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Continental Crust at Mantle Depths

Guest Editor: Jane A. Gilotti

The Realm of Ultrahigh-Pressure Metamorphism
Jane A. Gilotti

Continental Crust at Mantle Depths: Key Minerals and Microstructures
Hans-Peter Scherli and Patrick J. O’Brien

Constructing the Pressure–Temperature Path of Ultrahigh-Pressure Rocks
Hans-Joachim Massonne

Linking Time to the Pressure–Temperature Path for Ultrahigh-Pressure Rocks
William C. McClelland and Thomas J. Lapen

Deep Fluids in Subducted Continental Crust
Jörg Hermann, Yong-Fei Zheng, and Daniela Rubatto

Formation and Exhumation of Ultrahigh-Pressure Terranes
Bradley R. Hacker, Taras V. Gerya, and Jane A. Gilotti

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Who isn’t fascinated by caves and volcanoes? They are windows to the interior of the Earth. We know more about places on the Moon, and now Mars, than what lies 100 km beneath our feet. Jules Verne (1864) captured this interest when he fantasized Prof. Lidenbrock’s journey to the center of the Earth. The professor, if he seemed, climbed down a lava tube on the stratovolcano Snaefellsjökull in Iceland and had a series of entertaining adventures with a vast subterranean ocean, an ichthyosaurus, giant diamonds, and prehistoric humans before he was somehow ejected by an eruption and emerged at Stromboli in Italy! The fiction of this account is humorous, but played off scientific advances of its time. Verne’s 1864 idea of an earlier primitive human race is said to have been inspired by Lyell (1863), who was influenced by Darwin (1859). The implications of preserved ancient worlds (or time travel?), a cliché today, were novel then. But is the imaginatively strong rocks and lack of ductility implied by open voids at great depth that I want to discuss. What are the limits of this fiction? When it comes to high-pressure metamorphism, our imagination has sometimes been ductility-challenged.

Before the plate tectonics revolution fully took hold, experiments demonstrated that bluestone mineral assemblages are stable only at high pressure (HP) and low temperature. In combination with field studies, this led to the hypothesis that these crustal rocks were somehow buried to great depth (15–30 km), kept cool, and returned to the surface (Essene et al. 1965; Ernst 1965). How could that happen? The elegant explanation now provided by subduction of oceanic crust was not yet appreciated, and the interpretations of high P and low T were met with some skepticism. Alternate, shallow processes, such as tectonic overpressure, were proposed. If great lateral forces could move continents, could pressures much greater than the lithostatic load be applied to shallow rocks? But like Verne’s caves, tectonic overpressure requires that rocks have sufficient strength, which experiments and seismology have shown not to be the case, and HP metamorphism is now recognized as evidence for subduction.

This issue of Elements describes more recent and perhaps more remarkable advances in the petrology of UHP (ultrahigh-pressure) metamorphic rocks. UHP index minerals, including microdiamond and coesite, have been found in metasediments of at least 20 terranes that were buried to depths greater than 100 km, possibly much greater, and have somehow returned to the surface. This history and the tectonic implications are fascinating but uncertain, and are reminiscent of the earlier controversies regarding HP metamorphism.

An early tenet of plate tectonics was that only mafic ocean crust is dense enough to subduct to depths where it converts to denser-still eclogite, sealing its fate to sink deeper. Such material can only return from the mantle in small pieces— as xenoliths entrained in magma, or perhaps as exotic blocks lubricated by serpentinite. In contrast, continental crust was said to be forever, suggesting that continental growth is the ideal savings account: continuous deposits over the past 4.5 billion years but never withdrawals. Now, UHP mineral equilibria show that even granitic compositions and sediments become dense if buried to mantle depths in a Himalayan-style orogeny. Our savings are not secure; continental crust does subduct. Once this happens, its fate is uncertain. How deep can such rocks be buried and still return to the surface? How much never returns? How is exhumation possible? Are regionally distributed UHP occurrences such as Dabie–Sulu a continuous terrane or an association of UHP outcrops surrounded by other rocks? Ductility (again) suggests surprising new mechanisms, including mantle drips and mantle diapirs.

