 2014). Because antigorite undergoes virtually complete dehydration and release of boron in water-rich melts and/or silica-rich aqueous fluids at ~700°C (Harvey et al. 2014), it is, therefore, likely that any serpentinite-derived boron within arc rocks is derived from the base of the subducted lithosphere (Fig. 1C) where temperatures may be as low as 475°C beneath the volcanic front (Stern 2002). Importantly, boron released from the slab into the melt generation zone is quantitatively transferred to the arc rocks because boron is highly incompatible during mantle melting.

The elevated δ11B in arc rocks suggests that dehydration fluids are a major boron source, but other isotopes and trace elements (e.g. 10Be and Th) indicate that melting sediments supply an increasing portion of incompatible elements as the slab is subducted deeper. Indeed, the lowest δ11B values in the Izu arc (+1‰) lie furthest from the forearc and are more similar to sediments. They also have B/Nb ratios (~2.5) that are closer to sediments (~1) than aqueous fluids (>100) and the mantle (0.1) (Ishikawa and Nakamura 1994). The extent to which the sediment signal comes from melting versus extraction of fluid mobile elements by deeply sourced water is subject to debate (Stern 2002). Although enrichment of fluid-immobile species, such as 10Be and Th, in arc rocks requires sediment melting, most thermal models predict that subducted sediments are not heated sufficiently to melt phengite, the likely main boron host in the deeply subducted slab (Domanik and Holloway 1996).

Recycling into the Deep Mantle

The majority of boron entering the subduction zone is ultimately derived from seawater (either as sediment pore water or incorporated into hydrous minerals) and from continental crust (as clastic sediments). Much of this boron is recycled into seawater during dewatering of the slab during early subduction, or is recycled into arc crust in the form of arc volcanic and plutonic rocks (Moran et al. 1992). For any crustal and/or seawater boron to be recycled into the deep mantle it must be hosted in phases that are stable at greater pressures and temperatures than those within the arc magma generation zone. This either requires boron to be incorporated into minerals that are
stable under upper mantle conditions and/or that minerals in crustally derived subducted sediments are not broken down during descent into the mantle.

While most of the boron in subducted altered oceanic crust and the overlying sediments is lost to fluid phases during dehydration and passes into the sub-arc mantle before the slab descends into the deep mantle, there are boron-bearing minerals that may survive beyond the volcanic front and that may be subducted into the deep mantle. Of the secondary boron-bearing minerals formed in the subducted slab, the most stable is phengite, which can persist up to temperatures of >1,000°C and pressures up to 100 kbar (Domanik and Holloway 1996). Continued preferential extraction of high 11B fluids leads to phengite having 11B values as light as −18‰, but, importantly, it may still retain up to 50 ppm boron (Pabst et al. 2012; Halama et al. 2014). Thus, there is the potential for boron that has ultimately been derived from the continental crust and seawater (but with a much lighter 11B value) to be recycled into the deep mantle.

**SUBDUCTION ZONE BORON BUDGETS**

**Impact on Seawater Boron Isotopes**

Attempts to incorporate subduction zone processes into global seawater boron isotope budgets have relied on data from only a few sites, but the simplest interpretation of these data is that most of the boron expelled back into seawater at subduction zones has a 11B of +13‰, compared to +40‰ in seawater. A plausible mass-balance can be achieved between the amount and isotopic composition of boron entering the subduction zone in pore waters and adsorbed to sediments, and that which is expelled back into seawater in forearc fluids (You et al. 1995).

The amount of boron expelled back into seawater at convergent margins depends on the amount of sediment entering the subduction zone. Higher subduction rates may result in increased return of labile boron to the oceans and lower seawater 11B values, although the long residence time of boron in the oceans (~10–20 My) mitigates against large and rapid changes in seawater 11B values.

Reconstruction of seawater 11B values over the past 50 My (Raitzsch and Honisch 2013) suggests that there has been an ~3‰ increase in seawater 11B since the Late Eocene, superimposed on shorter-term oscillations of up to 2‰ (Fig. 2A). It is interesting to note, therefore, that over this period there appears to be a first-order correlation between time-averaged subduction rates (Fig. 2B) (Chen et al. 2015) and the reconstructed seawater 11B, with peaks in the latter coinciding approximately with lower subduction rates. This apparent coincidence is not proof of a causal link between subduction rates and seawater 11B, but the existence of subduction-rate reconstructions extending back ~180 My (Engebretson et al. 1992) provides a testable hypothesis if reconstructions of seawater 11B values can be reliably extended further back in time.

**Recycling into the Mantle**

There is a strong correlation between the budgets of fluid mobile elements, such as boron, entering subduction zones and the content of these elements in arc rocks (Plank and Langmuir 1993). However, mass-balance uncertainties are too large to constrain mismatches in inputs and outputs in subduction zones. Nevertheless, the question as to whether boron is recycled into the deep mantle may be addressed by searching for 11B signatures of subduction in ocean island basalts that are unequivocally derived from the deep mantle and that have other isotope signatures (e.g. in Sr, Nd or Pb) that suggest a contribution from recycled subducted slabs (White 2015).

The first requirement is, however, knowledge of the 11B value of the primitive mantle (i.e. the composition of the mantle before extraction of any crust). This has been a difficult problem to solve because the boron concentrations of mantle-derived rocks are low and easily perturbed by post-eruptive alteration of primary signatures by
circulating fluids and high-level assimilation of crustal material, including previously altered mantle-derived rocks. Recently, Marshall et al. (2017) undertook an ion-probe study of the boron isotope systematics of MORB and, together with consideration of other indices of alteration and assimilation, were able to determine that the δ11B value of the mantle from which MORB is derived (depleted MORB mantle) is ~7‰ ± 1‰, with a boron concentration of <0.1 ppm. Comparison with other stable isotope systems (White 2015) suggests this also likely represents the δ11B of primitive mantle. Because MORB probably derives from mantle previously depleted in elements enriched in the crust (White 2015) and because boron is highly incompatible, the boron concentration of the primitive mantle is probably higher than that of depleted MORB mantle.

Relatively few ocean island basalt (OIB) suites have been analysed for boron isotopes and much of the wide spread in δ11B values for individual sample suites has been ascribed to contamination of the magma source by high-level assimilation of altered rocks, rather than by variations in the mantle source. Thus, light δ11B values (as low as ~14‰) in some Icelandic melt inclusions have been attributed to the interaction of lavas with geothermal fluids (Brounce et al. 2012). In contrast, high-level crustal assimilation of altered oceanic crust is thought to be responsible for the high δ11B values (up to +12‰) in western Azores (Portugal) ocean island basalts. The lower values (~7.4‰ to ~3.3‰) observed in the eastern Azores are considered to more closely reflect mantle source compositions (Genske et al. 2014).

A compilation of ocean island basalt data (excluding those most obviously affected by high-level alteration/assimilation) is presented in Figure 3. Also shown are mixing trajectories between two potential subduction components: phengite and clastic sediments. Note that fractional crystallization may yield higher B concentrations, with no change in δ11B values. Many of the low δ11B OIB data could be construed to lie on a trend from mantle δ11B values to the phengite δ11B field (Fig. 3). In contrast, data from Hawaii (USA) (Tanaka and Nakamura 2005), the eastern Azores (Genske et al. 2014) and intraplate volcanic rocks from NE China (Li et al. 2016) trend to higher δ11B values than the primitive mantle. This may reflect mixing of a primitive mantle source with deeply subducted and recycled sediments, as previously suggested for the Hawaiian data (Tanaka and Nakamura 2005). Interestingly, potential mixing lines with recycled sediments (Fig. 3) form a better fit to the data if the sediment endmember has δ11B values that fall to the lower end of the range observed in clastic sediments. This would support the suggestion above that any subducted and recycled boron is likely to have a lighter δ11B value than material entering the subduction system. Further studies are required to determine whether the OIB data truly reflect mantle heterogeneities, but separating the potential role of high-level assimilation/alteration processes from variations in the original mantle source will be difficult.

**CLOSING REMARKS**

This review illustrates that boron more than lives up to its description of being “light and lively” in the upper portions of subduction zones. When it comes to deeper sections of the subducted slab, however, there are indications that there may be a more furtive side to its character, with some boron resolutely clinging on to refractory phases and returning to the deep mantle. This may be where boron behaviour in subduction zones has most promise of contributing to wider advances in Earth science. But there are several questions that must be resolved before this potential can be realised. While much information has been obtained from rocks metamorphosed under subduction zone conditions, overprinting by later fluids and the mobility of boron during retrograde metamorphism does complicate interpretations. Experimental studies of boron partition coefficients and of isotope fractionation between fluids and minerals and the amounts of these minerals formed under subduction zone conditions would help resolve these uncertainties. At present, there is little boron data available for ocean island basalts, particularly compared to other isotope systems. But advances in boron isotope geochemistry will likely require a combination of micro-analytical techniques and a better evaluation of potential contamination of mantle signatures by high-level crustal assimilation and alteration.

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**Figure 3** A compilation of ocean island basalt (excluding those most obviously affected by high-level alteration/assimilation) δ11B versus boron concentration data for mantle-derived rocks. Mixing lines show trends towards upper and lower δ11B values measured in clastic sediments (~5‰ and ~5‰) and phengite (~10‰ and ~18‰) using B concentrations of 100 ppm and 50 ppm, respectively. Tick marks are every 0.1‰ of sediments/phengite to a maximum of 5‰. FC = fractional crystallization trend; sed = sediment; pheng = phengite. Data sources: Hawaii (USA) (Tanaka and Nakamura 2005), Iceland (Brounce et al. 2012), East Azores islands (Portugal) (Genske et al. 2014), NE China (Li et al. 2016), mantle value and all other data – including Afar (Ethiopia), Galapagos (Ecuador), Loihi (Hawaii, USA), McDonald (McDonald Islands, Australia), Saint Helena (British Overseas Territory) – from Marshall et al. (2017). Phengite data from Pabst et al. (2012), Halama et al. (2014). Sediment data from Palmer and Swihart (1996).
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ELEMENTS ISSUES ON SUBDUCTION ZONES


Boron Isotopes: A “Paleo-pH Meter” for Tracking Ancient Atmospheric CO₂

E. Troy Rasbury¹ and N. Gary Hemming²

INTRODUCTION

The boron isotope composition of calcium carbonate shells of marine organisms has the unique potential to record surface ocean pH, allowing the calculation of atmospheric pCO₂ due to the established relationship between pH and the partial pressure of (atmospheric) CO₂ (pCO₂). This “paleo-pH meter” allows scientists to produce a record of the natural fluctuations of atmospheric pCO₂ over geologic time, which will help us better understand the impacts of the recent anthropogenic addition of CO₂ to Earth’s atmosphere. Towards this end, a tremendous effort to understand the systematics of boron uptake in marine carbonates is underway. Here, we review the potential of boron isotopes to constrain ocean pH and, thus, atmospheric pCO₂.

KEYWORDS: pH proxy, boron isotopes, pCO₂, foraminifera, brachiopods, paleoclimate

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Keywords: pH proxy, boron isotopes, pCO₂, foraminifera, brachiopods, paleoclimate

INTRODUCTION

The isotope ratio of light elements, such as oxygen and carbon, have proved extremely valuable for studies related to biological and geochemical processes due to the large mass difference between the isotopes of those elements. These light isotope systems are widely used in paleoclimate research, because climate processes result in a large range in isotope compositions of geologic and biologic materials. The past few decades have seen an impressive increase in the application of other stable light isotopes, each with its own potential for illuminating specific processes. Early studies of boron isotopes in marine carbonates had the goal of exploiting the large percent mass difference between ¹¹B and ¹⁰B, the two stable isotopes of boron, similar to the way carbon and oxygen isotopes have been applied. However, in contrast to those other stable isotope systems, the mass-dependent boron isotope fractionation between seawater and calcium carbonate shells is not the dominant controlling factor. Instead, the major control on boron isotope fractionation is related to the effect of pH on the aqueous speciation of boron and to an observed large offset in the isotopic composition between the two primary aqueous species. Incorporation of only one of these species into marine carbonates leads to a pH control on the isotopic composition of the carbonate minerals, and thus, the ability to estimate ocean pH in the past using well-preserved fossil shells. With an estimate of past surface ocean pH, and knowledge of one additional aquatic carbonate system variable (e.g. alkalinity, total dissolved inorganic carbon), then atmospheric pCO₂ can be calculated due to the strong coupling of the surface ocean and atmosphere. Due to this unique potential of the boron proxy for estimating pCO₂, a tremendous effort has focused on a more fundamental understanding of boron speciation and isotope fractionation and on boron incorporation into carbonate minerals in order to improve the application of this geochemical tool. Equally important are the analytical developments, including international comparisons between laboratories (Foster et al. 2013) as well as single laboratory comparisons between the two most used measurement methods, those of negative thermal ionization mass spectrometry (NTIMS) and of multi-collector inductively coupled plasma mass spectrometry (MC–ICP–MS) (Farmer et al. 2016). Progress in these areas is bringing us closer to the routine and widespread application of boron isotopes in geochemical studies. Here, we review the basis for the boron pH proxy and a sample of recent papers that illustrate the unique potential of boron as a pH proxy for seawater, and thus, for atmospheric pCO₂.

THE BORON pH PROXY

The aqueous speciation of boron is controlled by pH, with boron in trigonal (3-fold) coordination in boric acid [B(OH)₃] dominating at low pH and boron in tetrahedral (4-fold) coordination in borate [B(OH)₄⁻] dominating at high pH (Fig. 1). Boric acid has a preference for the heavier isotope, ¹¹B, whereas borate has a preference for the lighter isotope, ¹⁰B. This preference, or fractionation factor, predicts an isotope ratio of each boron species, which in turn reflects the proportions of boron species in an aqueous fluid having 3-fold and 4-fold coordination (Fig. 1). Incorporation of only borate in carbonate shells is the fundamental mechanism that allows the boron isotopic composition of marine carbonate fossils to record the pH of ancient oceans.

Boron Incorporation into Carbonates

The large offset between the boron isotope composition of seawater and marine carbonates was first observed in studies of modern biogenic and abiogenic minerals. The
The fraction of the two dominant aqueous boron species, B(OH)\(^+\) and B(OH)\(_3\)\(^-\), with pH shown in blue. The isotope composition of borate derives from a seawater value of \(\delta^{11}B = 39.6\%o\) (Foster et al. 2010) using the empirically derived fractionation factor of Klochko et al. (2006). \(\delta^{11}B = \frac{([^{11}B/^{10}B]_{\text{sample}}/[^{11}B/^{10}B]_{\text{standard}} - 1) \times 10^3}{\text{where the reference standard is NIST SRM 951 boric acid.}}\) Modified with permission of Elsevier from Hemming and Hanson (1992).

Laboratory investigations of boron isotopes have used inorganic carbonates synthesized under controlled pH conditions to evaluate boron incorporation (Xiao et al. 2006; Mavromatis et al. 2015; Noireaux et al. 2015; Uchikawa et al. 2015; Kaczmarek et al. 2016). Without exception, these studies show a strong dependence of the boron isotope composition on pH and a significant offset from the parent fluid. Hemming and Hanson (1992) theorized that the charged borate ion is attracted to the growing mineral surface, but is ultimately incorporated in 3-fold coordination. Based on nuclear magnetic resonance (NMR) data, calcite has both 3-fold and 4-fold coordinated boron, which has been interpreted either to represent an incomplete change in the borate ion at the mineral surface before incorporation (Sen et al. 1994) or that significant boric acid is assimilated (Klochko et al. 2009; Rollion-Bard et al. 2011; Cusack et al. 2015; Noireaux et al. 2015). However, even small amounts of boric acid would have a measurable impact on the \(\delta^{11}B\) of the resulting calcite, and this fact, combined with the expectation of greater accidental incorporation in rapidly deposited calcite, is at odds with the usual observed trend of greater deviation from the borate value with lower pH (Foster and Rae 2016). Using synchrotron X-ray nanoscale techniques on a single foraminiferal shell, Branson et al. (2015) showed no measurable 4-coordinated boron in foraminiferal calcite. Therefore, the only reasonable explanation to account for the observed isotope offset from the parent fluid requires a crystallographic control on modification of that species so that it can fit in the crystal lattice.

Culture experiments of foraminifera to test the boron proxy have yielded empirical data of boron isotopes in carbonates formed over a range of pH values. This has been summarized in detail in a recent review of the potential use of boron isotopes in foraminifera as a paleo-pH proxy (Foster and Rae 2016). Biogenic calcite does not give the isotope value of borate for the pH of the seawater in which it formed, yet it does have a systematic and predictable offset from the borate value. Determining this offset requires empirical calibrations to estimate pH. The reasons for this may be related to the control the organism has on the secretion of its shell (although this is seen in inorganic experiments as well), and it appears to be more pronounced for lower pH solutions. Perhaps organisms exert more of a control to raise pH when they are in lower pH environments, thus influencing this offset from the actual fractionation factor value. Another potential factor is that organisms often build their shells from amorphous calcium carbonate that subsequently crystallizes to calcite or aragonite. Could secondary processes related to the conversion to the crystalline phase partly control boron behavior? For example, it is easier to see how borate, without change in coordination, might be incorporated in amorphous calcium carbonate, and then remain in the structure even after conversion to the carbonate mineral. Henehan et al. (2016) have compiled new and published empirical data from planktic foraminifera using a graph of expected borate isotopic composition based on oceanographic conditions and the fractionation factor of Klochko et al. (2006) versus the boron isotope compositions of the foraminifera (Fig. 2). This clever plot assumes that all of the incorporated boron is borate. However, if small amounts of boric acid were systematically incorporated then this could be accounted for with the empirical equations. This compilation shows that some species plot offset from expected predictions, consistent with the site of incorporation having a higher-than-seawater pH, few plot on the one to one line,
and some plots at lower δ11B than predicted from measured oceanographic conditions. Possible reasons for these differences are discussed in Foster and Rae (2016).

Foraminifera culture experiments that monitored for changes in dissolved inorganic carbon show that the carbon speciation also changes depending on the changing conditions (such as pH) of the experiments (Allen et al. 2011). In a study that controlled for pH in some experiments and [CO₂] in others, and in each case holding the other parameter constant, Howes et al. (2017) demonstrated that whereas δ11B incorporated in carbonates is controlled by pH, [B] is controlled by [CO₃²⁻]. This makes sense in that the isotope composition is controlled by borate incorporation (regardless of quantity), whereas the borate ion competes for the crystallographic site that is occupied by CO₃²⁻. It is clear that there are some rich avenues for research to further our understanding of the boron pH proxy, and that boron isotopes also have the potential to be used to better understand the controlling factors in biomineralization.

Importantly, without exception, every published empirical study shows a large offset in the boron isotopic signature between the carbonate mineral and the solution from which it grew, and this offset varies systematically with the pH of the solution. Secondary factors exist, requiring the need for calibrations of each biological carbonate used in paleo-pH studies, but these do not invalidate the proxy.

**Application to Testing pH Change in the Marine Carbonate Record**

The high-resolution studies of glacial to interglacial changes in CO₂ determined from bubbles trapped in Greenland and Antarctic ice cores provide an excellent test of the potential for boron isotopes to accurately record atmospheric pCO₂. Several studies that examined the δ11B of planktic forams from ocean cores are remarkably consistent with the ice-core records of CO₂ (Fig. 3), giving confidence that boron isotopes can be used in deeper geologic time where ice-core records are not available.

**Figure 2** Expected boron isotope compositions of marine borate (as derived from planktic foraminifera) based on oceanographic conditions and the Klochko et al. (2006) fractionation factor versus the boron isotopic composition that was measured in marine organisms of cultured and wild foraminifera species (core-tops from the ocean floor); N. pachyderma, O. universa, G. inflata, G. siphonifera, P. obliquiloculata; tows (from the water column); G. siphonifera, O. universa; MOCNESS samples; O. universa, G. inflata; sediment trap; O. universa). Note that few analyses plot on the black one-to-one line. However, each planktic species has predictable behavior, making calibration curves (dark coloured lines) possible. Modified with permission of Elsevier from Hennehan et al. (2016).

**Figure 3** Summary of available δ11B-derived CO₂ data for the past 800 ky. (A) Time series of atmospheric CO₂ from Antarctic ice cores (red line) and from boron isotopes from Ocean Drilling Program (ODP) Site 668 (Mid-Atlantic off west Africa) (light blue squares) and ODP Site 999 (south Caribbean Sea) (aqua circles). Error bars are at 95% confidence. (B) Cross-plot of pCO₂ derived from boron isotopes with contemporaneous atmospheric CO₂ from ice-core records. Boron-derived pCO₂ is from three sites; ODP Site 999 and ODP Site 668 (as in 3A) and from GeoB1523 (a sediment core from the western tropical Atlantic). These plots show good agreement between the boron isotope studies on foraminifera, which are used to calculate pCO₂ based on the pH relationship, and the concentration of CO₂ trapped in air bubbles in ice from polar regions. Reproduced with permission of Annual Reviews from Foster and Rae (2016).
TAKING THE BORON pH PROXY BACK IN TIME

To apply the boron pH proxy through geologic time requires three things. First, that the isotope composition of seawater be estimated. Second, that there be a calibration of the carbonate being measured. Third, that the carbonate has not been altered by diagenesis. All of these requirements become increasingly difficult to meet in older samples, particularly for whole-rock samples. Fortunately, robust methods to screen for diagenetic alteration have already been well-established (Edgar et al. 2015; Stewart et al. 2015). As we will show, even though neither the seawater composition nor the detailed calibrations of biological carbonates are known throughout the Phanerozoic, careful studies of well-preserved fossils are placing limits on the system, and so are contributing to a better understanding on what controls secular variability as well as the magnitude of carbon cycle perturbations.