The six articles in this issue plus a perspective describe the global occurrence of UHP rocks, including their mineralogy and beauty, phase equilibria, the role of fluids, geochronology, and the processes that may form and exhume them. Ruling paradigms are challenged by new ideas. Taken together, these studies define with remarkable detail the pressure–temperature–time–fluid composition (P–T–t–X) paths taken by these rocks on their journey towards the center of the Earth and their surprising return. They are our best window on the subcontinental mantle.

John W. Valley†

† Principal Editor in charge of this issue

Cont’d on page 244 (references)
THIS ISSUE
The story told in this issue developed from a simple observation under the microscope and the curiosity of a scientist to identify the “weird inclusions” he was looking at (you can read about this discovery on page 246). The identification of these inclusions changed the way we thought the continental crust was behaving. Amazing! Guest Editor Jane Gilotti and the cast of authors she assembled tell this story admirably.

This issue contains the first article in what is hoped will be a series under the overall title Mineralogy Matters. The aim of the series is to address the question as to whether research in a particular area of mineralogy (broadly defined to include petrology and geochemistry) has made an impact. Has, in fact, mineralogy “mattered” in the case being discussed. The first subject concerns arsenic and the severe human health problems associated with arsenic contamination of drinking water in several parts of the world. This series is being edited by Past Principal Editor David Vaughan who would welcome suggestions for topics and offers to become involved in writing future articles in the series. He can be contacted via email at david.vaughan@manchester.ac.uk.

SURVEY HIGHLIGHTS
Shortly after the last issue went to press, I provided Seth Davis of the Geochemical Society with a short text to announce the issue in Geochemical News (I also provide such notices to all business managers/society news editors). He thought he would write a special item for Elements’ 50th issue the following week. I responded by suggesting that it would be interesting to ask people what their favorite issue was. Within a day, we had a survey ready to go, and we asked participating societies to distribute the Web link. Thanks Seth for making it happen!

The survey ran between June 18 and 28. In all, 527 of you responded. Thank you to everyone who participated in the survey and provided a wide variety of useful comments for the consideration of the editors and Executive Committee. For those who are curious, the top 10 favorite issues selected in the survey were (participants could provide up to 5 choices):

- Zircon: Tiny but Timely (v3n1, 2007)
- Rare Earth Elements (v8n5, 2012)
- Granitic Pegmatites (v8n4, 2012)
- Supervolcanoes (v4n1, 2008)
- Early Earth (v2n4, 2006)
- One Hundred Years of Geochronology (v9n1, 2013)
- Diamonds (v1n2, 2005)
- When the Continental Crust Melts (v7n4, 2011)
- Tourmaline (v7n5, 2011)
- Large Igneous Provinces (v1n5, 2005)

These popularity ratings have to be taken with a grain of salt, and the vast majority of the comments dealt with the difficulty of choosing only 5 favorites.

One responder wrote, “This selection is completely arbitrary. I found most of the issues extremely interesting, but often from different points of view – teaching, own research, interest for unknown fields, demonstrating to my university president/faculty members the importance of geosciences.” Another mentioned, “As a lecturer, numerous issues of Elements have provided excellent introduction to topics for advanced undergraduate courses. Several issues have provided overviews of areas new to me that are becoming important for my own research.”

The Editorial, Meet the Authors, Book Reviews, Perspectives, and Triple Point are the most-read regular features. But many of you reported reading Elements from cover to cover. 85% of respondents read the society news either always or sometimes: “I have found this to be a worthwhile section that generally has useful/interesting info,” commented a respondent. About 2/3 of the survey participants read the print version while the remainder use the online version, and some read both. More than half the respondents listed topics they would like to read about, and this extensive list represents a wealth of information that the editors will review attentively.

2012 IMPACT FACTOR
Elements’ impact factor for 2012 was 3.156, and its 5-year impact factor was 3.612. The 10 most cited articles from the time of publication to July 2013 are:


Pierrette Tremblay, Managing Editor

FROM THE EDITORS

BACK ISSUES OF ELEMENTS FOR TEACHING PETROLOGY

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**Do You Think Ions Like Queuing Up?**

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**EARTH SCIENTISTS ELECTED TO THE ACADEMIA EUROPAEA**

Four Earth scientists were recently elected as members of the Academia Europaea (www.acadeuro.org), an international, non-governmental, not-for-profit association of scientists and scholars. Members are drawn from some 35 European countries and eight non-European countries. Membership is currently around 2300 and covers the natural sciences, humanities, and letters. Founded in 1988, the Academia Europaea organizes workshops, conferences, and study groups; publishes the *European Review* and other academic materials; and provides expert advice on European science-policy matters.

**Peter Liss**, FRS, is a Professoral Fellow in the School of Environmental Sciences at the University of East Anglia in Norwich, UK, where he researches and teaches many aspects of environmental chemistry. His research interests are in global change, and he specializes in ocean–atmosphere interaction, particularly involving trace gases.

**Kristín Vala Ragnarsdóttir** is a professor of sustainability science at the Institutes of Earth Sciences and Sustainable Development, University of Iceland. After undertaking research on geothermal systems, the behavior of pollutants, and their link to health, she turned to sustainability studies. These range from city to national and world scale, with a focus on soils, communities, and well-being.

**Stephen Sparks**, FRS, is a professor of geology in the School of Earth Sciences at the University of Bristol and a leading authority in volcanology and igneous processes, including hazard and risk assessment. He is currently chair of the UK Advisory Committee on Mathematics Education and a member of the Technology Advisory Panel of the Nuclear Decommissioning Agency.

**Lars Stixrude** is a professor of geophysics and mineral physics at University College London. Through his research into the deep structure and evolution of the Earth as revealed by material behavior, he has helped to establish quantum mechanical simulation as a method for exploring the high-pressure behavior of planet-forming materials.

**SHEPARD MEDAL TO GEROLD WEFER**

Gerold Wefer of the University of Bremen, Germany, is the 2014 Shepard medalist for excellence in marine geology of the Society for Sedimentary Geology (SEPM). Gerold Wefer is a professor of marine geology. He founded MARUM, the Center for Marine Environmental Sciences at the University of Bremen, and was a director until November 2012. He received his diploma and PhD degree in marine geosciences from the University of Kiel, Germany. He has published more than 300 papers in the field of marine geosciences and has participated in about 30 major research cruises. He is a member of the German Mineralogical Society.
From the managing editor: In his iconic 1984 paper, “Coesite and pure pyrope in high-grade blueschists of the Western Alps: a first record and some consequences”—cited 711 times since publication and mentioned in 4 papers in this issue—Christian Chopin concluded his abstract with the following statement, “Eventually the role of continental crust in geodynamics may have to be reconsidered.” Rarely does a single paper have an impact that leads to the development of a whole new area of research. Chopin’s paper, and David Smith’s paper the same year, heralded a new field of research. I thought it would be interesting to get the story of how this discovery came about, and Christian graciously accepted to be interviewed.

What led you to study the Dora-Maira rocks?

In 1979, after my thèse de 3e cycle (French equivalent of the PhD) on the petrology of the Gran Paradiso massif (one of the three internal crystalline massifs of the Western Alps, along with the Monte Rosa and Dora-Maira massifs), I went for a postdoc at Bochum with Werner Schreyer to do experimental work at high pressure. Some of the rocks I had mapped for my thèse de 3e cycle were highly magnesian and offered promise as fine recorders of metamorphic evolution at high pressure through reactions among talc, chloritoid, garnet, carpholite, and chlorite, but these reactions had to be quantified. For more than 2 years, I did high-pressure experiments in the MASH system, working out the stability fields of the Mg end-members of chloritoid and carpholite. In the lab a whole group of people were working on various high-pressure and high-temperature phases. For example, Peter Mirwald and Hans-Joachim Massonne were working on the coesite-quartz transition, a classical pressure-calibration reaction, so I became familiar with these high-pressure phases.