The Boron Isotope Composition of Ancient Oceans

The boron isotope composition of the fluid, in this case seawater, must be known or assumed in order to calculate pH from the $\delta^{11}B$ of carbonates. One major feature of seawater that must be accounted for in models of secular change is that the $\delta^{11}B$ of seawater is remarkably heavier than the known primary input, i.e. river water, which has an estimated average $\delta^{11}B$ of 10‰ (Lemarchand et al. 2002). Future studies should also consider the importance of the subterranean groundwater estuary, which is equal in volume to rivers and is a diurnal reactor bed of geochemical processing. The greatest recognized sink is mid-ocean ridge (MOR) hydrothermal fluid–rock interactions (Simon et al. 2006). This, and all known fluxes out of the system, involves removal of isotopically light boron, which accounts for the major enrichment to 39.6‰ in present-day seawater. To better understand the secular variability of $\delta^{11}B$ in seawater, researchers have turned to process-based flux models (Lemarchand et al. 2002; Joachimski et al. 2005; Simon et al. 2006). From the accumulated boron isotope data, as well as the modeling studies, it is clear that a primary control on $\delta^{11}B$ of seawater is the removal of light boron. It is further clear that this control is primarily due to the reactive nature of the charged isotopically light borate ion that is more likely to be sorbed or incorporated through any of the alteration and precipitation processes that are removing boron. As a higher resolution record of secular variability emerges, factors that might control short-term changes in the $\delta^{11}B$ of seawater will come into focus.

Information on the secular variation of seawater in the Cenozoic is now emerging. A careful study using carbon isotopes to reconstruct the pH gradient demonstrates that $\delta^{11}B$ of seawater has changed by ~3‰ over the past 50 million years (Greenop et al. 2017). Interestingly, instead of a steady increase, it appears that seawater $\delta^{11}B$ shows a major jump between the Middle to Late Miocene of about 2‰ per million years (Fig. 4). This is a major consideration for using $\delta^{11}B$ to consider the magnitude of pH change, as the entire range for the glacial/interglacial cycles is about 0.6‰. Still, considering short (sub-million year) timescales, changes in the B/Ca and $\delta^{11}B$ can place bounds on pH and the changes in dissolved inorganic carbon that accompany perturbations of the carbon system. For example, Penman et al. (2014) used B/Ca and $\delta^{11}B$ in planktonic foraminifera to study rapid change across the Paleocene–Eocene Thermal Maximum, an interval that has long been known to have a major addition of light carbon associated with significant global warming. The boron results require there to be a rapid and sustained input of carbon to the system and represent a first estimate of the pH change associated with this climate event. Foster and Rae (2016) used a Monte Carlo approach to estimate the errors on the pH from this dataset and found that the actual $\delta^{11}B$ of seawater, and the pH prior to the perturbation, exert only a small influence on the estimates of the pH change. Importantly, the Paleocene–Eocene Thermal Maximum is considered to be a good analogue for the current rapid increase in CO$_2$ to the Earth’s atmosphere resulting from anthropogenic emissions.

Figure 4. Estimates of the secular variation in $\delta^{11}B$ in seawater over the past 22 million years. The $\delta^{11}B_{sw}$ curve was calculated using the variable pH gradient derived from $\delta^{13}C$. The median (red line), 68% (dark red band) and 95% (light red band) confidence intervals are plotted. ‘Pleist.’ = Pleistocene; ‘Olig.’ = Oligocene. Simplified from Greenop et al. (2017).
Foraminifera can be planktic or benthic and they tend to occupy narrow depth ranges. Decreasing temperature and increasing hydrostatic pressure though the water column allows more CO$_2$ to be stored with depth and, therefore, the pH and alkalinity shows a gradient. There is also a coherent and known relationship between oxygen isotopes and temperature. Anagnostou et al. (2016) used oxygen isotopes in foraminifera from ocean sediment drill cores to estimate the habitat depth and were able to apply the gradient in the measured $\delta^{11}$B to estimate the $\delta^{11}$B of seawater. Then, applying pH calibrations based on empirical data from foraminifera, they were able to reconstruct $p$CO$_2$ through the Eocene warm interval into the Neogene cooling. As with the Penman et al. (2014) study, Anagnostou et al. (2016) showed a clear change in the pH of the oceans over the studied stratigraphic depth interval despite uncertainties in the calibration and the secular variation of $\delta^{11}$B of seawater. This work shows >1,000 ppm CO$_2$ for the Early Eocene Climate Maximum at about 50 Ma, declining to less than 700 ppm by 40 Ma when glaciation is known to have started in Antarctica. This decline is coincident with a marked increase in $\delta^{18}$O, which suggests that the temperatures declined by 5°C. Anagnostou et al. (2016) used these relationships to consider the equilibrium climate sensitivity (temperature change in degrees centigrade for a doubling of atmospheric CO$_2$) and found that it is comparable to that of today.

Taking the pH proxy to the pre-Cenozoic is even more of a challenge. The boron isotope system is highly susceptible to diagenetic resetting, aragonite fossils are rarely preserved, and many of the fossils with calcite shells that appear to be good choices for preserving the original boron isotope signature are extinct, precluding the establishment of empirical pH–$\delta^{11}$B curves. Of the published pre-Cenozoic studies, brachiopods and rugose corals appear to have good potential as archives with relatively high boron concentrations. Trilobite fossils are typically calcite with very good exoskeleton preservation and could be good archives of boron isotopes, but no published data are available. Rugose corals and trilobites are extinct and have no modern representatives, but reliability could be tested by comparing fossils from different localities and different fossils from one horizon. Penman et al. (2013) examined a variety of modern brachiopods from known pH and found that there appears to be a species control on borate incorporation. This study also showed that B isotopes show variability across the brachiopod shell, as do C and O isotopes, which may also be a function of vital effects. Whereas these differences result in several per mil offsets from the borate curve, as well as differences from each other, there is a fairly solid 23‰ offset from seawater. Most of the measurements plot below the Klochko et al. (2006) borate curve, similar to non-symbiont-bearing benthic foraminifera as discussed in Foster and Rae (2016). To account for the differences among species, it is important to analyze the same species as well as different species from the same horizons to evaluate how different they might be. At this stage, the small differences among species are similar to the variation seen within similar time slices from the stratigraphic record. Future studies could target intervals of known change to see how boron isotopes respond, and it is expected that patterns will emerge that will offer important insights into the Earth system response to changing conditions. Emerging data from the Carboniferous–Permian glacial interval shows a major shift to values similar to the Neogene (Leggett et al. 2016) (Fig. 5). Whereas the ancient record is currently sparse, the existing data show much greater variability prior to the major proliferation of planktic calcifiers during the Mesozoic. The rise and diversification of calcifying organisms shifted carbonate deposition from the continental shelf to throughout the oceans. This innovation may have changed the regulation of ocean chemistry so that extremes in pH are now not allowed (Ridgwell 2005). The Joachimski et al. (2005) model for $\delta^{11}$B in the Paleozoic is an impressive fit to the compiled data (Fig. 5). As a higher resolution record of $\delta^{11}$B and elemental changes in seawater composition emerges, we expect that the nature of boron removal from seawater will offer a unique perspective into controls on seawater chemistry, as well as to changing atmospheric $p$CO$_2$.

![Figure 5](image-url)
SUMMARY

Boron isotopes in marine carbonates are already proving extremely valuable for paleoclimate studies. The prospects now look bright for testing models of the secular variability of the ocean and atmosphere and having a possible tool for studying the controls on biominalerization. Boron isotope composition of carbonates is demonstrably a measure of the pH of the fluids from which the carbonates formed. As with any proxy, calibrations are required. With a direct measure of the fractionation factor, and empirical data from culture experiments, we can now consider what are the controls on δ11B and B/Ca in biogenic carbonates. Clearly, taking this further back in time involves making assumptions about how extinct species controlled their local environment, and, perhaps even more difficult, the magnitude of secular variability. Application of the boron pH proxy to the Precambrian, before the advent of multicellular organisms, will require even more assumptions. Any study of Precambrian rocks must consider the control that diagennises imposes on the boron system. Typically, diagennesis would produce scatter such that multiple analyses from the same horizons, coupled with multiple geologic sections of the same age from widely separated parts of the globe, would be needed to test the reliability of this proxy in Precambrian records.

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Elements 248 August 2017
Naturally occurring borates are the major economic source of boron. Borates were first used over 4,000 years ago in precious-metal working and are now essential components of modern industry. Although borates have been exploited from other sources, three minerals from non-marine evaporites now form the major commercial sources of borate—borax, colemanite and ulexite. These major commercial deposits are associated with Neogene volcanism in tectonically active extensional regions at plate boundaries. The most important continental borate provinces are located in the USA, Argentina, Chile, Peru, and China, with the largest borate reserves in the world being found in western Anatolia (Turkey).

Keywords: economic borate deposits, non-marine evaporites, Turkish borate deposits

INTRODUCTION

Borates are the most important economic source of boron and have been used for millennia. Borax (see Table 1 for borate mineral formulae) was first used in Babylon (ancient Mesopotamia, now in modern Iraq) more than 4,000 years ago; indeed, its name is derived from the Persian burah (borak). At that time, the Babylonians brought borax from the Himalayas for use in the manufacture of jewellery. The Egyptians used borax in mumification, and by ~–300 AD the Chinese were familiar with borax glazes, as were the Arabs three centuries later. Borax was first brought to Europe in the 13th century by traders from Tibet and Kashmir (Ozol 1977; Travis and Cocks 1984; Kistler and Helvacı 1994; Smith and Medrano 1996; Garrett 1998; Helvacı 2005, 2015).

By the 1770s, the French had sourced borax from Purbet Province (India) and, at about the same time, natural boric acid (sassolite) was discovered in hot springs in the Maremma region of Tuscany (Italy). The discovery and commercial development of borate deposits accelerated during the 19th century. Chile started to mine borate from the Salar de Ascotán [salar means ‘salt flat’ in Spanish] in 1852, accounting for a quarter of the world’s annual supply of ~16,000 tonnes. In 1856, John Veatch discovered borax in Clear Lake, California (USA) (Kistler and Helvacı 1994). In Turkey, borate mining extends back to 1865 when borates were extracted from the Aziziye mine (Sultançayır) in the Balikesir province and was shipped to France for processing (Travis and Cocks 1984).

ECONOMIC MINERALOGY OF BORON

‘Borate’ has the industrial definition of, ‘Any compound that contains or supplies boric oxide (B_2O_3)’. But of the many known boron minerals only three are currently major commercial sources of borate: colemanite, ulexite and borax. All three are found within non-marine evaporites (Smith and Medrano 1996; Garrett 1998) (Table 1). Deposits containing these minerals are mined in a limited number of countries and are dominated by the United States and Turkey, which together supply 90% of the world’s borate (Table 2).

Borax is by far the most important mineral for the borate industry. This reflects the fact that borax is the most widely distributed and abundant borate mineral, with large tonnages present in the deposits at Boron (California, USA), Kirka (Turkey), and Tincalayu (Argentina) (Kistler and Helvacı 1994). In addition, borax crushes easily and dissolves readily in water, so processing costs are relatively low.

Ulexite is a mixed Na–Ca borate that has similar mineral processing properties to borax and is the usual borate used in the production of high-quality sodium-free glass for the fiberglass industry. While colemanite was historically produced in Death Valley (California, USA), large-scale production of high-grade colemanite is now restricted to the Emet Basin of Turkey (Helvacı and Alonso 2000; Helvacı 2005; Ortí et al. 2016).

ORIGIN OF BORATE DEPOSITS

All the world’s major economic borates are found in non-marine evaporite deposits located in extensional basins formed during the collision of tectonic terrains (Fig. 1) (Ozol 1977). Most of the commercial borate deposits

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in the USA, Argentina, Chile, Peru and Turkey are associated with continental sediments and acidic volcanism of Neogene age (Smith and Medrano 1996; Helvacı 2005). Many borates in Turkey, the USA and Argentina are also covered by carbonate cap rocks that aided their preservation (Helvacı 2005).

The Precambrian borate deposits of Liaoning Province (China) were initially classed as skarn deposits on the basis of their mineralogy (suanite, szaibélyite and ludwigite), but detailed field studies and boron isotope data indicate that they, too, are likely metamorphosed non-marine evaporites (Peng and Palmer 2002).

Borates have also been mined from skarn deposits (e.g. datolite from Dalnegorsk, Russia), active geothermal fields (e.g. sassolite from Lardarello, Italy) and marine evaporites (e.g. inderite from the Inder, Kazakhstan). However, none of these sources are currently of more than local significance (Kistler and Helvacı 1994).

Borate Deposits of Turkey

The world’s largest and best-studied borate deposits are those of western Anatolia (Turkey) (Helvacı 1995, 2015; Orti et al. 2016; Helvacı et al. 2017). The borate deposits themselves lie in an area covering 300 km east–west by 150 km north–south in western Anatolia, south of the Marmara Sea (Fig. 2). The main districts include the Bigadiç colemanite and ulexite deposits (Ca and Na borate); Sultançayır priceite deposits (Ca-type); Kestelek colemanite deposits (Ca-type); Emet colemanite deposits (Ca-type); and Kırka borax deposits (Na-type) (Figs. 2–4) (İnan et al. 1973; Helvacı et al. 1993, 2017; Helvacı 1995; Helvacı and Orti 1998; 2004; Garcia-Veigas et al. 2011; Garcia-Veigas and Helvacı 2013; Orti et al. 2016).

In Anatolia, the ultimate source of the boron is calc-alkaline volcanic rocks that were enriched in boron as a consequence of metasomatism and melting of the lithospheric mantle during continental collision (Ersøy et al. 2010).

**Table 1**

*IMPORTANT BORATE MINERALS IN COMMERCIAL DEPOSITS. AFTER GARRET (1998).*

<table>
<thead>
<tr>
<th>Boric acid</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sassolite</td>
<td>B(OH)₃</td>
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</tbody>
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<table>
<thead>
<tr>
<th>Ba-borates</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Colemanite</td>
<td>Ca₂[B₂O₅(OH)₄]·H₂O</td>
</tr>
<tr>
<td>Priceite</td>
<td>Ca₂[B₂O₅(OH)₃]·H₂O</td>
</tr>
<tr>
<td>Inyoite</td>
<td>Ca₂[B₂O₅(OH)₅]·4H₂O</td>
</tr>
</tbody>
</table>

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<tr>
<th>Na–Ca-borates</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Probertite</td>
<td>Na₂[Ca₃B₂O₇(OH)₆]·3H₂O</td>
</tr>
<tr>
<td>Ulexite</td>
<td>Na₂[Ca₃B₂O₇(OH)]·5H₂O</td>
</tr>
</tbody>
</table>

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<tr>
<th>Na-borates</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Tincalconite</td>
<td>Na₂[B₂O₅(OH)]·3H₂O</td>
</tr>
<tr>
<td>Borax</td>
<td>Na₂[B₂O₅(OH)]·8H₂O</td>
</tr>
<tr>
<td>Kernite</td>
<td>Na₂[B₂O₅(OH)]·3H₂O</td>
</tr>
</tbody>
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<tr>
<th>Mg-borates</th>
<th>Structural Formula</th>
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</thead>
<tbody>
<tr>
<td>Suanite</td>
<td>Mg₂B₂O₇</td>
</tr>
<tr>
<td>Szaibélyite</td>
<td>Mg₂[BO₃(OH)₂]</td>
</tr>
<tr>
<td>Inderite</td>
<td>Mg₂[B₂O₅(OH)]·5H₂O</td>
</tr>
<tr>
<td>Kurnakovite</td>
<td>Mg₂[B₂O₅(OH)]·5H₂O</td>
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</tbody>
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<tr>
<th>Mg–Ca borates</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Hydroboracite</td>
<td>CaMg₂[B₂O₅(OH)]·3H₂O</td>
</tr>
</tbody>
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<tr>
<th>Mg–Fe borates</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ludwigite</td>
<td>Mg₂[Fe⁺₂O₅(BO₃)]</td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th>Borate-chloride</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Boracite</td>
<td>Mg₂B₂O₅Cl</td>
</tr>
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</table>

<table>
<thead>
<tr>
<th>Borosilicates</th>
<th>Structural Formula</th>
</tr>
</thead>
<tbody>
<tr>
<td>Datolite</td>
<td>CaB(SiO₄)(OH)</td>
</tr>
</tbody>
</table>
The boron was then leached from the volcanic rocks by geothermal waters that collected and evaporated in playa lakes within extensional basins (Fig. 5). The mineralogy of the borate deposits reflects the composition of the geothermal fluids that are, in turn, dependent on the local geology (Helvacı 1995). For example, boron isotope data from the Kırka deposit suggest that colemanite precipitated from fluids of low pH (~8.2) compared to ulexite (pH ~8.6) and borax (pH ~8.8) (Palmer and Helvacı 1995). Strontium isotope data from across the Turkish borate province indicate that Ca-rich borates likely formed from the evaporation of geothermal fluids that had interacted with basement limestones (Palmer and Helvacı 1997; Floyd et al. 1998).

Turkey is currently the largest producer of borates and has the world’s largest reserves (Table 2). Production has more than doubled since 1980 to over one million tonnes per year, and further increases (particularly of borax from Kırka) are likely to lead to Turkey dominating world markets. Turkey is already the major world producer of colemanite, much of which comes from the Emet Valley.

**EXPLORING FOR BORATE**

Borate exploration uses all the tools available to the exploration geologist, with the recognition of trends of favourable host rocks and structures being an important guide to areas of possible interest. Borates are highly soluble, hence post-depositional dissolution of borate deposits by circulating meteoric water can lead to their dissolution. On the plus side, the mobility of borates also means that water sampling (from the surface and from wells) and vegetation surveys can yield useful information (Kistler and Helvacı 1994; Floyd et al. 1998; Helvacı 2005).

Geophysical surveys, particularly gravity and magnetics, are used to outline target basins or structures beneath sedimentary basin fill. Once geophysical, geological and geochemical surveys have identified promising targets, soil and rock-chip sampling techniques are used in exploration drill programs, with Sr, As, and Li as a common suite of elements to be assayed alongside boron (Helvacı et al. 1993, 2004; Palmer et al. 2004). Unlike most other elements, simple field assays of B₂O₃ can be undertaken using the original flame test and the simple wet-chemistry turmeric/curcumin test. Although layered evaporite deposits of borax, colemanite and ulexite are not generally sought at depths >500 m, boron-rich brines, particularly those associated with other salts of value, can be extracted from greater depths under certain circumstances (Kistler and Helvacı 1994).

**MINING OF BORATE**

Borate extraction and transport has a colourful history. For example, workers would wade into Himalayan lakes to harvest the lake “floor” and then transport the borax in

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**Table 2** THE RESERVE AND LIFE ESTIMATES OF THE WORLD’S BORATE DEPOSITS. After Helvacı (2005).

<table>
<thead>
<tr>
<th>Country</th>
<th>Economic Reserve (Mt B₂O₃)</th>
<th>Total Reserve (Mt of B₂O₃)</th>
<th>Estimated Life of Economic Reserve (years)</th>
<th>Estimated Life of Total Reserve (years)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Turkey</td>
<td>224,000</td>
<td>563,000</td>
<td>155</td>
<td>389</td>
</tr>
<tr>
<td>USA</td>
<td>40,000</td>
<td>80,000</td>
<td>28</td>
<td>55</td>
</tr>
<tr>
<td>Russia</td>
<td>40,000</td>
<td>60,000</td>
<td>28</td>
<td>69</td>
</tr>
<tr>
<td>China</td>
<td>27,000</td>
<td>36,000</td>
<td>19</td>
<td>25</td>
</tr>
<tr>
<td>Chile</td>
<td>8,000</td>
<td>41,000</td>
<td>6</td>
<td>28</td>
</tr>
<tr>
<td>Bolivia</td>
<td>4,000</td>
<td>19,000</td>
<td>3</td>
<td>13</td>
</tr>
<tr>
<td>Peru</td>
<td>4,000</td>
<td>22,000</td>
<td>3</td>
<td>15</td>
</tr>
<tr>
<td>Argentina</td>
<td>2,000</td>
<td>9,000</td>
<td>1</td>
<td>6</td>
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<tr>
<td>Kazakhstan</td>
<td>14,000</td>
<td>15,000</td>
<td>10</td>
<td>10</td>
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<tr>
<td><strong>TOTAL</strong></td>
<td><strong>363,000</strong></td>
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<td><strong>253</strong></td>
<td><strong>610</strong></td>
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saddlebags on sheep across the Himalayas to markets. There was borate extraction from what was known as the “Dante’s Inferno” of the Larderello (Italy) boric acid fumaroles. And there were the famous 20-mule teams used to transport borax from Death Valley to the Pacific coast in the western United States (Kistler and Helvacı 1994).