After being hired as a CNRS researcher at the École Normale Supérieure (ENS) in Paris in 1981, I systematically searched for these magnesian rocks. I had already done reconnaissance work on the Monte Rosa massif, where I had found magnesian assemblages that pointed to higher pressures than in Gran Paradiso. So the next step was Dora-Maira, and a literature search led me to the 1966 thèse d'état of Pierre Vialon on this massif. He described the assemblage pyrope-talc-chlorite, which, to me, with my fresh experimental background, seemed impossible in Alpine rocks of crustal origin, as pyrope-rich garnet had so far only been found in mantle rocks. I was very intrigued. In the fall of 1982, with colleagues Bruno Goffé and Bill Murphy and armed with the crude location map provided in the thesis, we set out to search for these rocks. We parked the car and spent over an hour walking around trying with no success. After returning to our starting point, we took a closer look at the outcrop next to the car and noticed unusual whitish nodules. They turned out to be garnet, but the garnet was so magnesian that it was almost white. Vialon was right! We sampled the outcrop and I had thin sections made.

How did the coesite discovery come about?

When I studied the thin sections, I noticed weird, high-relief, low-birefringence inclusions in pyrope with radial fractures around them and their breakdown into quartz. If pure pyrope was there, however unbelievable it seemed, why not coesite? There was one simple way to confirm this—probe them. We had an easily accessible, entirely manual electron microprobe at ENS. I sure remember the day I probed these inclusions and confirmed that they were pure SiO₂. So simple and so exciting. Intense jubilation!

At that time, coesite was known in impact rocks and in xenoliths in diamond-bearing kimberlites. So what would coesite be doing in crustal rocks? For the Alpine petrologist, the straightforward hypothesis was that it was metamorphic coesite, but this was also the idea with the farthest-reaching implications. So I took several weeks to consider alternative hypotheses. For example, could it be an impact product, a placer mineral, or a high-shear product? But in the end, the simplest hypothesis by far was the metamorphic one—with all the implications it carried.

Did you have trouble selling your idea to reviewers or other scientists?

No, probably because the petrographic evidence was so compelling. I gave a talk on the discovery at the European Union of Geosciences meeting in the spring of 1983. Afterwards, I was approached by David Smith (Muséum d’Histoire Naturelle de Paris) who thought he had a similar quartz texture in Norwegian eclogites he was studying. As he had access to a Raman spectrometer, we were able to get a confirmation of the coesite structure of a tiny, relict grain within a quartz inclusion in the Norwegian sample.
I am currently involved in a study of blueschists in Turkey. This interdisciplinary approach—each of us pushing the others to the limits of crystallography and chemical and, sometimes, the spec- troscopic approach—of a long-standing collaboration with crystallographers. Investigating structures like the beautiful series between ellenbergerite (purple stilpnomelane, staurolite, chloritoid, and dumortierite, accessory minerals, and new minerals) was just an exotic lens or, as it turned out, a part of a coherent, regional-scale metamorphic unit sharing these uncommon conditions of origin.

I then tackled the mineralogy, and this kept me occupied for another 10 years or so—these highly magnesium rocks were like Ali Baba’s cave. We described several near Mg end-members of known minerals like enstatite, richterite, chlorite, and dumortierite, accessory minerals, and new mineral suites like the beautiful series between ellenbergerite (purple stilpnomelane) and its blue-green phosphate counterpart. This was the beginning of a long-standing collaboration with crystallographers. Investigating the same object using two completely different and independent approaches—crystallographic and chemical—and sometimes the spectrosopic approach—each of us pushing the others to the limits of their method, is a very gratifying intellectual challenge, which I am still enjoying. Not always on high-pressure phases, admittedly, even if I am currently involved in a study of blueschists in Turkey.

What’s next in UHP metamorphism?

Ever deeper! Since 1989, there has been a steady stream of discoveries of UHP rocks, and continental subduction is now seen as a standard feature of collisional belts. But as we study rocks that have reached higher and higher pressure, and so higher temperature, it becomes increasingly likely that we will only observe retrograde products—and so evidence is more and more elusive.