Most of the world’s commercial borate deposits are now mined from open pits (Fig. 4). For example, the Boron mine in Kramer (California, USA) and the Kirka mine in Turkey are huge open pits that are mined by massive shovel excavators and trucks, plus front-end loaders for ore mining and overburden removal. The borate ores and overburden are first drilled and blasted and then a belt conveyor is used to move ore from the in-pit crusher to a coarse-ore stockpile from which it is reclaimed by a bucket wheel that blends the ore before it is fed to the refinery.

The Tincalayu deposit in Argentina is also mined from open pits. Here, the ore is transported 400 km by truck and rail to the Salta refinery. Some South American and Chinese salar (i.e. salt flat) operations also use hand labour to mine thin salar borates, generally after stripping of the overburden with a small bulldozer.

Borates are mined underground in the Liaoning Province of China and at the Billie and Gerstley mines in Death Valley. Borate brines are recovered at Searles Lake (California) and in the Qinghai Basin of China. Brines have also been extracted in the Inder region of Kazakhstan.

**BORATE MINERAL PROCESSING**

Processing techniques for borates are related to the scale of the operation and the ore type, with either the upgraded or refined mineral (borax, colemanite, or ulexite) or boric acid as the final product for most operations. Borax ores (e.g. from Boron, Kirka and Tincalayu) are generally crushed to ~2.5 cm and then dissolved in hot water/recycled borate liquor. The resultant liquor is clarified and concentrated in large counter-current thickeners, filtered, fed to vacuum crystallizers, centrifuged, and then dried. The final product is refined borate decahydrate (borax sensu stricto), borate pentahydrate (tincalconite) and fused anhydrous borax and can be used as a feed for the production of boric acid.

Colemanite concentrates are used directly in glass melts for the non-sodium fiberglass industry or are used as a feed for boric acid plants. Magnesium borates are generally concentrated, dissolved in acid to remove the magnesium, and then converted to boric acid or sodium borates.

Brines from Searles Lake (and also, presumably, from Qinghai) are recovered by either controlled evaporation or carbonation (Kistler and Helvacı 1994). The remaining borate liquor is fed to tanks containing borax seed crystals, which aid in the borate recovery. The resultant slurry is filtered, washed, redissolved, and fed to vacuum crystallizers that produce dehydrated borax products or boric acid.

While evaporite borate minerals and brines have relatively low energy (and, hence, low cost) production methods, borosilicates require much higher energy processing, something that has led to them becoming largely uneconomic. For example, ores from the Bor deposit (Dalnegorsk, Russia) with their relatively low $B_2O_3$ grades, are crushed, and then run through a complex plant that includes magnetic separators, heavy mineral separators, and flotation cells (Utekhin 1965). The concentrates are then dried, leached, and calcined before being converted to boric acid or to a sodium borate.

**USES OF BORON**

Boron is widely used in many industries, so that only a brief summary is possible here: more extensive details are provided in Crangle (2015). Borax pentahydrate and boric acid are the most commonly traded commodities. Boric...
Acid plants are operated by all the major borate producers. Glass fibre insulation is the major end use in the United States, followed by textile glass fibre and borosilicate glass, detergents, and ceramics. Boron fibre-reinforced plastics are used extensively for aerospace frame sheathing where they combine flexibility and light weight with strength and ease of fabrication. Minor uses that will likely increase include those in fertilizers, wood preservatives, alloys and metals, fire retardants, and insecticides (Garrett 1998).

Borates are also used in pharmaceuticals, cosmetics, anti-corrosion compounds, adhesives, abrasives, insecticides, metallurgical processes, and nuclear shielding. More recently, boron has been used in super magnets, where it is combined with rare earths, nickel and iron to produce alloys to make electromagnets for computer drives, high fidelity speakers, starter motors, and household appliances.

Borates are also increasingly used in “green” (i.e. environmentally friendly) applications by aiding recovery of heavy metals from industrial waste streams and by removing impurities from the polymers used in bleaching wood pulp for paper production.

Borates are also increasingly used in pharmaceuticals, cosmetics, anti-corrosion compounds, adhesives, abrasives, insecticides, metallurgical processes, and nuclear shielding. More recently, boron has been used in super magnets, where it is combined with rare earths, nickel and iron to produce alloys to make electromagnets for computer drives, high fidelity speakers, starter motors, and household appliances.

Figure 4 Field photos of Turkish borate deposits. (A) Simav open cast mine, in Bigadiç. (B) Old mine adit. Simav mine, Bigadiç. (C) Colemanite nodules intercalated with associated sediments. Tulu open pit mine, Bigadiç. (D) Ulexite ore lenses intercalated with associated sediments. Kurtpınar deposit, Bigadiç. (E) Borax and dolomitic clay alternations. Kırka open cast borax mine. (F) Massive crystalline borax lithofacies. Borax crystals are transparent and rectangular to equant and are surrounded by a silt/clay matrix. All photographs by C. Helvacı.

Figure 5 Generalized playa lake depositional model showing formation of borate deposits in Neogene basins of western Anatolia (Turkey). After Helvacı (2005).
Medical applications of borates include cancer research, where the large capture cross-section of the \(^{10}B\) isotope makes it an excellent neutron absorber that reacts with low-energy neutrons to give off short-range alpha particles that can be used for microsurgery in previously inaccessible areas of the brain. Current tests on boron analogues indicate they may also be effective in reducing serum cholesterol and other disease-causing proteins.

Borates were traded at relatively high prices into the late 19th century, but have become a relatively modestly priced industrial mineral commodity in recent years following the development of the large deposits at Boron (USA) and Kirka (Turkey). Prices are directly related to production costs, of which the largest is fuel for drying, dehydrating, and melting the refined ore into the industrial products. Industry prices for most products have held steady with the rate of inflation (Kistler and Helvacı 1994; Helvacı 2005).

Based on recent history, the major world consumers of borates will likely continue to be North America, Europe and Japan. Consumption of borates is expected to increase, spurred by strong demand in the Asian and South American agriculture, ceramic and glass markets. World consumption of borates was projected to reach 2.0 Mt B\(_2\)O\(_3\) by 2014, compared with 1.5 Mt B\(_2\)O\(_3\) in 2010 (Rio Tinto Inc. 2011; Roskill Information Services Ltd. 2010, O’Driscoll 2011).

Known reserves of borate minerals are large—particularly in Turkey, South America, and the USA—and production from Turkey and the USA will continue to dominate world markets (Table 2). Very few modern industries can get by without borates, and very few people can get by without their products. Hence, borates and their products will continue to play a vital role in the global economy.

ACKNOWLEDGMENTS

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Small molecules containing boron can play all sorts of roles in chemistry, biology and materials science. Molecular boron compounds display a wide range of unusual and fascinating structures, and their chemical reactivity can be very different from that of boron’s next-door neighbour carbon. Some of the reasons for this will be considered and illustrated through applications in energy, medicine and new materials. The boron dipyrrins, also known as BODIPYs, are a prime example. They are strongly fluorescent when excited by illumination and are widely used as fluorescent tags in biology and as biosensors. More recently, they have been studied for their energy transfer properties in light-harvesting applications.

**Keywords:** boron, boranes, fluorescent sensor, sugar sensor, BODIPY

**INTRODUCTION**

Boron occurs in nature largely as borate minerals. Borates in their simplest form occur as calcium or magnesium borates or borosilicates and are dominated by very strong B–O bonds, which at 536 kJ mol⁻¹ are amongst the strongest of the element–element single bonds. These strong bonds also dominate the aqueous chemistry of boron. Looking more broadly at the roles that boron can play in the modern world, we find that small molecules containing boron have a wide range of applications in chemistry, biology and materials science. These applications all have in common that boron is bonded to other elements other than oxygen, which opens not only a world of chemical transformations but also very different properties and applications than those of the simple borates that feature in roles as prosaic as washing powder and ant killer. Millions of tons of borates and their derivatives are used worldwide each year, much of it in glass and ceramics, as well as in the oil industry and agriculture (Ritter 2016). Borate may have had a key evolutionary role in stabilizing ribose, critical to forming prebiotic ribonucleic acid (RNA). Boron is an essential trace element in both plants and humans (Furukawa and Kakegawa 2017 this issue).

**POLYHEDRAL BORON CLUSTERS**

To begin with, consider boron bonded only to itself: in other words, pure, elemental boron. Although it can exist in several amorphous and crystalline phases, the most fascinating to chemists are the α- and β-rhombohedral phases, which contain icosahedral B₁₂ clusters. Although the isolation of pure phases of boron has been dogged by history and controversy, a remarkable set of boron hydride clusters are based on a whole range of polyhedral structures. The boron hydride cluster B₃H₅⁺⁺ resembles the icosahedral units in rhombohedral boron but with each boron capped by a hydrogen atom, allowing this cluster anion to be isolated as a molecular species (Fig. 1). A range of other boron cluster anions with related formulae BₙHₙ⁻ (n = 4–12) are known and all are high-symmetry clusters based on deltahedra (regular polyhedra with triangular faces). Neutral boranes with generic formulae BₓHₓ₊₄ and BₓHₓ₋₆ have structures based on the same deltahedra but with one or two of the vertices missing. When we compare these boranes to the similar series of binary hydrides—CaH₂ (alkanes), CaH₂ (alkenes) and CaH₂ (alkynes)—we find remarkable differences. Although boron and carbon are immediate neighbours in the periodic table, hydrocarbons are typically linear and branched chains or rings, whereas boron hydrides exist as polyhedral clusters (Fig. 1). Why is this?

It all comes down to the electron-deficient nature of boron, which has three valence electrons compared to carbon which has four. Carbon can form four bonds to achieve a closed shell octet, whereas boron can form only three bonds and accumulate six electrons. This is two short of the stable octet configuration. It can make up for its electron shortage by sharing the available electrons as much as possible, leading to curved and, ultimately, closed polyhedral structures. The molecular orbital (MO) theory description of the bonding in these clusters involves MOs both on the surface of and within the cluster, which have contributions from many boron atoms thereby allowing maximum sharing of the available bonding electrons. The MOs in simple hydrocarbons, on the other hand, can generally be described as having contributions from just two atoms, forming simple electron-pair bonds. The boron hydrides just don’t have enough electrons to go around. Even hydrogen gets into the sharing act: hydrocarbons contain simple C–H single bonds whereas boranes contain both simple B–H bonds and unusual B–H–B bridging hydrides, structures that cannot be explained by conventional bonding theories. Harvard chemist William Nunn Lipscomb (1919–2010) won the 1976 Nobel Prize in chemistry for “his studies on the structure of boranes illuminating problems of chemical bonding”. The use of boranes as reagents for chemical transformation was also recognised by a Nobel Prize awarded to Herbert Charles Brown (1912–2004) in 1979.
Applications of Boron in Biology and Medicine

Boron Neutron Capture Therapy

Borane clusters have potential applications, as yet clinically unrealised, in medicine. The stable boron isotope $^10$B has a very high neutron capture cross section for capture of thermal neutrons, leading to an excited $^{11}$B nucleus which decays to a high-energy α particle ($^4$He) and a $^7$Li nucleus: $^{10}$B + n → $^{11}$B$^*$ → α + $^7$Li + 2.31 MeV. If these energetic decay products are generated close to a tumour then ionisations occur which damage the tissue. This therapy, known as boron neutron capture therapy (BNCT) requires a high concentration of boron to be localised in the vicinity of a tumour. Borane clusters conjugated to a tumour-targeting group have been investigated for this. The simplest of these is BSH (B$_{12}$H$_9$SH$^-$)— others contain C$_2$B$_{10}$H$_{11}^-$ or C$_2$B$_9$H$_{12}^-$ clusters attached to nucleosides, porphyrins or sugars as the targeting agents. Good progress is being made with these, although, as with any new therapeutic agent, issues with solubility, toxicity and efficacy must be addressed along with the stability and accessibility of the neutron source (Luderer et al. 2015; Satapathy et al. 2015).

Boronic Acids

The only drug containing boron that is in current clinical use is bortezomib, approved in 2003 for the treatment of multiple myeloma and non-Hodgkin’s lymphoma. This compound is essentially a tripeptide containing pyrazinoic acid, phenylalanine and leucine with a boronic acid instead of a carboxylic acid at the “C-terminus”. This is the first example of an organoboron compound encountered in this discussion and it contains one B–C bond and two B–OH bonds. One of the best-known uses of boronic acids are as sugar sensors (Hansen and Christensen 2013). A particular example of this is discussed later. A further, very important use of boronic acids is in Suzuki–Miyaura coupling, the most commonly used carbon–carbon bond-forming reaction in the pharmaceutical industry and also widely used for polymerisation reactions (Sakamoto et al. 2009; Blakemore 2016). Akira Suzuki won the 2010 Nobel Prize in chemistry for the development of this important chemical transformation.

Fluorescent Boron and the BODIPYs

The boron dipyrrins, abbreviated to the ‘BODIPYs’, are a group of small, highly fluorescent molecules based on the parent molecule (the core of all BODIPY structures) 4,4-difluoro-4-bora-3a,4a-diaza-s-indacene, which contains a BF$_2$ core bonded to a dipyrrin group (Fig. 2A). They are widely used as dyes, notable for their small Stokes shift, high fluorescence quantum yields, and sharp excitation and emission peaks and high brightness. In Figure 2B, a sample of a typical BODIPY shows that the solid is orange-red but the solution version of the compound is a vividly fluorescent yellow-green, even to the naked eye. BODIPY dyes absorb light (a photon of energy) at a characteristic wavelength (forming a transient excited state) and the fluorescence occurs when this energy is re-emitted as light. The emitted light (fluorescence) has a longer wavelength than the absorbed light: the difference is the Stokes shift. BODIPY dyes serve as fluorescent indicators for pH, metal ions, anions, biomolecules, reactive oxygen species and other chemical reactions and physical phenomena (Boens et al. 2012).

Fluorescent Tags for Biomolecules

The parent BODIPY is a scaffold which is modified by appending substituents to the dipyrrin periphery to improve stability and solubility and to tailor the emission properties (Kowada et al. 2015). From this has developed a rich synthetic chemistry for the production of derivatives used in a wide range of applications. BODIPY dyes can penetrate cell membranes and can be used for cell and in vivo imaging. Their fluorescence response can switch between ON and OFF, depending on the mechanism of interaction between the surroundings and the BODIPY excited state. A typical architecture is BODIPY–linker–chelator, in which the chelator is designed to recognise the target analyte. In a reductive photoinduced electron transfer (PET) mechanism, the chelator acts as an electron donor and the excited state BODIPY as an electron acceptor. When the chelator is free, this electron transfer quenches (‘turns off’) the BODIPY fluorescence (Fig. 3A). However, when the chelator recognises the target, it no longer quenches the BODIPY and the fluorescence is turned ON (Fig. 3B). When the donor/acceptor properties are reversed, then oxidative PET can result, and fluorescence is turned OFF when the chelator binds to the target. A second mechanism is the Förster-resonance energy transfer (FRET), which occurs by energy (rather than electron) transfer between the BODIPY and a donor or acceptor.
BODIPYs can be used for single molecule and super-resolution microscopy, a technique for visualizing individual proteins and biomolecules. Examples are the commercially available LysoTracker® Green (excitation/emission maxima 504/511 nm) and LysoTracker® Red (excitation/emission maxima 577/590 nm) probes, both developed for fluorescence microscopy of lysosomes (subcellular organelles). They can be modified to fluoresce at different wavelengths by variation of the substituents on the BODIPY core, and are sensitive to pH. The dyes are weakly fluorescent in neutral or alkaline conditions, but their fluorescence is greatly enhanced in the acidic environment of lysosomes when the terminal nitrogens on the side chain (highlighted in green and red in Figs. 3C and 3D) are protonated (equivalent to the chelator in Fig. 3B binding to its target, in this case H⁺). The second red highlight in LysoTracker® Red illustrates how addition of the electron-rich pyrrole unit to the dipyrrin framework dramatically shifts the absorption and emission wavelengths and, hence, the colours (Fig. 3).

Sugar Sensing

The B–F bonds in BODIPY are very strong and, as a result, chemically inert. They stay intact in all the applications for which BODIPY dyes are used. Modifications to BODIPY’s by attaching groups to modify the fluorescence properties or by targeting the analyte occur on the dipyrrin carbon backbone. Further modifications could be induced by replacing the fluorine (F) substituents on boron, although the extremely strong B–F bonds make this chemically challenging. However, by using an appropriately strong Lewis acid (see below for a discussion of these) to activate the B–F bonds, substitutions can be made, for example with chlorine or oxygen to make Cl-BODIPY or O-BODIPY, respectively. The B–Cl and B–O bonds are more reactive, and with the right substrate will undergo chemical reactions at the boron centre. In this way, the boron itself can be used as the recognition unit for the target analyte.

Boronic acids were mentioned above—they are organo-boron compounds containing two B–OH bonds and one B–C bond (denoted “R”). Sugar molecules contain several C–OH groups and, when in water, boronic acid and sugars can form links though B–O–C bonds. If the organic group R on the boronic acid has a “reporter” function, for example fluorescence turning ON or OFF upon the formation of the boronic acid–sugar bonds, then this allows the system to sense the presence or absence of a sugar (Fig. 4). In very recent research from our own laboratory, we have combined the concept of boronic acids as sugar sensors with substitution at the boron centre in O-BODIPY to make direct BODIPY–sugar conjugates (Fig. 5). Using glucose as the sugar, we can isolate several examples containing glucose in different ring forms and with 1:1 and 2:1 BODIPY:glucose ratios. These retain their excellent fluorescence properties. We are currently investigating their possible applications for recognising and targeting specific sugars and to be developed as probes for polysaccharide structure and function (Liu et al. 2016).
BORON IN ENERGY AND MATERIALS

Light Harvesting

BODIPYs were discussed above for their applications as fluorescent sensors. The mechanisms by which BODIPY fluorescence is modulated are typically by photoinduced electron transfer (PET) or by Förster resonance energy transfer (FRET – energy transfer between two light-sensitive molecules). In systems which are tailored for FRET, BODIPYs have been applied to light harvesting. Their good light-absorption properties, coupled with their ability to transfer energy via FRET, make them useful for incorporation into molecular systems engineered to capture light energy and transform it to an alternative form in which it could be used or stored. The important steps in these light-harvesting antenna systems are the absorption of light by an antenna, followed by energy transfer, which in turn drives electron transfer from a donor to an acceptor. This produces an electron–hole pair, which, if it has a sufficiently long lifetime, can be drawn off into an external electrical current. The photosynthetic reaction centre in chlorophyll is the source of inspiration from which this approach is derived. In an elegant example of this principle, a molecular construct features BODIPY units as the antennae, a zinc porphyrin (closely related to the iron porphyrin or heme unit found in hemoglobin) as the electron donor, and a C60 fullerene as the electron acceptor (Fig. 6) (Maligaspe et al. 2010). The BODIPYs absorb light and they transfer this energy to the porphyrin, which drives electron transfer to the fullerene. This is just one example of the ways in which BODIPY ‘sensitizers’ are being used as antennae in light-harvesting systems—and there are many more.

Boranes as Fuels

We have considered above the boron hydrides, or boranes. Boranes share with the hydrocarbons very high heats of combustion, forming boron oxide, B2O3 + H2O, similar to the formation of CO2 + H2O upon combustion of hydrocarbons. For example, burning ethane (C2H6) produces 1,560 kJ/mol of energy, while burning diborane (B2H6) produces 2,138 kJ/mol. Boron hydrides can achieve higher energy densities than hydrocarbons, and so-called “zip fuels”—a family of jet fuels containing boranes as additives—were investigated during the cold war era. However, both the fuels and the exhaust were toxic and the boron carbide by-products of incomplete combustion caused problems with turbine blades. Their use was discontinued. The lighter members of the borane family, for example diborane (B2H6), are pyrophoric, which means that they spontaneously combust on contact with air. This property has been exploited in the case of triethylborane (an organoboron derivative), which was used to ignite the slippery and high flash-point jet fuel JP-7 used in the SR-71 Blackbird’s jet engine.

Hydrogen Storage

One of the most exciting possibilities of a post–fossil fuel world is the use of hydrogen as a fuel. Currently, hydrogen is transported and stored as a compressed gas. The steel cylinder used to store compressed hydrogen gas adds a lot of weight to the total system (for example, on-board storage in a hydrogen-powered car), poses the risk of working with high pressures, and cannot achieve an energy density as high as liquid gasoline. A safer, more efficient, way of storing hydrogen might be via chemical hydrogen storage. This concept requires a lightweight, hydrogen-rich material that can release hydrogen on demand under mild conditions, and be recharged by reversing the process, i.e. absorbing hydrogen to reform the hydrogen-rich phase.

![Image](image.png)

**Figure 6** In this BODIPY–porphyrin–fullerene molecular system for light harvesting, the BODIPY molecule acts as a sensitizer, absorbing a photon of light. This light energy is transferred to a zinc porphyrin electron donor and is used to drive electron transfer to the fullerene electron acceptor. This molecular chain is an example of how light energy can be converted to a flow of electrons and, ultimately, an electrical current.
Ammonia borane (BH\(_3\)–NH\(_3\)) contains 19.6% hydrogen by weight, releases hydrogen under mild conditions (temperatures around 100 °C) and has been intensively investigated as a chemical hydrogen storage material (Heldebrant et al. 2008).

**Boron Nitride**

If all the hydrogen is removed from ammonia borane, then the resulting chemical product is boron nitride (BN). This material is fascinating for several reasons, but first let’s think about it from fundamental principles. Boron, carbon and nitrogen have 3, 4 and 5 valence electrons, respectively. Hypothetical C\(_2\) and BN fragments each have 8 valence electrons. Extending this analogy, bulk carbon and bulk boron nitride should be isoelectronic and show similar chemical and materials behaviour. This turns out to be exactly the case. Just as carbon can exist as diamond and graphite allotropes, so boron nitride can exist in two similar phases (Fig. 7). The cubic form (sphalerite structure) is isostuctural with diamond, and although not quite as hard, has better thermal and chemical stability. Hexagonal BN has a graphite structure and is a good lubricant—again, its higher stability renders it useful under conditions too harsh for graphite itself. It has a high shear and is used as an additive in cosmetics to give them a pearly lustre. An exciting recent development in carbon chemistry is the production of carbon nanotubes—these are sheets of graphitic carbon rolled to make nano-sized tubes, and they have many applications. Just as might be expected from the relationship between BN and carbon, BN nanotubes are also known, but have rather different properties. Carbon nanotubes are metallic or semiconducting, while BN nanotubes are insulators. Buckminsterfullerene (C\(_{60}\)) is a cluster of 60 carbon atoms with the same symmetry as a soccer ball; BN fullerenes are also known, but are often observed as multiwalled, concentric structures (Zhi et al. 2008). All these new nanostructures are the subject of intense research as chemists and materials scientists work to understand their properties and develop new applications.

**Boron Compounds in Catalysis: Frustrated Lewis Pairs**

The electron deficiency typical of boron compounds manifests itself as strong Lewis acidity. Lewis acidity is a broader concept than simple proton acidity (also known as Bronsted acidity). Bronsted acid–base concepts define an acid (like hydrochloric acid, HCl) as a proton donor, and a base (like hydroxide ion, OH\(^-\)) as a proton acceptor.

The Lewis acidity concept recognises that a proton donor is also an electron pair acceptor and uses this as a definition of acidity. Thus, a Lewis acid is an electron pair acceptor and a Lewis base an electron pair donor. Trivalent boron compounds (denoted BX\(_3\) where X is any atom or group attached to boron) are very good Lewis acids. They contain only a sextet of electrons (three B–X bonds each requiring two electrons) and have a high driving force to accept a further pair of electrons (a Lewis base electron pair donor) to achieve an octet. A simple example is the reaction between BF\(_3\) (Lewis acid) and NH\(_3\) (Lewis base) to form the BF\(_3\)--NH\(_3\) complex which contains a new B–N bond. Ammonia borane (BH\(_3\)--NH\(_3\)), described above in the discussion on hydrogen storage, is an example of a Lewis acid–base complex.

Recent work in this sphere has extended this concept to what are termed “frustrated Lewis pairs” (FLPs). A boron Lewis acid with very bulky groups attached (BR\(_3\) where the R groups are large and take up a lot of space) coupled with a similarly bulky Lewis base results in an FLP. The bulky molecules want to form a complex with a new bond to boron but are prevented from doing so because the groups around

![Figure 7](image1.png)

**Figure 7** Cubic and hexagonal phases of boron nitride (BN) and a multiwalled BN nanotube. Reproduced from Zhi et al. (2008) with permission of the Royal Society of Chemistry.

![Figure 8](image2.png)

**Figure 8** Illustration of “frustrated Lewis pairs”. The bulky groups on boron and phosphorus mean the boron of the Lewis acid (C\(_{6}F_{5}\))B cannot get close enough to the phosphorus of the Lewis base P'Bu\(_3\) to form a B–P bond, resulting in a “frustrated Lewis pair”. If H\(_2\) is present, the pair reacts with hydrogen, with boron accepting a hydride (H\(^-\)) and phosphorus accepting a proton (H\(^+\)). Shown is the resulting ion pair (left) [(C\(_{6}F_{5}\))B]\(^-\) and (right) [HP'Bu\(_3\)]\(^+\) formed from the reaction of (C\(_{6}F_{5}\))B and P'Bu\(_3\) with H\(_2\). From Welch and Stephan (2007).
each partner take up too much space. The FLPs turn out to be very reactive combinations – the Lewis acid and Lewis base centres want to react with each other, but they can’t. So, instead the FLPs will react with other small molecules. In the example shown in Figure 8, the boron of the Lewis acid (C₅F₅)₃B cannot get close enough to the phosphorus of the phosphine Lewis base P₄Bu₅ (a phosphorus atom bonded to three branched organic groups) to form a complex with a B–P bond, but instead the FLP reacts with hydrogen, with the boron accepting a hydride (H⁻) and phosphorus accepting a proton (H⁺) (Welch and Stephan 2007). This uncoupling of H₂ into H⁺ + H⁻ is difficult to accomplish by other means. Although it burns readily (explosively!), hydrogen gas (H₂) is a relatively inert molecule and must be activated towards chemical reactivity, usually by catalysis. A catalyst is not consumed in the reaction but provides a pathway for the reaction to occur. Hydrogenation, or transfer of H₂ to other molecules to produce new chemical compounds, is of enormous importance in all kinds of chemistry ranging from drug synthesis to food processing. Typical catalysts are based on heavy elements such as palladium, which are useful on a laboratory scale but expensive and unsustainable on an industrial scale. Remarkably, the FLP/H₂ system using boron compounds as the Lewis acids turn out to be excellent hydrogenation catalysts (Stephan and Erker 2015). The significance of this is that expensive palladium catalysts could be replaced by a much cheaper and more readily available element like boron, avoiding the use of heavy metals altogether.

CONCLUSIONS

Modern boron chemistry, particularly molecular organoboron compounds, is coming of age with applications in new materials, sensing, medicine, catalysis, and energy all developing apace. In a world where there is increasing focus on future sustainability, one important driver is the development of chemical systems that do not rely on heavy metals for important transformations and processes. Boron, one of the lightest elements in the Periodic Table, fits the bill for this very well. The examples above illustrate some of the possibilities being pursued in current boron research. Some ideas have been around for a while (boron neutron capture therapy) whereas others are very new (frustrated Lewis pairs for metal-free catalysis and BODIPY compounds in light harvesting).

Tripping the light fantastic – the important applications of boron materials described above derive either from boron’s properties as a light-weight element or its ability to form fluorescent (light-emitting) organoboron compounds. Without a doubt, there will be more to come.

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Borate and the Origin of RNA: A Model for the Precursors to Life

Yoshihiro Furukawa and Takeshi Kakegawa

According to the RNA World hypothesis, ribonucleic acid (RNA) played a critical role in the origin of life. However, ribose, an essential component of RNA, is easily degraded: finding a way to stabilize it is critical to the viability of the hypothesis. Borate has been experimentally shown to have a strong affinity for ribose, and, thus, could have protected ribose from degradation in the formose reaction, a potential process for prebiotic ribose formation. Accumulation of borate on Hadean Earth (prior to ~4,000 Ma) might have been a key step in the chemical evolution of the biotic sugar. Proto-arcs are suggested as a geological setting sufficiently rich in borate to stabilize ribose during the Hadean.

Keywords: Hadean Earth, proto-arc, ribose, RNA, prebiotic

INTRODUCTION

Many questions remain concerning the prebiotic spontaneous formation of the building blocks of life and their polymerization to form functional polymers on Earth prior to ~4,000 Ma, i.e., during the Hadean. More specifically, according to the RNA World hypothesis, ribose (a type of sugar) [(1) in Fig. 1] played a critical role. However, it is one of the most unstable molecules among all the major potential building blocks. Thus, both the spontaneous formation and the accumulation of ribose is thought to be essential for the origin of life. In this article, we review experiments showing how borate plays an important chemical role in the formation and accumulation of ribose and of borate’s role in nucleoside phosphorylation, a critical step in assembling a phosphate and a nucleoside to form a monomeric unit of RNA. Furthermore, this article discusses the surface environments on Hadean Earth and introduces a plausible geological scenario for how and where borate might have accumulated during the Hadean.

PREBIOtIC CHEMISTRY ON BORATE AND RIBOSE

The RNA World Hypothesis and the Difficulty of Stabilizing Ribose

 Sugars are an indispensable part of the functional biomolecules that are used for the storage and expression of genes, for cell membranes, and for carrying energy. In ribonucleic acid (RNA) and deoxyribonucleic acid (DNA), ribose or 2-deoxyribose forms a structural framework with phosphate and is connected with nucleobases to form the sequence of the gene code. RNA is usually a single-stranded molecule that has a sequence of nucleobases comparable to DNA. The potential importance of RNA in the origin of life was proposed in the 1960s and later named the RNA World hypothesis (Crick 1968; Joyce 1989). In all living forms, gene information is stored in DNA as a sequence of nucleobases, whereas proteins are constructed from the gene information via RNA. Proteins catalyze many biochemical reactions, including the formation of DNA and RNA.

Thus, the three complex biopolymers of RNA, DNA, and proteins work together in all living forms.

It does not seem plausible that these three complex biopolymers arose simultaneously and then self-assembled into a complementary system within a cell compartment on prebiotic Earth. But, a scenario has been proposed whereby one type of polymer (RNA) works both as catalyst and gene-code template such that the system composed of RNA might have been ancestral to the present DNA–RNA–protein system of life (Crick 1968). Subsequently, researchers discovered that several RNAs catalyze biochemical reactions, as do enzymes.

Ribose is an aldopentose—a five-carbon monosaccharide with an aldehyde functional group—and the sole sugar in RNA (Fig. 1). It has many structural isomers, i.e., sugars having the same chemical composition but different structures, which can be seen in such compounds as xylose [(2) in Fig. 1], lyxose [(3) in Fig. 1], arabinose [(4) in Fig. 1], ribulose, and xylulose. They all form in the formose reaction in which formaldehyde [(5) in Fig. 1] and glycolaldehyde [(6) in Fig. 1] react in alkaline solutions with a cation catalyst such as Ca$^{2+}$ and Mg$^{2+}$ (e.g., Shapiro 1988). Experimental formation of detectable amounts of ribose in the formose reaction has been reported by Shapiro (1988). However, the reaction is sequential and the successive polymerization consumes previously formed sugars, including ribose. Ultimately, all the products polymerize into a brown caramel substance, a complex mixture of sugar polymers and their degradation products. Furthermore, the yield of ribose is limited in the formose reaction products compared with other aldopentoses because ribose is the least stable aldopentose (Larralde et al. 1995). Due to this low stability of ribose, some researchers have questioned the spontaneous accumulation of ribose and the subsequent formation of RNA on the prebiotic Earth (e.g., Shapiro 1986; Larralde et al. 1995).

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Borate Stabilization of Ribose may Be Critical to Forming Prebiotic RNA

Experiments support the suggestion that the preservation of ribose might have been mediated by borate. Borate is an oxianion of $B^{3+}$ and, in a wider sense, ‘borate’ refers to any compound containing an oxianion and hydroxyd anion of boron, e.g. $B(OH)_{3}$ and $B(OH)_{4}^{-}$. Thus, in this wider definition, the term ‘borate’ is also used to refer to minerals containing boron oxide/hydroxide, such as colemanite [Ca$_{5}$B$_{4}$O$_{9}$(OH)$_{3}$·H$_{2}$O]. In the present paper, oxianions of $B^{3+}$ in solution, such as $B(OH)_{3}$ and $B(OH)_{4}^{-}$, are referred to as ‘borate’, whereas solids containing borate, such as colemanite, are referred to as borate minerals.

Speciation of borate in solution depends on the solution pH: at pH < 9, trigonal $B(OH)_{4}^{-}$ is the dominant species, whereas at pH > 9, tetragonal $B(OH)_{4}^{-}$ dominates. The $B(OH)_{4}^{-}$ species can combine with a hydroxyl to form an ester (Van Duin et al. 1984), with cis-diols, in particular, forming a stable cyclic ester (Fig. 2B). Thus, sugars typically form complexes with tetragonal $B(OH)_{4}^{-}$. Research into how pentose–borate complexes form has shown that borate combines with the 1,2-diol and with the 2',3'-diol of ribose to form various ribose–borate complexes (Chapelle and Verchere 1988) (Fig. 2B). In aqueous solutions, each aldopentose appears in five different configurations ($\alpha$-furanose, $\beta$-furanose, $\alpha$-pyranose, $\beta$-pyranose, and a linear aldehyde form). The proportions of ribose at equilibrium in water are 9% in the aldehyde form, 70% in the $\alpha$- and $\beta$-pyranose form, and 21% in $\alpha$- and $\beta$-furanose form (Fig. 2). When ribose forms a complex with borate, all ribose molecules that are fixed in the furanose form are far less reactive than when in the aldehyde form, thereby decreasing the degradation rate of ribose (Chapelle and Verchere 1988). Among the four aldopentoses, borate forms complexes preferentially with ribose (Chapelle and Verchere 1988; Furukawa et al. 2013).

The formose reaction is promoted in high-pH solutions (Fig. 2C). However, the stability of ribose and other sugars decreases with increasing pH (Larralde et al. 1995) because the reactivity of ribose increases with increasing pH. The dissolved borate species $B(OH)_{4}^{-}$ does, in fact, lead to the condensation of glycer aldehyde and glycolaldehyde to form ribose in better yields than the reactions in borate-free solutions (Ricardo et al. 2004). The stability of ribose itself was shown to increase in borate solutions (Scorei and Cimpoiaşu 2006). Furukawa et al. (2013) compared the effects of borate, $B(OH)_{4}^{-}$, on all four aldopentoses and found that ribose is selectively stabilized by borate in a concentrated borate solution (80 mM) but the other aldopentoses continued to degrade. The strong affinity of borate does selectively stabilize ribose, the least stable of the aldopentoses, yet ribose is the only aldopentose found in RNA. Dissolved silicate, Si(OH)$_{4}^{-}$, has also been proposed as a stabilizer of sugars in the formose reaction under different conditions from those experienced by borate (Lambert et al. 2010). Quantitative comparison experiments showed that silicate certainly improves the stability of pentoses, but the effect is smaller than that of borate and does not lead to the selective stabilization of ribose (Nitta et al. 2016). Phosphate is also an essential component of RNA because it combines with ribose to form the sugar–phosphate backbone of RNA. But, the effects of dissolved phosphate on the stabilization of pentoses are negligible (Nitta et al. 2016). These results suggest that borate is the most effective simple compound for stabilizing ribose in abiotic environments.

Experiments also reveal that borate can affect the phosphorylation of ribonucleoside, a reaction for which a phosphate group combines with nucleoside, itself composed of a ribose and a nucleobase. This reaction is a critical step in the assembly of ribonucleotide, a monomeric unit of RNA. During phosphorylation of ribonucleoside, phosphate randomly forms esters at three different hydroxyl positions in ribonucleoside: 2', 3', or 5'-hydroxyl, as shown for the adenosine structure in Figure 3. The products of phosphorylation at 3'- and 5'-hydroxyl are the ribose–phosphate linkages found in terrestrial biota. Curiously, the 2'-hydroxyl form of ribose–phosphate has not been reported.

Ribonucleoside can form a complex with borate at its 2',3'-diol position when in water and also with formamide [(7) in Fig. 3] (Furukawa et al. 2015; Kim et al. 2016). As illustrated in Figure 3, the bound borate inhibits phosphorylation at 2'- and 3'-hydroxyl, which results in the selective phosphorylation at the 5'-hydroxyl to form 5'-monophosphate [(8) in Fig. 3] (Furukawa et al. 2015; Kim et al. 2016). Activated 5'-monophosphate can form long ribose (1). Ribose is a minor product. Successive reactions degrade ribose into brown caramel.
oligonucleotides when dried in the presence of montmorillonite, a clay mineral catalyst (Ferris et al. 1996). Thus, the formation of 5'-monophosphate would be an important step to forming primordial RNA. And although long oligomers can be formed from 2',3'-cyclic monophosphate, further investigations are needed to understand exactly how. Unlike borate, dissolved silicate has almost no effect on the selection of the phosphorylation site of a ribonucleoside (Furukawa et al. 2015).

Borate also mitigates another serious problem in phosphorylation: the low reactivity of phosphate minerals. There is not sufficient phosphate dissolved in natural aqueous environments for phosphorylation to easily proceed because most phosphate is bound in the relatively insoluble minerals of the apatite group. However, Kim et al. (2016) showed that the magnesium phosphate borate mineral lüneburgite \([\text{Mg}_3\text{B}_2\text{O}_5(\text{OH})_2\text{PO}_4\_2\_6\text{H}_2\text{O}}\) is effective in phosphorylating a nucleoside: it can selectively yield good amounts of nucleoside 5'-monophosphate in aqueous solutions. In this latter case, borate is extracted from lüneburgite and subsequently bound to the 2'-hydroxyl and 3'-hydroxyl of ribose. The phosphate released from lüneburgite is then utilized for phosphorylation of a nucleoside before it can precipitate as insoluble phosphates. The formation of Mg-borate minerals during the Hadean has been suggested by Holm (2012). Thus, borate could have mediated selective phosphorylation on the Hadean Earth.

BORATE IN THE EARLY ARCHEAN AND HADEAN

Borate-rich Environments in the Early Archean

The strong chemical affinity between ribose and borate suggests that ribose could have accumulated in places where borate is highly concentrated. Enrichment of borate is commonly found in modern continental evaporite basins, followed by the precipitation of borate minerals, e.g. colemanite. Such evaporite basins have been considered as ideal localities to promote prebiotic ribose formation...
(Ricardo et al. 2004). But Grew et al. (2011) questioned whether continental evaporites were present during the Hadean. This skepticism has now resulted in contradictory models as to where prebiotic ribose might have formed.

The surface environments of early Mars are often considered as “suitable” for prebiotic ribose formation. The NASA Curiosity rover detected 10–100 ppm B in calcium sulfate veins in Mars’ Gale Crater (Gasda et al. 2016), which is comparable to amounts present in terrestrial clay-rich sediments (~100 ppm). This discovery supports the suggestion that the first prebiotic ribose may have formed on ancient Mars (Kirshvink et al. 2006). This model presumes not only that the water-rich ancient Earth could not concentrate borate and, therefore, was unsuitable for ribose genesis, but also that any RNA generated on Mars then survived the trip from Mars to Earth. However, there remains as much ambiguity regarding the availability of concentrated borate and the feasibility of the formose reaction on early Mars as on early Earth.

The Hadean Earth has attracted the interest of researchers in ribose genesis. Modern marine sediments can contain up to 258 ppm B (Williams et al. 2001). Seawater alteration of oceanic volcanic rocks is often accompanied by boron enrichment, particularly when associated with ultramafic rocks (Boschi et al. 2008). Boron in altered ultramafic rocks is released during the dehydration of a subducting plate, borate accumulating in the released alkaline fluids. The borate-rich alkaline fluids discharge on the seafloor to form mud volcanoes in the forearc regions. Holm (2012) suggested that such borate-rich alkaline fluids were present even in a Hadean subduction zone, and such fluids were responsible for ribose formation. However, relatively few scientists believe that a modern-style subduction system, with its dehydration at specific depths and concomitant borate release from altered rocks, was present during the Hadean.

Did Prebiotic Ribose Formation Occur in a Proto-arc?

The presence of an accreted ophiolite complex in the Isua Supracrustal Belt (ISB) of west Greenland provides evidence for plate tectonics in the early Archean (Furnes et al. 2007). A proto-arc model has been proposed to explain tectonic evolution of the 3.8 Ga to 3.7 Ga ISB (Nutman et al. 2015). In this model, segments of oceanic crust were accreted to form a proto-arc, while tonalite–trondhjemite–granite (TTG) suites were generated by melting accreted materials at the base of the proto-arc (Fig. 4).