The recent discoveries of diamond in Alpine oceanic rocks and of what is interpreted as coesite pseudomorphs after stishovite in the Luobusa chromitite of Tibet are fabulous. I feel the same excitement as when I discovered coesite. This is the primacy of observation: a simple observation suddenly reveals huge gaps in the understanding we have of our planet. Like vertigo. Just compare our understanding of continental behavior 25 years ago with the present one, and imagine the progress 25 years after the Luobusa findings: our understanding of how the mantle works might then be radically different.

Some references paving the way to the coesite finding, and later related references:


Meanwhile, I had submitted a manuscript documenting my work to Contributions to Mineralogy and Petrology. The only negative comment the reviewers made was that the paper was long, but I wanted to provide a thorough petrological description. The paper was published in 1984, and David Smith’s paper was published in Nature a few months later. After publication, I discovered that these pyrope megacrystals were actually already known within the Alpine community and that there were some samples in museums and collections. This shows how an extraordinary object can remain inconspicuous and unnoticed if there is no context to view it in. My good fortune was to be the one looking at these rocks with both a field and an experimental background. Serendipity or just “helping luck”?

Did this publication influence your career?

Yes, indeed. I spent the following 10 years mapping the extent of these magnesium rocks and clarifying the geological setting (with PhD students Caroline Henry and Gilla Simon, and colleagues in Bochum, Jerusalem, Kiel, Montpellier, and Torino). What was the relationship between this oddity and the country rocks that apparently had no special attributes (granitic gneiss with rafts of marble, metabedite, and eclogitic mafic rocks)? Was it just an exotic lens or, as it turned out, a part of a coherent, regional-scale metamorphic unit sharing these uncommon conditions of origin?

I then tackled the mineralogy, and this kept me occupied for another 10 years or so—these highly magnesium rocks were like Ali Baba’s cave. We described several near Mg end-members of known minerals like enstatite, richterite, chlorite, and dumortierite, accessory minerals, and new mineral suites like the beautiful series between ellenbergerite (purple stilpnomelane) and its blue-green phosphate counterpart. This was the beginning of a long-standing collaboration with crystallographers. Investigating the same object using two completely different and independent approaches—crystallographic and chemical, and sometimes the spectrosopic approach—each of us pushing the others to the limits of their method, is a very gratifying intellectual challenge, which I am still enjoying. Not always on high-pressure phases, admittedly, even if I am currently involved in a study of blueschists in Turkey.

Christian Chopin was born in 1955 and grew up in Lyon, France. During family holiday trips through the Massif Central, across a horst and graben structure, to recent volcanoes and old leucogranites, he may have got an early feeling for Earth matters. After passing the national selection exam to enter the École Normale Supérieure (ENS) in 1974, he studied Earth sciences at the two nearby universities, Paris 6 and 7. He had teachers like F. Albarède, C. J. Allègre, V. Courtillot, and K. Lambeck, but he was attracted to metamorphic petrology through J. Touret, G. Guitard, and J.-R. Kiénast. During these formative years, he profited from the early laboratory access offered by ENS to its students. In Martine Lagache’s group, he familiarized himself with experimental petrology and field mineralogy. He completed an Alpine thesis under the guidance of Pierre Saliot, studying the phase relations of Mg-Al-rich rocks at high pressure. He held a two-year postdoc position in Bochum, attracted by the enthusiastic personality of Werner Schreyer and a very active high-pressure experimental group. This stay marked the beginning of collaborations and friendships that shaped his career. He was hired by CNRS as a researcher at ENS Paris in 1981.

Exciting years followed, in his long scientific collaboration with Bruno Goffé. Goffé worked on lower-grade high-pressure rocks—and hunted carpholite worldwide—while Chopin studied the higher-grade ones, focusing on the Dora-Maira Alpine massif. Chopin became editor of the nascent European Journal of Mineralogy in 2001, and he has been head of the Laboratoire de Géologie at ENS since 2006. He is a firm believer in the publishing role of learned societies as an inexpensive alternative to monopolistic publishing houses.
Newly recognized occurrences of ultrahigh-pressure minerals in ultrahigh-temperature felsic granulites and in chromitite associated with ophiolite complexes lead to speculation about the recycling of supracrustal materials through deep subduction, mantle upwelling, and return to the Earth’s surface. This idea is supported by possible “organic” light carbon isotopes observed in diamond and moissanite in kimberlite xenoliths and chromitite. These findings presage another renaissance in the study of UHP granulite facies lower-crustal basement and ophiolites and in our understanding of the geodynamics of continental subduction and mantle cycling.