Tourmaline, a chemically diverse group of borosilicate minerals, has been widely reported in the ISB (e.g. Appel 1995; Mishima et al. 2016). Based on boron isotope compositions, Grew et al. (2015) suggested that the concentration of boron necessary for the generation of abundant tourmaline in the ISB was attained in a partially isolated basin by hydrothermal processes in a proto-arc setting (Fig. 4). Boron could have been initially extracted by deep fluids from the TTG suites, from accreted sediments (shown brown with white dots in Fig. 4), and/or from mafic/ultramafic rocks (shown in green and blue with white dots in Fig. 4). These deep fluids were discharged into the ancient oceans as hydrothermal fluids. Nutman et al. (2016) reported primary evaporitic carbonate in the ISB that could have been deposited from alkaline brines in a shallow and partially isolated basin on the proto-arc. Therefore, an early Archean proto-arc could have provided marine environments that were both boron-rich and alkaline.

Hadean zircon crystals have been found from Jack Hills in Australia. These pre–4 Ga zircons have higher oxygen isotope ratios than zircons in oceanic crusts, they have similar U/Yb ratios to Phanerozoic and Archean continental and island arc crusts, and they have higher Li concentrations than normal magmatic ocean-crust zircon. Such geochemical characteristics of Hadean zircon indicate that they formed from a granitic parent magma in TTG-like proto-continental crust (Valley et al. 2010). The Hadean zircons do not necessarily show that a proto-arc was present during the Hadean, but a proto-arc is nonetheless a plausible candidate to produce Hadean juvenile crust.

White dots represent boron-rich clays. TTG = tonalite–trondhjemite–granite suite.

**Figure 4** Proto-arc model for the early Archean and Hadean, and the proposed locations of Hadean boron-rich environments (Grew et al. 2015; Nutman et al. 2015).
We suggest that environments created by a Hadean proto-arc were ideal not only for TTG genesis but also for prebiotic ribose formation. In isolated and shallow basins on the proto-arc, evaporation may have helped to concentrate borate, supplemented by any continued influx of borate from hydrothermal fluids (Fig. 4). Formaldehyde, the source material of the formose reaction, is a water-soluble volatile and is formed by photochemical reactions between CO₂ and H₂O (Fig. 1). Formaldehyde in seawater in a shallow basin can be concentrated spontaneously through azeotropic evaporation (up to ~4 mol/L, theoretically). The water in this postulated isolated and shallow basin would be alkaline, as has been inferred for the ISB shallow basin, although the first open oceans were most likely acidic (Russell 2007). Therefore, such isolated alkaline conditions favoured the formation of sugars by the formose reaction. Concentrated borate in such an alkaline basin might have helped to form and preserve ribose selectively, as well as to form oligonucleotides through phosphorylation.

Boron-rich and alkaline environments are also expected locally around mud volcanoes on the slopes of a proto-arc (shown in yellow in Fig. 4), similar to the model proposed by Holm (2012). The presence of alkaline fluids at mud volcanoes during the early Archean is indicated by variable zinc isotope compositions from ISB serpentines (Pons et al. 2011). Furthermore, deep marine sediments in the proto-arc would have provided a boron-rich alkaline environment (Mishima et al. 2016). Thus, the formose reaction could also have proceeded in relatively deep marine environments around Hadean proto-arc. As the result, the spontaneous formation and accumulation of ribose could have been promoted in Hadean proto-arc environments. Preferential stabilization of ribose by borate in prebiotic Earth might explain why ribose became the sugar component in nucleic acids.

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Holm NG (2012) The significance of Mg in prebiotic geochemistry. Geobiology 10: 269-279
What has the MSA Council been up to?

The second Mineralogical Society of America (MSA) Council meeting of 2017 was held 19–20 May 2017, so I am reporting here on some of the more interesting activities afoot. First, the meeting stretched over two days because we decided that some issues, such as the future of MSA and its forthcoming centennial celebration in 2019, needed more time for discussion and brainstorming than a one-day meeting would allow. Planning for a centennial celebration event moves forward under the leadership of Peter Heaney, who has announced his activities and an invitation to participate in planning through the MSA-talk list-server. An event in June 2019, probably in Washington DC will be a feature, but sessions at IMA2018, Goldschmidt2018, GSA2018 and perhaps elsewhere are planned to focus on the next 100 years of the MSA, including the status of our sciences and their relevance to society. Contributions of ideas, effort, and support are encouraged for our centennial and related celebrations.

The main activities of MSA continue to be publishing and outreach, the latter via the highly regarded lecture program, student grants, Mineralogy-4-Kids, and a few other resources. To keep the outreach programs healthy and growing, we need to maintain funding and engagement. Thus, council is seeking ways to support these valuable programs more substantially, particularly with targeted sponsorships, stronger endowments, or new ones. This requires searching for benefactors and supporters who can enhance annual giving or who can provide legacies. We are working on expanding the Benefactors Committee, a small group of people who will engage with corporations, members, and mineral collectors and dealers. Clearly, this connects with a Capital Campaign organized around the Centennial Celebration. We encourage members to continue their generous support of the MSA and to communicate your ideas on how the MSA can be made financially stronger.

Another concern has been the representation of the MSA at meetings, because we do not sponsor our own meetings. MSA participates in both Geological Society of America (GSA) meetings and international Goldschmidt conferences through cosponsorship of sessions and social receptions. However, members may have forgotten that when volunteering a session to these meetings, they can suggest MSA as a cosponsor and connect members to the sessions. We will be reassembling a Meetings Committee to assist in organizing sessions with an MSA flavor and identifying volunteered sessions that are appropriate for MSA cosponsorship. From time-to-time the MSA has been represented with a booth at regional GSA meetings, which are strongly attended by students. We believe these meetings are an excellent venue to identify MSA to students and promote membership. We will be setting up a program to provide materials from the MSA Office for representatives to set up a table to be advocates for the society at these regional meetings. Expenses of manning the booth and the attendees’ registration will be reimbursed. Details are in development, but we hope this will be an attractive opportunity for MSA membership and as a means of encouraging students to attend these meetings.

I hope this letter gives you some sense of what MSA Council has been concerned with lately, things that go beyond the normal responsibilities of the separate organizing committees, approving budgets, reviewing ongoing activities, and the other traditional activities.

George Harlow
2017 MSA President
“Roebling Lecture: The Effects of Solid–Solid Phase Equilibria and Partial Melting on the Oxygen Fugacity of the Upper Mantle.” At 3:30 p.m., Thomas W. Sisson will present, “Dana Medal Lecture: Magma Generation in the Quaternary Cascades.” At 4:00 p.m., Dustin Trail will present, “MSA Award Lecture: An Accessory Mineral and Experimental Perspective on the Evolution of the Crust.” At 4:30 p.m., George Harlow will give his MSA Presidential Address. The MSA/GS/MGVP Joint Reception will round off the day at 5:45 p.m.–7:30 p.m.

Topical sessions have been proposed for awardees:


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**MSA CONTRIBUTORS AND BENEFACTORS**

Many members contribute to MSA by including a contribution with their annual dues and/or by responding to special appeals. Depending on the wishes of the member, the money is deposited with the principal of the MSA Endowment, MSA Outreach, MSA Mineralogy/Petrology, J. B. Thompson, Edward H. Kraus Crystallographic Research, Bloss, or General Operating Funds. The income of these funds is used to support MSA’s research grants in crystallography, mineralogy, and petrology; publishing of the American Mineralogist; the MSA Undergraduate Prizes; the Mineralogical Society of America Award; the Distinguished Public Service Award; the Dana Medal; the Roebling Medal; the website; and the lectureship program. If you have not done so previously, you may use the Contributions to MSA form on the MSA home page (http://www.minsocam.org) or contact Mineralogical Society of America, 3635 Concorde Pkwy Ste 500, Chantilly, VA 20151-1110 USA phone: +1 (703) 652-9950 fax: +1 (703) 652-9951 e-mail: business@minsocam.org. Cost is $30 ($22.50 members MSA, GS, CMS).

**SHORT COURSE ON PETROCHRONOLOGY**

Organizers: Matthew Kohn (Boise State University, USA); Martin Engi (University of Bern, Switzerland); Pierre Lanari (University of Bern).

Dates: 20–21 October 2017

Location: Washington State Convention Center (WSCC), Seattle (USA).

Petrochronology uses geochemistry, textures, thermodynamics, and various types of modeling to integrate the ages of individual minerals in a petrogenetic context. Examples include the use of crystal domain-specific trace-element patterns or thermometers in minerals such as zircon, garnet, and feldspar to link an age to an overall P–T–t path or the evolution of a magma or metamorphic rock. The course will review petrochronologic methods, both conceptual and analytical, and illustrate how accessory and major minerals may be used to understand igneous and metamorphic processes.

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**NEW TITLE: REVIEWS IN MINERALOGY AND GEOCHEMISTRY**

**Volume 83: Petrochronology: Methods and Applications**

Matthew J. Kohn, Martin Engi, and Pierre Lanari, editors.


What is “petrochronology”? Petrochronology is the study of rock samples that links time (i.e. ages or duration) with specific rock-forming processes and their physical conditions. A single date is virtually useless in understanding the history of magma crystallization or metamorphic pressure–temperature evolution. Petrologists and geochronologists strive to understand rock-forming processes and the time and the rates at which they occur by integrating numerous ages into the petrologic evolution of a rock. Petrochronology: Methods and Applications (v83 in the RIMG series) covers phase relations and reaction sequences in petrochronology; local bulk composition effects on metamorphic mineral assemblages; diffusion; petrochronology by electron microprobe, laser-ablation inductively coupled plasma mass spectrometry, secondary ionization mass spectrometry analysis, and thermal ionization mass spectrometry techniques; specific examples of petrochronology using zircon, baddeleyite, monazite, allanite, xenotime, apatite, titanite, rutile, and garnet; and the chronometry and geospeedometry of magmatic processes using chemical diffusion in olivine, plagioclase and pyroxenes.

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**NEW TITLE**

**Care and Documentation of Mineral Collections**


This work is an attempt to provide information and guidance on all aspects of caring for and documenting mineral collections. It is aimed at professionals and amateurs alike and is dedicated to everyone who shares a love of minerals and those who care for and about collections. Topics include: Collection Organization, Documentation Ancillary Collections, Preventive Conservation, Collection Organization, Storage, Hazards, Safety, and Risks, Administrative Policies, Private Collections, and Bibliography and Resources.

Description and ordering online at www.minsocam.org or contact Mineralogical Society of America, 3635 Concorde Pkwy Ste 500, Chantilly, VA 20151-1110 USA phone: +1 (703) 652-9950 fax: +1 (703) 652-9951 e-mail: business@minsocam.org. Cost is $30 ($22.50 members MSA, GS, CMS).
**ELSEVIER PHD STUDENT RESEARCH GRANT WINNERS**

The International Association of GeoChemistry (IAGC) is happy to announce the recipients of the 2017 Student Research Grants, sponsored by Elsevier and the IAGC. The PhD Student Research Grant program assists geochemistry PhD students to acquire geochemical analyses in support of their dissertation research. Every year, we have many strong research proposals from students from around the world, and every year the awards become even more competitive. This year we allocated more funds so we could distribute five awards. The success of these grantees demonstrates the high caliber of their research. Congratulations to our grantees!

**Bryce Mitsunaga** (University of California, Los Angeles, USA). “A Reconstruction of Temperature and δ18O Data since the Last Glacial Maximum using Soil and Gastropods from the Chinese Loess Plateau.”

Bryce Mitsunaga graduated from Williams College (Massachusetts, USA) with a BA in geosciences and is currently a PhD student in the department of Earth, Planetary, and Space Sciences at the University of California, Los Angeles. Bryce is exploring several applications of the carbonate “clumped” isotope thermometer: one project involves a reconstruction of central Asian climate during the last ice age using δ18O, δ13C, and multiple heavy-isotope CO2 data from soil carbonates and fossil terrestrial snail shells. The second project proposes to characterize conditions at the Meso-Neoproterozoic boundary through analyses of CO2 and trace metals from billion-year-old Lake Superior stromatolites in North America. He is also studying the systematics of CO2 isotopologue thermometry through establishing baseline values of artificially reordered minerals. By this, he hopes to better quantify the fractionation that occurs during carbonate dissolution in acid.

**Maxence Guillermic** (Institut Universitaire Européen de la Mer, France). “Past Evolution of Ocean Carbon Sources and Sinks in Response to Climate Change.”

Maxence Guillermic is a PhD student at the Institut Universitaire Européen de la Mer (IUEM, France), with co-advisors at the University of California, Los Angeles (USA) and the University of Cambridge (UK). Maxence is working at the intersection of marine geochemistry and paleoceanography. He reconstructs Cenozoic pH and pCO2 changes using boron isotopes (δ11B, which is a pH proxy) and trace element analyses (e.g. B/Ca, Mg/Ca) on multiple foraminifera species, and will learn about so-called clumped isotopes (a temperature proxy). The goal of his thesis is to understand the role of past changes in marine carbon sources and sinks during critical climate transitions when there is evidence for changes in atmospheric greenhouse gas levels. Maxence earned an MSc in marine chemistry from IUEM in 2015 in which he characterized the isotopic composition of germanium in seawater.

**Suzette Timmerman** (Australian National University, Australia). “Diamonds – Time Capsules of Volatiles and the Key to Dynamic Earth Evolution.”

Suzette Timmerman earned her BSc in Earth sciences in 2012 and MSc in solid Earth in 2014 at the VU University Amsterdam (Netherlands). She is currently doing her PhD at the Research School of Earth Sciences at the Australian National University (Australia). Her work focuses on the origin and cycling of volatiles in the mantle by studying diamond samples from Brazil, Southern Africa, and Australia. Suzette uses diamond samples with ages ranging from 3.2 Ga to 0.07 Ga to study noble gas compositions in the mantle through time. Noble gas analyses will be complemented by cathodoluminescence imaging, nitrogen content and carbon isotope analyses, major element analyses of mineral/fluid inclusions, and trace element analyses to constrain the growth environment and the diamond-forming fluid. She will also compare lower mantle/transition zone and upper mantle diamonds for their noble gas compositions and will examine eclogitic and peridotitic diamonds to evaluate if noble gases were subducted down into the diamond stability field. This will help to develop a better high-resolution model of the structure of the Earth’s mantle and its evolution.

**Kirstin Washington** (University of Southern California, USA). “Weathering and Climate from the Middle Devonian to the Upper Permian.”

Kirstin Washington earned her Bachelors in environmental sciences (2011) and MS in applied geosciences (2012) from the University of Pennsylvania (USA). She is currently a PhD student in the Department of Earth Sciences at the University of Southern California (USA). Her research focuses on understanding past and present chemical weathering processes. She utilizes dissolved δ7Li ratios of modern river water and hydrothermal fluids to investigate the relationship between low- and high-temperature rock/water interactions. Additionally, she is pairing δ7Li compositions of ancient carbonates and clumped isotope thermometry to understand the relationship between climate, chemical weathering, and biotic changes over geologic timescales. She measures δ7Li ratios via multicollector inductively coupled plasma mass spectrometry (MC–ICP–MS) and carbonate clumped isotopes using a specially configured mass spectrometer.

**Mabrouk Sami** (University of Vienna, Austria). “Rare Metal Granites, Central Eastern Desert, Egypt: Geochemistry and Economic Potentiality Red Sea Mountains, Eastern Desert, Egypt (Nubian Shield in East Africa).”

Mabrouk Sami earned his BSc (Hons) in Earth sciences and MSc in geochemistry/exploration from Minia University (Egypt). He is currently a PhD student in the Department of Lithospheric Research at the University of Vienna (Austria). He studies the mineralogy, geochemistry and geochronology of rare metal–bearing granitoids in the Central Eastern Desert of Egypt. His work focuses on unravelling the timing and sources of rare metals [such as Nb, Ta, Th, U, Sn and rare-earth elements (REEs)] that become enriched in highly fractionated granitic rocks using whole-rock chemistry (major, trace and REEs), U–Pb zircon and Sr–Nd radiogenic isotopes. The composition of rare metal economic minerals will be determined by electron microprobe analysis and laser ablation inductively coupled plasma mass spectrometry. Mabrouk has already used a combination of these different geochemical methods to understand the petrogenesis and magmatic processes that controlled the formation of certain Egyptian highly fractionated granitoids and their associated rare metal mineralization.
THE OMAN DRILLING PROJECT: A MILESTONE IN THE “MOHOLE TO MANTLE” (M2M) PROJECT

Japanese scientists and Japan’s deep-sea scientific drilling vessel Chikyū are deeply involved in the Oman Drilling Project (Oman DP; http://www.omandrilling.ac.uk/), which is itself part of the International Continental Scientific Drilling Program (ICDP). From December 2016 to March 2017, Phase I drilling of the southern Oman ophiolite (Fig. 1) resulted in a total of 1,500 m of hard-rock cores being recovered. Measurements of the geophysical properties and geological description of the cores will be carried out on board the Chikyū in the summer of 2017 by shipboard scientists who applied to be involved from all over the world. The project has been nicknamed ChikyūOman. These cores have been sent to Japan for further study.

The crust–mantle boundary, called the Moho Transition Zone (MTZ), in this region is thought to represent an active reaction zone where melts from a mid-ocean ridge basalt (MORB) accumulated and reacted with peridotites to form dunites (e.g. Boudier and Nicolas 1995; Kelemen et al. 1997; Korenaga and Kelemen 1997; Koga et al. 2001; Akizawa et al. 2012; Nicolle et al. 2016; Rospabé et al. 2017). Drilling into the MTZ is planned as Phase II of the Oman DP, and should take place from November 2017 to March 2018 (Fig. 1). The relationship between the MTZ and the major seismic-reflection boundary that is the Mohorovičić (Moho) discontinuity is still open to debate. The cores drilled through the Oman MTZ, and the geophysical logging of the boreholes, will provide a unique opportunity to evaluate and clarify the relationship between the Moho and the MTZ. This data will be essential for any future Moho projects – drilling from the crust down to the Moho – one of which may be part of a future International Ocean Discovery Program (IODP) drilling project. The ultimate goal of the Oman DP is to help carry out the IODP’s “Mohole to Mantle” (M2M) project, which aims to drill through a complete section of oceanic crust in the Pacific Ocean and into the underlying mantle (Kelemen et al. 2013). In this regard, the Oman DP and ChikyūOman can together be regarded as a milestone in the progress towards the M2M project.

Eiichi Takazawa
Niigata University / JAMSTEC

REFERENCES


JOURNAL OF MINERALOGICAL AND PETROLOGICAL SCIENCES

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Original Articles

Abuite, CaAl2(PO4)3F2, a new mineral from the Hinomaru-Nago mine, Yamaguchi Prefecture, Japan – Satomi ENJU and Seichiro UEHARA

Precipitates within olivine phenocrysts in oxidized andesitic scoria from Kasayama volcano, Hagi, Japan – Terumi EJIMA, Mari YONEDA, Masahide AKASAKA, Hiroaki OHFUJI, Yoshiaki KON, Mariko NAGASHIMA and Yoshihiro NAKAMUTA

Letters

Sintering nanocrystalline diopside from pulverized diopside crystals – Yumiko TSUBOKAWA and Masahiro ISHIKAWA

Carbogenic fluid inclusions in a garnet–pyroxene granulite from Austhovde in the Lützow–Holm Complex, East Antarctica: Implications for a decompressional P-T path – Kazuki TAKAHASHI and Toshiaki TSUNOGAE
THE CANADIAN MINERALOLOGIST (IS NOT DEAD)

With apologies to Mark Twain, but reports of our demise are greatly exaggerated. As I am sure you, the reader, know, the business collapse of our typesetter and their attempts to hide the extent of their troubles resulted in the journal being more than a year behind. However, at the time of writing – 1 June 2017 – the September 2016 issue was online, the November 2016 issue was due to go online in mid-June, and our new typesetter (Allen Press) was confident that all remaining issues, including the July 2017 issue, will be online by the time you read this at the end of July.

Our revival is largely due to the superhuman efforts of our editorial team: Managing Editor Mackenzie Parker, who didn’t take a day off at Christmas (but is threatening to go to Disneyland in September), and Editorial Assistants Jordan Roberts and Donald (“DJ”) Lake, who put their Masters theses on hold to help save the journal. I will profile in a future article those who comprise what has to be the youngest, most enthusiastic, and perhaps unusual, editorial team anywhere. I also thank our authors for their patience and understanding, our associate editors for standing by us, and the team at Allen Press, who until recently had to contend with damaged files from the previous typesetter but who went well beyond the normal to help us catch up. A special thanks goes to the MAC Council for their unwavering support during a very difficult time.

The great news for authors is that our average submission-to-publication time has fallen to under four months. So … send us your manuscripts, especially if you want them published quickly.

To celebrate our rebirth and to communicate with authors our exciting ideas for the future we are planning some special events at the upcoming 2017 Geological Society of America Annual Meeting, to be held 22–25 October in Seattle (Washington, USA); at the 2018 Resources for Future Generations (RFG) conference to be held 16–21 June in Vancouver (Canada); and at the 2018 International Mineralogical Association conference to be held 13–17 August in Melbourne (Australia). There is also talk of a barbeque at the Vancouver meeting. See you there!

Sincerely yours, Lee A. Groat
Editor, The Canadian Mineralogist

2017 MAC AWARDS

The Mineralogical Association of Canada (MAC) is pleased to announce its award winners for 2017.

Hawley Medal Winners

The Hawley Medal is awarded to the best paper published in the Canadian Mineralogist. The 2017 award went to David Jenkins, Albert Chan, and Darby Dyar for their paper, “Partitioning of Chlorine between NaCl Brines and Ferro-Pargasite: Implications for the Formation of Chlorine-rich Amphiboles in Mafic Rocks”, which appeared in the January 2016 issue of Canadian Mineralogist (v54, pp 337–351).

Chan, Jenkins and Dyar conducted hydrothermal experiments to measure the partitioning of chlorine between brine and amphibole. The careful characterisation of the reactants and products and the development of a thermodynamic model to relate amphibole chemistry and brine chemistry allowed the results to be applied to high-grade metamorphic rocks and to seawater–ocean floor alteration. The work provides an excellent example of the application of mineralogy to understanding Earth processes.
Peacock Medal to Heather E. Jamieson

The Peacock Medal, the highest award bestowed by the Mineralogical Association of Canada, is awarded to Heather E. Jamieson of Queen’s University (Kingston, Ontario, Canada) for her outstanding contributions to the minerals sciences.

Heather E. Jamieson is a professor at Queen’s University in Geological Engineering and Geological Engineering and seconded 50% to the School of Environmental Studies. She received her undergraduate degree from the University of Toronto (Canada) and her PhD from Queen’s. She held an NSERC post-doctoral fellowship at the Geological Survey of Canada. Heather’s expertise is in the area of environmental geochemistry and mineralogy, particularly the mineralogical controls on the mobility and bio-accessibility of metals and metalloids such as arsenic, antimony, the rare-earth elements and lead in mine waste. She has pioneered the application of synchrotron-based microanalysis and quantitative mineralogy to metal speciation in mine tailings, soils and sediments. She and her graduate students have recently demonstrated the persistence and pervasive presence of arsenic trioxide from historic roaster stack emissions in lake sediments and soils in the Yellowknife region (Canada). Much of her fieldwork is in the Canadian North, but she has also conducted research in Nova Scotia (Canada), Chile, Peru, USA, Spain and Australia. She has supervised more than 40 graduate students, all of whom are now working as academics, environmental consultants or regulators. She has recently coedited and contributed a chapter to the book Arsenic: Environmental Geochemistry, Mineralogy and Microbiology (volume 79 of the Reviews in Mineralogy and Geochemistry series).

Young Scientist Award to Siobhan (Sasha) Alexandra Wilson

The Young Scientist Award is given to a young scientist who has made a significant international research contribution and a promising start to a scientific career. This year’s awardee is Siobhan (Sasha) Alexandra Wilson, who is a Senior Lecturer in the School of Earth, Atmosphere and Environment at Monash University in Melbourne (Australia) and an ARC [Australian Research Council] Discovery Early Career Researcher Award Fellow.

Sasha Wilson obtained her BSc (Honours) in physics from McMaster University (Ontario, Canada) in 2003 and her MSc and PhD in environmental geochemistry from the University of British Columbia (Canada) in 2006 and 2010, respectively. Sasha held a NASA Postdoctoral Fellowship at the University of California (USA) node of the Astrobiology Institute from 2010 to 2011. She has been a faculty member at Monash University since 2011. She received the 2016 E. S. Hills Medal from the Geological Society of Australia for her contributions to geochemistry. Sasha leads the Environmental Geochemistry Experimental Laboratory at Monash University. Her team’s applied work focuses on tailoring element cycles for carbon, metal and metalloid sequestration within minerals in geo-engineered landscapes, mining environments and mineral processing circuits. On the fundamental side, her group is developing the use of alteration minerals in meteorites and fossils for (palaeo) environmental reconstruction, working to understand the role of gas–mineral reactions in sedimentary systems, and elucidating the relative roles of microbial metabolism and organic geochemistry in organo-mineralisation.

WELCOMING NEW MEMBERS OF THE MAC COUNCIL

The MAC Executive approved the nomination of the two candidates below for the two positions of councillor for 2017–2020. As no additional nominations were received from the membership, the nominated candidates were declared elected by acclamation.

Councillors 2017–2020

Kriss Leftwich is an application scientist at PROTO Manufacturing (Canada), where she contributes a geological/mineralogical perspective to powder X-ray diffraction products. Under PROTO, she also runs grant and community outreach programs, including the PROTO Advantage Grant and donating time/resources to local schools to encourage students to engage in science, technology, engineering and mathematics (STEM) programs. She has a BS (2010) in geology from Western Kentucky University (USA). Between 2008 and 2010, her undergraduate research focused on sequestration and storage of the radioactive waste products of Cs and Rb by synthesized and natural zeolites (adviser: Dr. Aaron Celestian). In 2008, under the direction of Dr. Denton Ebel, she participated in an NSF-funded “Research Experience for Undergraduates” at the American Museum of Natural History (New York, USA) studying the modal mineralogy of the CV chondrites Vigarano, Grossnaja, Allende, and Leoville using an electron microprobe for elemental mapping. In 2015, she obtained an MS at Indiana University (USA) in mineralogy (adviser: Dr. David Bish). This work contributed to the investigation of hydration cycles of minerals and their potential influence on the (bio-)availability of water on Mars. Her focus in this work was on salt minerals’ hydration cycles (MgCl2·nH2O, NaMg(SO4)2·nH2O, and KClMgSO4·nH2O systems), with the thesis “Hydration/Dehydration Behavior of Minerals under Mars-Relevant Conditions”. Her industrial experience also includes asbestos analysis via polarized-light microscopy and a variety of wet-chemistry analytical techniques.

Aaron J. Lussier is a research scientist in mineralogy at the Canadian Museum of Nature (Ottawa, Canada). He has completed a BSc in geology (Honours) in 2003 at the University of Manitoba (Canada), an MSc at McGill University (Canada) in 2006, and a PhD at the University of Manitoba in 2011. His doctoral research, conducted under the advisership of Dr. Frank C. Hawthorne, focused on the crystal chemistry of light-ion-bearing tourmaline minerals. Upon receiving an NSERC Post-doctoral Fellowship Award, he worked with Dr. Peter C. Burns at the University of Notre Dame (Indiana, USA) on aspects of the crystal chemistry of uranium minerals. In early 2017, he joined the Canadian Museum of Nature. Dr. Lussier’s current research interests focus on the discovery and characterization of new mineral species, investigating the importance of nanomineral phases in geochemical transport processes, and understanding mechanisms controlling compositional variability in zoned minerals during crystal growth. Aaron also received a Distinguished PhD Dissertation Award in 2012, the Winthrop Spencer Gold Medal in 2012, the Faculty of Earth Science PhD Thesis Prize in 2012, a NSERC PhD Post Graduate Scholarship for 2006–2008 and a NSERC Canada Graduate Scholarship for 2004–2005. In addition to his recurring contributions to the Canadian Mineralogist, Dr. Lussier has published several papers with the American Mineralogist, Mineralogical Magazine, and Periodico di Mineralogia.
Mineralogical Society of Great Britain and Ireland

www.minersoc.org

MINERALOGICAL SOCIETY NEW BOOK TITLES

This issue of *Elements* sees a veritable feast of new book content in the joint European Mineralogical Union–Mineralogical Society series, the EMU Notes in Mineralogy.

Two new volumes have been published in the EMU Notes in Mineralogy series:

**Volume 17—Redox-Reactive Minerals: Properties, Reactions and Applications in Natural Systems and Clean Technologies**

Minerals are naturally occurring inorganic solids that make up the solid part of most solar terrestrial planets. Redox-active elements such as iron, manganese, titanium and sulfur in these minerals allow them to engage in a wide range of electron-transfer reactions, including those mediated by biota or processes involved in palaeo-weathering and biogeochemical cycling. The importance of redox-reactive minerals in many natural and industrial processes has been demonstrated by a plethora of scientific publications and industrial applications in recent decades. In this book, the influence of redox-reactive minerals on key biogeochemical processes and opportunities for their application in environmental technologies are outlined and illustrated in 14 comprehensive chapters. The book will be a key reference for Earth science students, geologists, geochemists and engineers and other researchers and practitioners in this rapidly growing interdisciplinary field and includes the following content:

- Chapter 5. “Biogeochemical Redox Processes of Sulfide Minerals.” D.J. Vaughan and V.S. Coker
- Chapter 6. “Geochemical Proxies for Biogeochemical Cycling and Ocean Anoxia.” C.L. Peacock, A. Lalonde, and K. Konhauser

The book is available from the Mineralogical Society online bookshop: www.minersoc.org (click on bookshop) at a price of £55 (institutions) and £40 for individuals (+ shipping). Copies are also available from the Mineralogical Society of America and from Amazon.

**Volume 18—Mineral Fibres: Crystal Chemistry, Chemical–Physical Properties, Biological Interaction and Toxicity**

Asbestos is probably one of the most studied substances ever. Asbestos is synonymous with argument and controversy: it is magic but feared, essential but dreaded, a strategic natural raw material but a source of concern and hazard; it is banned but still used safely, and so the list goes on. Asbestos-related diseases are certainly of significant concern in terms of occupational and public health. Asbestos World Health Organisation officials estimate that 125,000,000 people worldwide are exposed annually to asbestos in occupational settings, and >100,000 people die annually of diseases associated with asbestos exposure. The use of asbestos has been banned in most developed countries, but chrysotile asbestos is still used in many developing countries. This book presents the state-of-the-art in the vast multidisciplinary research field of asbestos and of mineral fibres in general. The protagonists of the book are the mineral fibres, with their immense complexity and poorly understood biochemical interactions. The approach of the chemist/mineralogist/crystallographer puts the fibre in focus, whereas the approach of the biochemist/toxicologist/doctor assumes the perspective of the organism interacting with the fibre. The perspectives of both the ‘invader’ and the ‘invaded’ must be considered together to establish a conclusive model to explain the toxicity of mineral fibres. In fact, this sharing of different perspectives and working in a multidisciplinary way is the key to understanding the mechanism of asbestos-induced carcinogenesis. With this in mind, the state-of-the-art in the field of mineral fibres is illustrated and discussed in this volume, with a multidisciplinary approach taking into account all the different scientific strands (biology, chemistry, epidemiology, mineralogy, physics, toxicology etc.). The different views have been considered in an attempt to assemble the pieces of the jigsaw and to present the reader with an up-to-date and complete picture.

- Chapter 1. “Introduction.” A.F. Gualtieri
- Chapter 3. “Crystal Habit of Mineral Fibres.” E. Belluso, A. Cavallo and D. Halterman

Chapter 6. “Surface and Bulk Properties of Mineral Fibres Relevant to Toxicity.” F. Turci, M. Tomatis and A. Pacella


Chapter 8. “In Vitro Biological Activity and Mechanisms of Lung and Pleural Cancers Induced by Mineral Fibres.” B. T. Mossman and A. Pugnaloni


The book is available from the Mineralogical Society online bookshop: www.minersoc.org (click on bookshop) at a price of £55 (institutions) and £40 for individuals (+ shipping). Copies are also available from the Mineralogical Society of America and from Amazon.

Impact Factor
As we await the annual arrival of the Journal Citation Reports (JCR) (impact factors for 2017 will be old news by the time you read this), we ponder on the ever-increasing number of ways in which our journals are assessed: scientific impact, social media impact, sales impact and reputation. Clarivate, the organization responsible for JCR, took several months to index issues of several mineralogy journals from late 2016 (papers from the December 2016 issue of Clay Minerals were finally listed in Web of Science in May 2017). Competitor journals in the commercial realm are entirely up-to-date. No responses other than holding messages were received from Clarivate to multiple enquiries about progress. Readers are asked to keep this in mind when considering the numbers produced by agencies such as Clarivate.

FORTHCOMING SOCIETY MEETINGS
Training Course: The Application of Analytical SEM (EDX) and EPMA (WDX) in the Earth Sciences (http://www.nhm.ac.uk/business-services/training/application-of-analytical-sem-and-epma.html)
27 February – 2 March 2018
Natural History Museum, London, UK

European Microbeam Analysis Society (EMAS) 2018 Workshop
End-June 2018
Bristol, UK

Granulites and Granulites
10–13 July 2018
Ullapool, Scotland, UK

IMA 2018 (www ima2018.com)
13–17 August 2018
Melbourne, Australia

MEETING: REDOX-ACTIVE MINERALS IN NATURAL SYSTEMS
The ‘Redox-Active Minerals in Natural Systems’ meeting was held at the University of Manchester (UK) at the Manchester Institute of Biotechnology on 21–22 June 2017. It was a very interesting, cross-disciplinary meeting of four of the Society’ special interest groups (Clay Minerals Group, Environmental Mineralogy Group, Geochemistry Group, and Geomicrobiology Network). Each of these special interest groups sponsored a session at the meeting and delegates were encouraged to move between sessions.

Keynote lectures, including the Society’s Hallimond Lecture, were presented at the meeting. Abstracts for these lectures can be found at www.minersoc.org/redox.html

Mineralogical Society Hallimond Lecturer: Barrie Johnson (Bangor University Wales), ‘Redox Bio-Transformations of Inorganic Species Dictate the Dynamics of Extremely Acidic Environments’

Geomicrobiology Network: Amelia-Elena Rotaru (University of Southern Denmark), ‘Syntrophic Acetate Oxidation Between Geobacter and Methanosarcina from the Bothnian Bay Facilitated by Conductive Minerals’


Geochemistry Group: Susan Little (Imperial College, London), ‘Pseudo-redox Control on the Oceanic Budget of Zn and Zn Isotopes’


SOCIETY AWARDS 2017

Prof. Hilary Downes, MSGBI President, presented the 2017 awards to winners Prof. Bruce Yardley (Collins Medal) and Dr Vicky Coker (Max Hey Medal), during the recent meeting ‘Redox-Active Minerals in Natural Systems’ held at the University of Manchester, UK.

The Mineralogical Society-Schlumberger Award will be presented to Prof. Maggie Cusack at a future meeting of the Society. The citations and responses will be published in a forthcoming issue of Mineralogical Magazine.
The Meteoritical Society's finances continue to be on a sound footing, and both the operating fund and our investment fund are currently very healthy. A large portion of the operating budget relates to the publication of *Meteoritics and Planetary Science* (MAPS), our international monthly journal of planetary science which covers topics that include the origin and history of the Solar System, planets and natural satellites, interplanetary dust and the interstellar medium, lunar samples, meteors, meteorites, asteroids, comets, craters, and tektites. The MAPS journal has been published by Wiley since 2010, and our income from Wiley closely matches the expenses of the editorial office at the University of Arizona (USA). The editorial office is managed by Editor Tim Jull.

Society memberships include subscriptions to MAPS and *Elements*. Membership with subscription to only the electronic version of MAPS has become a popular option, although more than half of our membership still purchases the printed version. Collection of membership dues for 2018 will begin in October 2017. I encourage members to pay their dues in a timely manner because this helps greatly with financial planning. Healthy finances depend on a stable number of memberships.

Our investment fund includes four separate endowed funds and continues to do as well as we can expect with the current market situation. Many society members contribute generously to supporting all of these funds, and your donations are always greatly appreciated. The Nier Fund supports the annual Nier Prize, which recognizes outstanding research by young scientists in meteoritics and closely allied fields. This year’s recipient (2017) is Dr. Francis McCubbin of the Johnson Space Center (USA). The Gordon A. McKay Fund supports an award to the Center (USA). The editorial office is managed by Editor Tim Jull.

The General Endowment Fund supports a variety of outreach projects. Over the last year, this fund has been used to provide travel support for students to attend meetings on four different continents: workshops on Chondrules in the Protoplasmic Disk (UK), Extraterrestrial Materials (UK), and Chondrules as Astrophysical Objects (Canada); the International Workshop on Shock Metamorphism (Australia); the 1st British Planetary Science Congress (Scotland); and the Meteoritics and Planetary Science sessions of the 3MA [Magmatism, Metamorphism and Associated Mineralizations] Colloquium (Morocco). Endowment Funds were also used to support travel for students to attend the Meteoritical Society meeting in Berlin (Germany). This year, endowment funds will be used to fund students and post-doctoral scholars to attend the society’s annual meeting in Santa Fe. Some of the money used has been contributed directly as part of the annual membership renewal. We always welcome suggestions and ideas for ways in which the General Endowment Fund can be utilized to promote the goals of the society and enrich its activities.

A total of over $15,000 was donated to the various funds from our generous members. Your contributions provide direct support that helps to strengthen our international community.
EMU RESEARCH EXCELLENCE MEDAL

One of the means by which the European Mineralogical Unions (EMU) fosters and encourages research in the mineralogical sciences is to present a silver medal each year. The “EMU Research Excellence Medal” is presented to young scientists (not older than 40 years) who have made significant contributions to research and who are active in strengthening European scientific links. During the period 2012–2016, Richard Harrison, Diego Gatta, Razvan Caracas, Encarnación Ruiz-Agudo, István Kovács, and Sylvie Demouchy were honoured with this prestigious distinction. By tradition, the medal is presented at an awards ceremony during an international meeting, such as the Goldschmidt meeting or a combined meeting of EMU member societies. Dr Demouchy will receive her medal and present her award talk at the 2017 Goldschmidt conference in Paris (France). The award winner for 2018 will also be announced at the Goldschmidt conference.

Every year, usually with a deadline in May, the EMU Medal Committee calls upon the member societies and all European mineralogists for nominations. The nomination process is quite straightforward and requires only a cover page (available at http://eurominunion.org/wp-content/uploads/2016/12/cover-page-EMU-award.pdf); a cover letter from the nominator outlining the candidate’s qualifications in light of the criteria for the award; supporting letters from at least two, but no more than four, co-sponsors; and a complete CV, including the nominee’s complete publication list.

All members of the EMU societies are encouraged to consider nominating suitable candidates from among their colleagues, to recognise their outstanding scientific contributions to the mineralogical sciences (in the broadest sense).

Please feel free to contact the President of EMU, Michael Carpenter (mc43@esc.cam.ac.uk), at any time with questions or suggestions about the EMU Research Medal.

For more information, visit eurominunion.org/?page_id=152
FROM THE PRESIDENT

Later this year, the conference Exploration ‘17 (www.exploration17.com) will be convened in Toronto (Canada). This event is the sixth decennial mining exploration conference, which has been held in the seventh year of every decade since 1967. I hope to attend and am a coauthor on a paper titled “Advances in Exploration Geochemistry, 2007 to 2017 and Beyond” that will be published in the Exploration’17 conference proceedings. In pursuing background details for this paper, I referred to the previous decennial abstract, “Major Advances in Exploration Geochemistry, 1998–2007” by Cohen et al. (2007), along with the similarly titled paper in our journal, Geochemistry: Exploration, Environment, Analysis (GEEA) (Cohen et al. 2010). I also referred farther back to one of the earliest online AAG newsletter articles to see what the state-of-play was during these times. In Explore issue No. 15 (December 1974) was an article authored by Carpenter (1974) titled, “Status of Exploration Geochemistry in U.S. and Canadian Universities”. Interestingly, the one clear common thread to all of these aforementioned articles was the lack of future geochemists coming through the third-level education system. Exploration geochemistry courses were few and far between. While the early newsletter article was only referring to North America, I can safely say that the same challenges existed in Australia and many other countries. Our recent AAG member survey identified this risk to a key area of our applied research and, although I don’t want to give too much away for the upcoming decennial paper, I think it is safe to assume that this theme continues.

“At present, most personnel training is done by geochemical departments in government organizations and industry groups. Most schools in the United States and Canada do not offer geochemical training, particularly at graduate levels, due to faculty limitations, lack of budgetary support, and the erroneous impression that applied geochemistry is not sufficiently academic.” Cavender, W. (1968) – a review article in Mining Engineering quoted by Carpenter (1974).

The more things change, the more things stay the same, it would seem. So, while concepts, applications, technology and many other things have come a long way forward in applied geochemistry, our ability to train future geochemists has come full circle. This is not completely disheartening and should be viewed as a clear guide. It is solid evidence pointing to where we as a community and the AAG need to do better. If you are reading this and in academia or in a current training or mentoring role, please know that you are possibly the most critical part of future geochemistry, and I hope you are able to support or grow your educational offerings and continue to bring more students into our discipline.

The AAG student awards are being updated, and there will be more funding available to attend the June 2018 International Applied Geochemistry Symposium in Vancouver (Canada) which will be part of the larger Resources for Future Generations conference (RFG2018). I fully anticipate that the AAG will provide an excellent platform for students to present their work. So, please make sure to mark it in your calendar and get prepared well in advance. More details are available at the RFG website (www.rfg2018.org), as well as on the AAG website. The AAG will circulate details for abstract submission and travel awards in the near future.

An update from the most recent AAG council meeting shows the AAG website will be shifting to a more easily operated platform, which should make renewals, and a number of other issues that members have raised, easier to deal with. Hopefully, AAG members will not notice too much of a change from the front end. One clear point from the council meeting was that new AAG councillors are needed for next year (2018). If you are a Fellow and would like to be more active in the AAG, please let me know.