UHP MINERALS IN NEW TECTONIC ENVIRONMENTS

The discovery of minerals and microstructures indicative of ultrahigh-pressure (UHP) metamorphism in a variety of new tectonic environments is providing insight into the fate of subducted crust. Two of the most recent findings of UHP minerals in ultrahigh temperature (UHT) granulites and in chromitites associated with ophiolite complexes are highlighted below. Also presented is a schematic cross section of the outer shells of the Earth, showing the recycling of crustal materials in various tectonic regimes (Fig. 1). These findings, together with many other well-documented occurrences of global UHP orogens, reveal that microdiamond, coesite, and other UHP phases are more common than previously thought in both Alpine- and Pacific-type orogens.

Occurrences of microdiamond (+ coesite) as inclusions in kyanite, garnet, and zircon from felsic granulites in the northern Bohemian massif (e.g. Kotková et al. 2011) together with earlier findings of microdiamond, coesite, and nano-size α-FeO2-structured TiO2 polymorph in pelitic gneisses of the central Erzgebirge suggest that a large part of the Bohemian massif crustal basement has been exhumed from mantle depths of >150 km and subjected to mid-crustal high-temperature (HT) to UHT granulite facies recrystallization. Moreover, the occurrence of diamond and coesite inclusions in garnet and kyanite of UHT felsic granulites from northern Africa are unusual as these rocks document much higher P-T conditions (P > 4.3 GPa, T > 1100°C), exhibit topotaxial overgrowths of diamond and coesite, lack palisade quartz around relict coesite, and have intergrowths of coesite and phengite possibly after K-cymrite (Ruiz-Cruz and Sanz de Galdeano 2012, 2013). The close association of mantle-derived garnet peridotites with such UHP-UHT granulites suggests that these peridotite bodies became interdigitated with deeply subducted continental crust under UHP conditions rather than being teectonically emplaced at shallow crustal levels.

More startling is the fact that UHP minerals have been discovered in podiform chromitites in ophiolite. For example, diamond, moissanite, possible coesite pseudomorphs after stishovite, Fe–Ti alloys, osbornite, cubic boron nitride, TiO2 II, and zabonite occur as nano- to micro-scale inclusions in podiform chromitite from the Luobusa ophiolite, Tibet (Yang et al. 2007; Li et al. 2009; Dobrzhinetskaya et al. 2009). In situ microdiamond (+ moissanite) inclusions in chromite grains also have been recognized in several ophiolitic massifs along the 1400 km long Yarlung–Zangbo suture between India and Asia, and in the Polar Urals (Yang and Robinson 2011). These UHP minerals and chromite containing exsolution lamellae of coesite + diopside (Yamamoto et al. 2009) suggest that the chromitites formed at P > 9–10 GPa and at depths of >250–300 km. Thin lamellae of pyroxene in chromite, similar to those from Tibet, have been documented in chromitites in the northern Oman ophiolite (Miura et al. 2012). The precursor phase most likely had a Ca-ferrite or Ca-titanite structure; both are high-pressure (HP) polymorphs of Cr-spinel at P > 12.5 and 20 GPa (at 2000°C), respectively (Chen et al. 2003). Apparently, these UHP-mineral-bearing chromitites had a deep-seated evolution prior to extensional mantle upwelling and partial melting at shallow depths to form the overlying ophiolite complexes.