Finally, it is with regret that we learned of the passing of distinguished Chinese geochemist Professor Xie Xueqin (1923–2017). He will be greatly missed in the geochemistry community. When I was a young geochemist in 2007 in Oviedo (Spain), I clearly remember his speech when he received the AAG Gold Medal. His list of achievements were most impressive.

Ryan Noble, AAG President

REFERENCES


RECENT ARTICLE PUBLISHED IN EXPLORE

The following is an abstract for an article that appeared in issue 175 of the Explore June newsletter.

“Evidence of Geothermal Activity Near the Nazko Volcanic Cone, British Columbia, Canada, from Ground and Surface Water Chemistry”

Ray Lett1 and Wayne Jackaman2

Travertine deposits and CO2-rich gas seepages, known indicators of geothermal activity, are common in two wetlands, informally named the North and South Bogs, near the Nazko volcanic cone, British Columbia, Canada. Although travertine and the CO2-rich gas seepages suggest sub-surface geothermal activity, the bog water temperature is less than 23 °C. Lithium, Sr, Rb, Si and B contents are elevated in bog ground and surface water, but concentrations are lower than those reported in the hot springs at global geothermal fields. Chloride and Hg could not be detected in the bog water. Water at the base of a small travertine cone associated with a strong CO2-rich gas seep in the North Bog has an unusually low (<6 °C) temperature with elevated B contents up to 436 ppb and Li up to 380 ppb. Thermodynamic modelling predicts aragonite, calcite and chalcocite can precipitate from bog water and a chalcocite thermometer suggests higher water temperature up to 68 °C in the past. Anomalously Li, Rb, Sr and B content are indications for a deeper, warmer fluid that cooled during movement to the surface, but δ18O and δ34S isotope data and absence of Cl– suggests the bog water is mainly meteoric. The δ13C values, however, indicate that the CO2-rich seepage gas may be from a deep, magmatic source.

The full article can be viewed at: https://www.appliedgeochemists.org/index.php/publications/explore-newsletter

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FROM THE PRESIDENT

Dear Members of the DMG,

Time is flying by, more than half of 2017 is gone, and we are already looking forward to the GeoBremen meeting to be held 24–29 September 2017 in Bremen (Germany). The conference’s overarching theme and title is, “The System Earth and its Materials – From Seafloor to Summit”, and as such, the meeting will provide a multidisciplinary stage on which to explore the various sub-themes of the Earth and material sciences.

I invite all DMG members to attend our annual business meeting on 25 September 2017. All the important issues of concern to our society will be discussed. Thus, if you would like to raise a certain topic or you have any questions relevant to the society, please come to the meeting. Members can approach almost every board member personally because most of them will be in Bremen for the entire meeting.

At the annual business meeting, we will also finalize the nominations for the 2017 elections. The board has already prepared a list of persons who have agreed to stand for election, but the nomination of other/alternative candidates is still possible. The list of candidates was published in the June issue of Geowissenschaftliche Mitteilungen (GMIT) (see www.gmit-online.de).

One of the highlights of the meeting is the presentation of the DMG awards. The Abraham Gottlob Werner Medal is the highest award given by the DMG and is for outstanding original research (the silver medal) or distinguished service to the mineralogical sciences (the gold medal). In addition, there are three awards for young scientists: the Paul Ramdohr Award, which is for the best oral student presentation at the annual meeting; the Victor Moritz Goldschmidt Prize, which is for outstanding mineralogical contributions; and the Beate Mocek Prize, in memory of the late Beate Mocek (1962–2010), which is for young female scientists who specialize in petrology and geochemistry.

I hope to see you in Bremen!

All the best, and Glückauf,

Reiner Klemd (DMG President)
ANNOUNCING THE WINNERS OF THE EAG PHOTO CONTEST, “WONDERS OF GEOCHEMISTRY”

We are pleased to announce the three winners of the 2017 Photo Contest, “Wonders of Geochemistry”. We asked the photographers to tell us more about their winning pictures, so read on to find out the stories behind these images, which capture beautifully some of the “Wonders of Geochemistry”.

“The Encrusting the Mantle”, by Marco Brenna (Lecturer at University of Otago, New Zealand)

In January 2017, I joined a field expedition to Red Mountain, Mount Aspiring National Park in New Zealand. Red Mountain is the exposed portion of the Dun Mountain ophiolite belt, the place of origin of the rock name “dunite”, which consists mostly of olivine. My colleague at the University of Otago, Dr James Scott, is leading several projects dealing with the properties of and processes that occurred in the lithospheric mantle beneath New Zealand. I went along with him and one of his PhD students, Stephanie Junior, to sample portions of the mantle exposed high up in the Southern Alps. The landscape is rocky and, due to its chemical make-up (mostly Mg, Fe and Si), no vegetation covers the ground – this resulting in a Martian-like red landscape. Because of its contrast, my eyes were drawn to a patch of white ground. With the thought in mind that New Zealand was once famed for its pink and white terraces, and hoping to discover something analogous, we explored the white patch, which however turned out to be “just” a carbonate spring. After this first one, we found a few more of these springs, which occur along an alignment and are, therefore, likely controlled by some local fault that forms a pathway for fluid flow. Looking down on the ground, I saw a colourful combination of peridotite fragments encrusted with white carbonate, and snapped. The question remains, however: Why should a carbonate spring occur within an ultramafic crustal domain?

“The Color Palette of Dallol”, by Electra Kotopoulou (PhD student at CSIC-UGR, Spain)

The Danakil depression lies 120 m below mean sea level in NE Ethiopia. This vast, salty plain, composed of a thick evaporitic sequence, was created by several transgressions of the Red Sea. Danakil is situated at the extension of the Main Ethiopian Rift, one of the three branches of the Afar triple junction system (the other two being the Red Sea and the Gulf of Aden) that is tearing apart the continental crust, resulting in incipient seafloor spreading. In this dry, remote, and harsh area of Ethiopia, where daily temperatures in the winter can exceed 50 °C (the name “Ethiopia” derives from the Greek words “aιθω” and means “sunburnt”), mantle plume activity related to the continental rifting has created a unique hydrothermal system within the evaporitic sequence, known as the Dallol dome.

Calcite precipitates on colorful dunite and serpentinite pebbles at a spring within the Dun Mountain ophiolite, Red Mountain, Southern Alps (New Zealand).

The Fe aqueous species and saline minerals give the most spectacular colours in Dallol’s acidic terraces.

Hydrothermal activity in Dallol is expressed by numerous springs, miniature geysers, fumarolic fields, and phreatic eruptions. The pristine spring water is hyper-acidic, hyper-saline and oxygen-free; it is discharging at a temperature around 107 °C; and it has more than 25 g/L of Fe. The solid phases that are precipitating are composed mainly of halite and Fe nanophases and these form chimneys, pillars, terraces, and many other structures. As oxygen diffuses slowly in this hyper-saline system, both the Fe aqueous species and the Fe mineral precipitates are oxidized to produce this impressive palette of colours, ranging from transparent, to white, veraman (a type of blue-green), lime, green, yellow, gold, orange, red, chestnut, caramel, and ochre!
“Hardness Removal by Crystal Sticks”, by David Benavente (Associate Professor at University of Alicante, Spain)

My colleagues from the applied electrochemistry group at my university suggested that I should study precipitates on stainless steel because they (my colleagues) were investigating electrochemical softening methods to remove hardness from natural waters. This attempt seemed amazing and new to me because I had been studying salts in monuments and stalactites for a long time. I thought, “Easy task. A bit ugly, though”. I did not know what the scaling was like or what the precipitate that spoils my kettle or washing machine was like.

We characterised the precipitate using scanning electron microscopy with energy dispersive X-ray spectroscopy and X-ray diffraction. Simple is beautiful. Calcium and magnesium ions were eliminated from the water to form different mineral phases. Calcium is removed from water as calcite and aragonite, whereas magnesium is precipitated as brucite. The calcite presented trigonal-shaped crystals, the aragonite had needle forms, whereas the brucite precipitated as spherulites. It was amazing how hardness could transform itself. All the crystal shapes seemed to be in perfect balance, coexisting in harmony.

2018 EAG AWARDS – SEND IN YOUR NOMINATIONS

Recognizing deserving scientists from all generations is crucial. It can really make a difference to one’s career (see blog post “What does it change to receive an award” at blog.eag.eu.com). Yet it can’t be done without nominations. So, make a difference and send a nomination for one of the EAG awards.

The Urey Award recognizes outstanding contributions that have advanced geochemistry over the span of a career.

The Science Innovation Award differs by subject area every year according to a five-year cycle. In 2018, the award is in honour of Nicholas Shackleton for his work in climatology and recognizes important and innovative breakthroughs by scientists within 30 years from the start of their PhD (which must have been completed). Hence, candidates for the 2018 award should have started their PhD in 1987 at the earliest.

The Houtermans Award recognizes a single exceptional contribution to geochemistry, published as a single paper or as a series of papers on a single topic. This award is bestowed to scientists within 12 years from the start of PhD (which must have been completed). Hence, candidates for the 2018 award should have started their PhD in 2005 at the earliest.

The GS/EAG Geochemical Fellows Award is bestowed upon outstanding scientists who have made major contributions to the field of geochemistry.

Nomination deadlines: 31 October for the GS/EAG Geochemical Fellows and 15 November for all other awards. All details are available at www.eag.eu.com/awards/nomination.
The Geochemical Society (GS) awards are named after some of the pioneers in the field—Victor Goldschmidt, Alfred Treibs, Frank W. Clarke, and Clair Patterson. Today’s geochemists continue to blaze new trails of discovery, and we need your help to recognize these innovative scientists. Nominating a colleague, student, or mentor for an award is an act of real generosity that highlights their achievements and can also inspire others. Anyone, with the exception of GS board members and those directly involved in the award selection process, may submit a nomination. This includes young geochemists as well as more senior scientists.

Considerable progress has been made regarding the diversity of nominees in recent years, but more progress is still needed. The cultural richness represented by GS members from 70 countries should also be reflected in the awards that we grant for scientific achievement. This is important not only in the interest of equity but also to ensure that all the young scientists who participate in the society and attend Goldschmidt conferences recognize their potential future selves in the persons being honored.

Please consider submitting a nomination this year by the 31 October 2017 deadline. Information on how to submit an award nominations package can be found at the GS’s website: www.geochemsoc.org/awards/makeanomination/.

The society is accepting nominations through Oct. 31 for the following:

The **V. M. Goldschmidt Award** is the society’s highest honor. This award is presented for major achievements in geochemistry or cosmochemistry, consisting of either a single outstanding contribution or a series of publications that have had great influence on the field. It is named after Victor M. Goldschmidt (1888–1947) whose classification of the elements in the Earth and meteorites and pioneering work on crystal chemistry laid the basis of modern geochemistry. The importance of this award has been recently reinforced by a generous gift from former Goldschmidt award winner Prof. Gerald Wasserburg: the recipient will now be able to travel to the Goldschmidt conference to receive his or her award as a guest of the conference.

The **C. C. Patterson Award** recognizes an innovative breakthrough of fundamental significance in environmental geochemistry, particularly in the service of society, consisting of either a single outstanding contribution or a short series of papers published within the last decade. Clair C. Patterson (1922–1995) developed the uranium–lead dating method. Using lead and uranium isotopic data from the Canyon Diablo meteorite, he calculated the first accurate and precise age for the Earth.

The **F. W. Clarke Award** recognizes an early career scientist for a single outstanding contribution to geochemistry or cosmochemistry, published either as a single paper or as a series of papers on a single topic. Frank Wigglesworth Clarke (1847–1931) was a chemist who determined the composition of the Earth’s crust.

The **Alfred Treibs Award**, presented by the Geochemical Society’s Organic Geochemistry Division, is given for major achievements, over a period of years, in organic geochemistry. The legacy of Alfred Treibs (1889–1983) consists of his classic papers on porphyrins, which provided the starting point of organic geochemistry.

**MEETING ASSISTANCE PROGRAM**

The Geochemical Society’s Meeting Assistance Program provides support for symposia or conferences related to geochemistry. All GS members are eligible to apply. Awardees receive US$2,000 and the society may award up to four per year. The GS Program Committee reviews applications twice a year; the next deadline is 30 September 2017. For more information, visit: tinyurl.com/GeoChemMAP.

**GS BOARD OF DIRECTORS OPEN POSITIONS**

The Nominations Committee of the Geochemical Society is seeking nominees for the positions of vice president and two directors for terms beginning in January 2018. 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 should be communicated by 15 September 2017 to any member of the Nominations Committee or to the GS business office at gsoffice@geochemsoc.org. More information regarding the duties and responsibilities of board positions can be found on the society’s website.

**VICTOR MORITZ GOLDSCHMIDT: FATHER OF MODERN GEOCHEMISTRY**

The term “geochemistry” had existed for 100 years when Victor Goldschmidt built upon technical developments of the time, as well as advances in physics and chemistry, to revolutionize the field by adding a theoretical underpinning to it, turning it into a mature science. Grossman (1993) expressed Goldschmidt’s importance thus: “It is astonishing, even to experienced geochemists, just how many of the important concepts in this field originated with Goldschmidt”. Goldschmidt’s was an interdisciplinary approach: “The field of geochemistry,” Goldschmidt wrote, “ranges widely over the broad ground of modern science, from astrophysics and nuclear and atomic physics to geology, oceanography, and biology...” (Goldschmidt 1954). We take a brief look at the life of this seminal figure.

Victor Moritz Goldschmidt was born in 1888 in Zurich (Switzerland) to a family of scientists of Jewish heritage. When his father was appointed Chair of Chemistry at the University of Oslo, the entire family moved to Norway. Victor was 13. He was drawn to nature in Norway, became interested in mineralogy, and profited from vacations in the countryside to study rocks. It is interesting that while traveling in Europe with his family in 1906, he saw a spectacular eruption of Vesuvius (Italy) and sent specimens back to his teachers.

When he entered the University of Oslo (Norway) his first research was on contact metamorphism in the Kristiania region of southern Norway. The results were published in 1911 in the classic monograph,
which detailed the application of physical chemistry to metamorphic petrology.

Beginning in 1922, he began establishing the conceptual basis for geochemistry. In his nine monographs—known collectively as the *Geochemische Verteilungsgesetze der Elemente* (Geochemical Laws of Distribution of the Elements), which he published between 1923 and 1938—Goldschmidt laid out the fundamental laws of geochemistry and crystal chemistry.

In 1929, he was recruited to the University of Göttingen (Germany); there, he built and staffed a mineralogical institute where he spent several highly productive years. During these years, he conducted research in geochemistry with an emphasis on problems relating to the distribution of the rare elements between the solid crust of the Earth, the atmosphere, and the hydrosphere. The study was later expanded to the broader problem of the absolute abundance of all elements in the Earth, planets, and universe (Johnson 1985). He was nominated for a Nobel Prize during this time, the first of 11 nominations.

The rise of Nazism interrupted this productive work. As a Jew, he knew that he could be dismissed from the university at any time, but he initially resisted leaving. The situation became increasingly oppressive, however, and he eventually saw the writing on the wall. That is not merely a rhetorical statement: a sign saying, “Jews not desired” was posted outside his office, and he reluctantly decided to leave. He resigned from the University of Göttingen in 1935 and returned to Oslo.

In Norway, he continued his research, publishing the ninth part of his *Geochemical Laws*, which he called his “Ninth Symphony.” In it, he arrived at a table of cosmic abundances, from a combination of meteoritic and solar data, which provided the basis for later theories of the origin of the elements. “Goldschmidt’s perception of the fundamental significance of meteorite compositions for geochemistry is another example of his scientific genius” (Mason 1992). This work provided the foundation for two later Nobel Prizes in physics to other scientists.

The dire world situation again intervened: Germany invaded Norway in 1940, and, in March 1942, all Jews in Norway were decreed to be “illegal immigrants.” Twice he was arrested by the Gestapo; he was nearly boarded onto the prisoner ship *Donau*, but was pulled aside at the last moment and released thanks to the intervention of colleagues. The prisoners boarded that day were to be taken to Auschwitz, a concentration camp.

After this close call, he decided to flee with the help of the Norwegian Resistance. In December 1942, he and about 40 other refugees were smuggled over the frontier to Sweden.

In neutral Sweden, he was offered the chair of mineralogy at Uppsala University but he was determined to help in the war effort and decided to go Britain, where he felt that his knowledge of technical developments in Norway would be of value to the Allies. During his years in Britain, he worked on his *Geochemistry* opus, as well as lecturing extensively. He received many honors during this time: he was named a Foreign Member of the Royal Society in 1943, and, in 1944, he received the Wollaston Medal, the highest honor of Geological Society of London.

He returned to Oslo in 1946 but his health, never strong, had suffered greatly during the war. He died in March 1947 at the age of 59 from a cerebral hemorrhage.

At his death, he left his comprehensive treatise, *Geochemistry*, in draft form; it was completed by Alex Muir and published in 1954. It made Goldschmidt’s work known to an English-speaking audience and became the standard text on geochemistry for many years (Glasby 2006).

According to his biographer, Brian Mason, “Goldschmidt’s insight and intuition, his ability to plan and expedite extensive research programs, and not least his recruitment and inspiration of devoted research associates, revolutionized geochemistry” (Mason 1992). The Geochemical Society named its highest award, the Goldschmidt Medal, to recognize him.

In 1988, one hundred years after he was born, the first Goldschmidt Conference was held in Baltimore, Maryland (USA) and was attended by 463 geochemists. The program stated, “It is the intent of the participating societies that there should be a continuing series of conferences under this distinguished name.” That wish has been fulfilled. Goldschmidt Conferences, organized by the Geochemical Society and the European Association of Geochemistry, have grown to be the premier meetings in geochemistry. They are now attended by some 4,000 scientists annually.

**REFERENCES**


V. M. Goldschmidt sitting in his office in the Mineralogisk-Geologisk Museum in Oslo in the 1920s.

**Die Kontaktmetamorphose im Kristianiagebiet**, which detailed the application of physical chemistry to metamorphic petrology.
Over the years there have been a number of published peer-reviewed proceedings from annual meetings that record technical developments in interpretive analytical methods and significant scholarly research contributions in the broad categories of natural, applied, and materials science. We can lump all of these into the term ‘clay science’. There is an interesting trend to note, however, about the changing sectors where clay science publications are concerned. In his presidential address at the Edmonton meeting, Professor Srodon presented research he had conducted on papers published in ‘clay science’ in the journals Applied Clay Science, Clay Minerals, and Clays and Clay Minerals over the last 50 years, from the ‘natural’ and ‘materials science’ sectors. There is a perfectly linear inverse correlation as shown on the graph below:

The increase in the number of papers published in the ‘materials science’ sector has been mirrored by an equal decrease in the number from the ‘natural science’ sector. A recent count suggests that the number of materials science papers is more than double that from the natural science sector. Is this something clay scientists and society members should be concerned about? In my opinion, it depends.

The importance and social relevance of clay mineralogy and clay science cannot be overstated. Clay mineral surfaces are the most reactive mineral surfaces in the geosphere and contribute, almost exclusively, to bulk-rock specific surface area (Srodon and McCarty, 2008). Illite and illite-smectite are major constituents of mudstone, making up ~40%, and they form at least 10% of other sedimentary rock types (Srodon 2009). Shales and mudstones make up to 70% of Earth’s sedimentary record (Garrels and Mackenzie 1971). A rigorous understanding of the structural and compositional relationships of the wide variety of clay species, especially mixed-layered types, is absolutely critical for understanding near-surface processes, including those in the ‘critical zone’, conventional soil science, environmental remediation, and hydrocarbon exploration and development. Geological hazards from swelling clays cause more economic loss than earthquakes, floods, and volcanos combined. Those who study the fundamental structure and composition of clay minerals – factors that control the clay’s physical properties – are still hugely important in terms of the future of our science. In addition, clays are a major material in industrial manufacturing and value-added products, such as food additives, cosmetics, cat litter, drilling fluids, catalysts, and many more. And no wonder! Clay particles are often at the nanometer-scale, with large basal surface to edge aspect ratios, large specific surface areas, and large cation exchange capacities. Clay science continues to serve an enormously important role in the broader science horizon and should be taken into consideration in large-scale research projects where clays are encountered.

The field of clay mineralogy is actually a subdivision of clay science. Rigorous methods of teaching clay mineralogy include education in systematic categories of the various clay species, methods of sample preparation, data collection by X-ray diffraction (structure), and supporting spectroscopic methods (composition). Modern methods of analysis, including computer simulation of diffraction data, are generally taught in the natural science sector in geology departments in US universities. The top professors in such departments don’t last forever. They retire, they die, or they may change disciplines. But universities do not seem to replace such clay mineralogists. Do the authors in the materials science sector have appropriate levels of fundamental clay science education? I suspect many are self-taught in this respect. If not, and self-teaching becomes what must be done to complete materials science goals and projects, is there enough access to quality references, guidelines, and ‘how-to’ modules so that the materials scientists can be sure they are using the most modern and effective methods? Probably not.

In addition to the resources already offered by The Clay Minerals Society, there is a website created by Professor Dave Mogk of Montana State University (http://serc.carleton.edu/NAGTWorkshops/mineralogy/clay_mineralogy.html). Dave works in high-temperature granulite metamorphism mineralogy/petrology and says that he lacks a formal education in systematic clay mineralogy but recognizes the extreme importance of the field. Dave worked to create the aforementioned website where students and other scientists can find systematic information on how to deal with characterization and understanding of the materials themselves and the analytical methods that are needed to determine accurate structure and compositional relationships in clay-bearing materials. Dave and the host organization of the National Association of Geological Teachers (NAGT) welcome input from any and all knowledgeable clay scientists on how to improve this site with the most relevant information. In particular, we would like to see a ‘How-To’ best practices section that systematically takes the reader through sample preparation, data collection, and analysis and that can be a repository of relevant references. My hope is that The Clay Minerals Society can partner with NAGT and other professional societies who have a vested interest in the field and in doing this right. Please contact me (mccardog@gmail.com) or Mary Gray at The Clay Minerals Society office (cms@clays.org) with any suggestions. Let’s make sure that up-to-date resources are available and easy to find for this important field of science.

Douglas K. McCarty (mccardog@gmail.com), President, The Clay Minerals Society

REFERENCES


NOTE Please find a detailed report about the 54th Annual Clay Minerals Society Conference that was held in conjunction with the Oil Sands Clay Conference on 5–8 June 2017 in Edmonton, Alberta in the Meeting Report section of this issue.
MEETING REPORT

54th ANNUAL MEETING OF THE CLAY MINERALS SOCIETY

The 54th Annual Meeting of The Clay Minerals Society (CMS) was held 2–8 June 2017 at the Northern Alberta Institute of Technology (NAIT) (Edmonton, Alberta, Canada) in conjunction with the Oil Sands Clay Conference. The meeting was organized by the Centre for Oil Sands Sustainability (part of NAIT) and The Clay Minerals Society. The meeting was a success, with more than 130 attendees, 66 abstracts submitted – 51 oral presentations and 15 posters. Session topics included, “Clays in Oil and Gas”; “Clay/Organic Interaction and Clay-Polymer Interaction”; “Clays in Mining”; Structure and Properties of Clays”; “Clay and Environmental Quality”; “Clay in Geotechnical Engineering”; Clays and Soil Formation”; and “Clays in Water/Solid Separation Processes”.

Passing of the Gavel

During the meeting, Dr. Jan Srodoń (Institute of Geological Sciences, Poland), CMS President, passed the presidential gavel to Dr. Douglas K. McCarty, a recently retired senior staff geologist at Chevron ETC (Houston, Texas, USA). Dr. McCarty has been very active in The Clay Minerals Society. He is a former associate editor of Clays & Clay Minerals and the 2011 recipient of the Pioneer Award, as well as student research and travel awards.

The Clay Minerals Society Marion L. and Chrystie M. Jackson Mid-Career Clay Scientist Award. Dr. McCarty worked for 20 years researching mineral analysis techniques, wireline log physics, mineral-structure composition relationships and physical properties. More recently, he has worked on the characterization of nanometer-scale pore systems in unconventional tight-rock reservoirs. Dr. McCarty holds visiting appointments at the Polish Academy of Science and Purdue University (Indiana, USA).

CMS Awards

During the meeting, several awards were conferred by the CMS. They included the George W. Brindley Clay Science Lecture Award, the Pioneer Award, as well as student research and travel awards.

The George W. Brindley Clay Science Lecture Award recognizes a clay scientist who will infuse the CMS with new ideas, someone who is both a dynamic speaker and who is involved in innovative research. The 2017 award was conferred on Dr. Sridhar Komarneni, a Distinguished Professor of Clay Mineralogy in the Department of Ecosystem Science and Management and Materials Research Institute at the Pennsylvania State University (USA). He presented a lecture entitled, “Structure–Property Relationship of Synthetic and Modified Clays and Clay–Organic Nanocomposites for Environmental Protection”.

The Pioneer Award was bestowed on Dr. Fred Longstaffe, Distinguished University Professor and Canada Research Chair (Tier 1) in Stable Isotope Science and the Director of Laboratory for Stable Isotope Science, Department of Earth Sciences, Western University (Ontario, Canada). The Pioneer Award was established to recognize research contributions that have led to important new directions in clay minerals science and technology.

Five students each received a CMS Student Research Award: Jeffrey Hannon (Reynolds Award Winner for highest-ranking application), Timothy Henderson, Sarick Matzen, Jomih Monsurat Omolola and Boyoung Song. In addition, seven students each received a Student Travel Award (pictured above left to right): Bhabananda Biswas, Fashina Bidemi, Timothy Henderson, Seungyeol Lee, Paulina Maziarz, Ruhaida Rusmin and Katherine Rothwell (Blair Jones/Jane Flynn recipient for highest ranking application).

Best Student Presentation Winners

Winners of the Best Oral Presentation Award were Aleksandra Govedarica (1st place), Timothy Henderson (2nd place), and Ruhaida Rusmin (3rd place). Best poster presentation winners were Anna Koteja (1st place), Pauline Maziarz (2nd place), and Xuoli Lee (3rd place). Winners received a certificate and free CMS membership for 2018.

10th Canadian Powder Diffraction Workshop

The 54th Annual Meeting of The Clay Minerals Society started with the 10th Canadian Powder Diffraction Workshop, which was held 2–4 June, was sponsored by Canadian National Committee for Crystallography, and was hosted at NAIT. The workshop was organized by Patrick H. J. Mercier, who is a senior research officer at the National Research Council Canada (Ottawa, Ontario) and Chair of the Canadian National Committee for Crystallography. The following lecturers and instructors are thanked for their time and expertise: James F. Britten, Michael A. Gharghouri, Jacques Huot, Anita Lam, Xinsong Lin, Patrick H. J. Mercier, Bussarakorn Patarachao, Kristian Ufer, Robert B. Von Dreele, and Pamela S. Whitfield. The workshop reviewed the basics of powder diffraction and informed participants on current trends.

Oil Sands Workshop

On 4 June, the Oil Sands Workshop was held on NAIT’s main campus. The workshop brought together professionals and students of oil sands, bringing them up to speed on current issues, technologies, and approaches. The workshop discussed the following topics: clays in oil sands geology; methods for measuring the clays that are used in the oil sands industry; the impact of clays on bitumen extraction; the impact of clays on flocculation and transport of fines-dominated slurries; tailings dewatering mechanisms and the influence of clays; tailings dewatering technologies in oil sands; and a review of research needs and outstanding questions.

NEXT ANNUAL CMS MEETING

The next annual CMS meeting (the 55th) will be held 11–14 June 2018 at the University of Illinois at Urbana-Champaign (USA). The title and the theme of this meeting will be “New Visions in Clay Science”.

1811-5209/17/0013-0283-$0.00  DOI: 10.2138/gselements.13.4.283
Twenty years ago, most people relegated tourmaline to the “accessories” category and ignored it in petrological analyses. This view has since changed dramatically, and tourmaline is now widely used as an extraordinary archive of petrologic processes and host-rock formation conditions, allowing for element sources, temperature, pressure, fluid composition, pH, and provenance to be constrained. Although this transformation was already underway in 1997, the first Tourmaline Conference (June 1997)—organized by Milan Novák (Moravian Museum; Masaryk University, Czech Republic) and Frank Hawthorne (University of Manitoba, Canada)—acted as a catalyst. This meeting brought together an international group of scientists to discuss tourmaline research and to advance tourmaline science, and this led to a host of fruitful collaborations. Over the years, this meeting attained mythical status among tourmaline researchers, and a second edition was long overdue.

Tourmaline 2017 participants from Europe, Asia, Africa, and North and South America, with conveners Jan Cempírek (front left), Milan Novák (center with sign). Photo: Radek Škoda.

In June 2017, at the 20th anniversary of the first conference, Jan Cempírek (Masaryk University) and Milan Novák reconvened 61 scientists from 17 countries at the same location near Nové Město (Czech Republic) to assess progress in tourmaline research, to discuss new challenges, and to catalyze community efforts for advancing tourmaline science. The meeting was a huge success, not least because the format allowed for abundant discussion—helped by world-renowned Czech beer—thereby promoting cross-fertilization among crystallographers, petrologists, mineralogists, and isotope geochemists. The relaxed atmosphere also encouraged students to fully participate in these discussions. With students and early career scientists making up nearly half of the attendees, the appeal of tourmaline research to the next generation is clear.

A series of eight keynote addresses over the three-day conference highlighted the state-of-affairs, challenges, and future directions for tourmaline research in mineralogy, petrology, and geochemistry. These were interspersed with numerous contributed presentations and posters. With the experience of having attended both meetings, Darrell Henry (Louisiana State University, USA) began with a historical perspective on the issues leading to the 1997 conference and a broad overview of progress since that time. The large increase in publications and the utility of tourmaline as an indicator mineral. The meeting also provided a forum for the International Mineralogical Association (IMA) Subcommission on Tourmaline Nomenclature to discuss new ideas and modifications. The complete program can be found at www.tourmaline2017.cz. A special issue of the Journal of Geosciences will be dedicated to tourmaline, and we invite contributions from the wider tourmaline research community to this issue. The deadline for submissions is 30 September 2017. Please contact Jan Cempírek (info@tourmaline2017.cz) for more information.

Tourmaline inspires all generations: (left) Renata Čopjaková, (center) Petr Gadas, and (right) Tonis Škovodová. Photo: Barb Dutrow.

Social events allowed ample time for interactions among colleagues, spawning new collaborations and debating every aspect of tourmaline science. The highlights were the pig roast, a trip to the Zelená Hora UNESCO heritage site, and the baroque castle Ždár nad Sázavou. A fabulous field trip to eight classic tourmaline localities in the eastern part of the Bohemian Massif followed, led by Milan Novák and Jan Cempírek with Petr Gadas, Radek Škoda, and Renata Čopjaková. Outcrops permitted all of the attendees to collect tourmalines to their heart’s delight: from abyssal pegmatites to orthogneisses to metacarbonates to NYF (i.e. rich in elements Nb, Y, and F) pegmatites to nodular granites. The comprehensive accompanying field guide supplemented overviews given by tourmaline workers at each locality. Cultural highlights of the trip included a visit to the St. Barbara church in Kutná Hora—one of the few churches in the world with murals of miners and a statue of a miner inside the church—and the Church of Bones in Kutná Hora.

With the success of the conference, another Tourmaline Conference is in the works. Hopefully, in less than 20 years.

Barb Dutrow, Louisiana State University, USA
Vincent van Hinsberg, McGill University, Canada
Jan Cempírek, Masaryk University, Czech Republic
Klaus-Dieter Grevel, Jena University, Germany
The short course entitled Petrochronology: Methods and Applications was held 22–23 (Saturday and Sunday, respectively) April 2017 in Vienna (Austria). It was co-organized by Pierre Lanari (University of Bern, Switzerland), Matt Kohn (Boise State University, USA) and Martin Engi (University of Bern), who also served as editors of the new volume (v83) of the Reviews in Mineralogy and Geochemistry (RiMG) series entitled Petrochronology: Methods and Applications. Sponsors of the short course included industry partners (SELFRA, CAMECA, ESI) and scientific societies (Geochemical Society, European Association of Geochemistry, European Geosciences Union, la Société Française de Minéralogie et Cristallographie), which awarded six travel grants and offered reduced registration fees to eleven students. This short course brought together 85 participants from 25 countries, including graduate students, early career scientists, and senior researchers.

On Saturday, Chris Clark (Curtin University, Australia) provided a clear review of the use of equilibrium phase diagrams in petrogenetic modeling, including accessory minerals. Pierre Lanari then addressed issues of incomplete equilibration and potential pitfalls for thermobarometry, which was followed by Matt Kohn, who skillfully presented the effects (merits and perils) of diffusion, and Ralf Dohmen (University of Bochum, Germany), who gave a comprehensive overview of techniques used to study magmatic processes (chronometry and speedometry). In the afternoon, zircon – the most commonly used accessory mineral in petrochronology – was highlighted by Daniela Rubatto (University of Bern). Blair Schoene (Princeton University, USA) discussed opportunities and obstacles of U–Pb and Sm–Nd rock dating by thermal ionization mass spectrometry before Andrew Kylander-Clark (University of California, Santa Barbara, USA) gave a practical demonstration of laser ablation split-stream inductively coupled mass spectrometry monazite dating – which he did on-line from Vienna with his lab in California (USA)!

The morning session on Sunday was dominated by garnet, with Mark Caddick and Besim Dragovic (Virginia Tech, USA) taking the participants through a passionate review across observational, modeling and dating techniques. Petrochronological applications involving titanite and rutile were then presented, respectively, by Matt Kohn and Ellen Kooijman (Museum of Natural History, Stockholm, Sweden). After lunch, Urs Schaltegger (University of Geneva, Switzerland) turned our attention to igneous systems, with a special focus on zircon. Axel Schmitt (University of Heidelberg, Germany) described the use of the secondary ionization mass spectrometry analysis. And to finish this short course, Emilie Janots (University of Grenoble, France) presented insights into recent experimental results on mechanisms of monazite dissolution and reprecipitation.

Overall, this RiMG short course was a scientific and social success. It promoted fruitful discussions among students and researchers between the presentations and during the social parts of the program. A second short course on this topic will follow in Seattle (USA) 20–21 October 2017 (http://seattle2017.petrochronology.org). The RiMG volume itself (v83, Petrochronology: Methods and Application) is available for purchase via the Mineralogical Society of America’s website (http://www.minsocam.org/msa/RiM/v83.html).
**CALENDAR**

**2017**

**July 31–August 4** 13th International Topical Meeting on Nuclear Applications of Accelerators (AccApp’17), Quebec City, Quebec, Canada. Web page: accapp17.org/program/

**August 4–9** Magmatism of the Earth and Related Strategic Metal Deposits, Mias, Russia. Web page: emsmd.ru/

**August 6–10** Microscopy & Microanalysis 2017 Meeting, St. Louis MO USA. Web page: microscopy.org/

**August 12–13** Workshop: Melt Inclusions: Methods and Applications, Portland, OR USA. Web page: iavcei2017.org/preA_5.html


**August 20–24** DC, USA. Web page: www.acs.org


**August 20–29** 12th International Eclogite Conference (IEC), Åre, Sweden. Web page: www.geology.lu.se/IEC

**August 21–27** XXIV Congress and International Assembly of the International Union of Crystallography, Hyderabad, India. Website: www.iucr2017.org

**September 3–6** Joint Congress of the SIMP, SGI, Aiv, and SOGei, Pisa (Italy), Web page: www.geosciences.it/pisa2017

**September 12–14** Annual Meeting of Japan Association of Mineralogical Science, Ehime, Japan. Details forthcoming

**September 13–17** Conference on Accessory Minerals (CAM-2017), Vienna, Austria. Web page: www.univie.ac.at/Mineralogie-CAM-2017/

**September 14–15** Vitrogeowastes, Alicante, Spain. Web page: tarsa.eu/vitrogeowastes/

**September 17–22** Applied Isotope Geochemistry 12 (AIG-12), Copper Mountain, CO, USA. Website: www.appliedisotopegeochemistry.org

**September 18–22** DMG PhD Short Course: “Mineralogy, Mineral Physics, and Seismology of the Earth’s Mantle”, Bayreuth, Germany. Web page: depict-group.org/short-course.

**September 18–22** International Kimberlite Conference (11IKC), Caborne, Botswana. Web page: www.11ikc.com

**September 18–22** Basalt 2017, Kadan, Czech Republic. Web page: www.basalt2017.cz


**October 9–13** DMG Short Course: “In Situ Analysis of Isotopes and Trace Elements by Femtosecond LA-ICPMS”, Hannover, Germany. Contact e-mail: sweyer@mineralogie.uni-hannover.de

**October 15–20** International PhD School: “Carbon Forms, Paths, and Processes in the Earth”, Como, Italy. Web page: ctpp.lakecomoschool.org


**October 19–24** 24th Session of the Petrology Group of the Mineralogical Society of Poland: “Isotopes as Tools to Understand the Earth and Environment”, Wroclaw, Poland. Web page: ptmin2017.ing.uni.wroc.pl

**October 20–21** MSA–GS Short Course: Petrochronology, Seattle, WA USA. Web page: seattle2017.petrochronology.org/


**November 9–13** DMG Short Course: “In Situ Analysis of Isotopes and Trace Elements by Femtosecond LA-ICPMS”, Hannover, Germany. Contact e-mail: sweyer@mineralogie.uni-hannover.de


**November 14–17** Rayons X et Matière, Villeneuve d’Ascq, France. Web page: www.rayonssetmatiere.org

**November 26–December 1** MRS Fall Meeting, Boston, MA, USA. Web page: www.mrs.org/fall2017/

**December 11–15** AGU Fall Meeting, New Orleans, LA USA. Web page: fallmeeting.agu.org/2016/2017-fall-meeting-new-orleans/

**2018**

**January 21–26** 42nd International Conference and Expo on Advanced Ceramics and Composites (ICACC’18), Daytona Beach, FL, USA. Web page: ceramics.org/icacc2018

**March 18–22** 255th ACS National Meeting & Exposition, New Orleans, LA, USA. Web page: www.acs.org

**May 20–23** AAPG 2018 Annual Convention, Salt Lake City, UT, USA. Web page: www.aapg.org/events/conferences/ace.

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TRIBUTE TO PAUL H. RIBBE 1935–2017

Paul Hubert Ribbe, a giant in the field of mineralogy, passed away 24 June 2017 at the age of 82. Just eight weeks earlier, he was preceded in death by Elna Ribbe, his wife of almost 59 years. Paul was born 2 April 1935 in Bristol, Connecticut (USA), to the Reverend Walter and Grace Ribbe. He obtained his BS from Wheaton College (Illinois, USA) and his MS from the University of Wisconsin, Madison (USA), both in geology. He was the first American Fulbright Scholar admitted to Magdalene College, University of Cambridge (UK), where he worked at the Cavendish Laboratory with the legendary crystallographer Helen Megaw. He was awarded a PhD in 1963 for his research on the crystal structure of plagioclase feldspars. Following a short post-doc (University of Chicago, USA) and an assistant professorship (University of California, Los Angeles, USA), in 1966, Paul and Elna moved to Blacksburg (Virginia, USA) where he joined the Department of Geology at Virginia Tech. Paul became part of a powerhouse of talent in mineralogy and petrology that included Donald Bloss, Gerald Gibbs, Charles Gilbert, and the late David Wones.

Over a remarkable 30-year career, Paul Ribbe distinguished himself as one of the world’s greatest feldspar crystallographers. He is well known for his 1963 transmission electron microscopy study with Stephen G. Fleet of Cambridge University, which showed that the properties of moonstone are due to alternating lamellae of orthoclase and albite. Paul was President of the Mineralogical Society of America (1986–1987) and was awarded both the MSA Distinguished Public Service Medal (1993) and the Schlumberger Award from the Mineralogical Society of Great Britain and Ireland (1995). He also had a mineral named after him: ribbeite, a Mg–Mn$^{2+}$-orthosilicate.

Paul Ribbe’s most enduring impact on the world of mineralogy resulted from his visionary role as editor of MSA’s Reviews in Mineralogy series. This series began in 1974 when Paul edited a book entitled Sulfide Mineralogy under the heading of “Short Course Notes”, which contained articles by P. B. Barton, J. R. Craig, C. T. Previtt, V. Rajamani, S. D. Scott, and B. J. Wuenisch. Under Paul’s leadership, this book was later reprinted as Volume 1 of Reviews in Mineralogy. This was the first of 53 volumes that Paul handled, developing into what we know today as the Reviews in Mineralogy and Geochemistry series, with more than 84 volumes in this series to date. Known for excellence and comprehensiveness, these books have been sold or distributed to libraries worldwide.

It is fair to say that these books have touched the scientific life of nearly every mineralogist, petrologist, and geochemist in the world since 1974. The mineralogical community owes a great debt of gratitude to Paul Ribbe for his untiring dedication and for setting the very high standards as the Editor of this landmark series of reviews.

Paul’s intellect was monumental, certainly in things scientific, but more important to him was his family (he had three kids, nine grandkids, and six great grandkids), friends, those in need, and his Christian faith. He was a skilled counselor to many, both in and out of science. He was a master orator, with an ingenious and clever mind. Paul also had a dry wit. Mostly, he was admired and loved by family, former colleagues and students, and friends.

Mineralogy has lost a truly remarkable person.

Nancy L. Ross (Virginia Tech)
Michael F. Hochella Jr. (Virginia Tech)
Gordon E. Brown Jr. (Stanford University)

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Data from: F. M. Deegan et al, Scientific Reports 6, 30774 (2016).

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