Just where diamond in chromitites formed and whether or not diamond is involved in the recycling of oceanic/continental lithosphere rich in C and volatiles are open questions. The tectonic setting of these ophiolites reflects mantle upwelling and recycling of subducted oceanic/continental materials. The formation of diamond in the subcontinental lithospheric mantle is likely related to the oxidation of asthenosphere-derived, methane-rich fluids (Malkovets et al. 2007). The preservation of diamond is also controlled by the oxygen fugacity of the Earth’s mantle (Stango et al. 2013). Some Brazilian diamonds have “organic” light carbon isotope values (δ13C = –25‰ to –14‰) and contain microto nano-inclusions of “superdeep” mineral associations (Wirth et al. 2007, 2009; Walter et al. 2011). These inclusions include phase egg [AlSi4(OH)] + stishovite, spinel + nepheline–kalsilite, wüstite + ferropericlase, native iron + magnesite, α-FeO2-structured TiO2, wollastonite-II, cupidine, tetragonal almandine–pyrope, and various halides derived from precursor phases stable at depths of >700 km. Walter et al. (2011) also identified two new minerals (NAL, an aluminum silicate phase, and CF, a calcium ferrite phase) previously known only from experiments. Majorite-bearing diamonds from South African kimberlites also record “superdeep” mantle environments (Griffin 2008). Eclogite-associated kimberlite diamonds frequently have light δ13C values (–22‰ to –6‰) and contain coesite and garnet inclusions with high δ18O values (+6‰ to +16‰); the antecorrelation between C and O isotope ratios suggest a recycling origin (Schulze et al. 2003, 2013).

PERSPECTIVES

These new findings should certainly renew interest in the exploration of UHP minerals and rocks in ophiolite and granulite terranes. The isotopic and inclusion characteristics of kimberlitic diamonds provide compelling evidence for deep subduction of oceanic lithosphere, recycling of surface “organic” carbon into the lower mantle, and exhumation to the Earth’s surface, probably via a deep-mantle plume. Diamond and moissanite from chromitites associated with ophiolites in southern Tibet and the Polar Urals have extremely light δ13C values, –29‰ to –18‰ (Yang and Robinson 2011), much lighter than most peridotite-associated kimberlitic diamonds (–8‰ to –2‰). Although the origin of such light isotopic compositions in diamonds is the subject of debate, numerous studies of carbon isotope compositions of superdeep kimberlitic diamonds from Brazil and Siberia suggest that they were derived from deep-mantle cycling of oceanic crust (e.g. Taylor and Anand 2004; Bulanova et al. 2010; Walter et al. 2011). Composite mineral inclusions in Brazilian diamonds indicate crystallization at lower-mantle conditions; for example, inclusions of tetragonal almandine–pyrope were suggested to be a retrograde phase of Mg-perovskite stable at P > 30 GPa (Armstrong and Walter 2012).

Over the last decade, global mantle seismic tomography has been used to image slab stagnation; geochemical evidence of recycled material in the peridotitic mantle and the entire subduction / mantle plume cycle has been also documented. High-pressure experi- ments have revealed that reidite (a high-pres- sure polymorph of zircon) in a subducting slab is stable at P < 20.5 GPa and 1500 °C (Tange and Takahashi 2004). In fact, crust-derived, quartz- bearing zircons in garnet peridotite xenoliths from the Trans–North China orogenic belt (Liu et al. 2010, xenocrystic zircons in mantle xenoliths in Namibia and China (Liat et al. 2004; Zheng et al. 2006), and abundant, crust- derived, recycled zircons in orogenic perido- tites from the Urals (Bea et al. 2001) have been described. Pidofit chromites associated with the ophiolites of Tibet, the Polar Urals, and Oman, mentioned above, contain rare supra- crustal zircon, corundum, feldspar, garnet, kyanite, sillimanite, quartz, and rutile, and have much older U–Pb zircon ages than the formation ages of ophiolites (Robinson et al. 2012; Yamamoto et al. 2013). Paleozoic and Proterozoic zircons have been found in gabbroic rocks in the axial zone of the Mid-Atlantic ridge (Pilot et al. 1998; Skolotnev et al. 2010). This direct evidence of crustal recy- cling into the mantle should lead to another research renaissance, which will integrate the efforts of geophysicists, geochemists, mineral physicists, and geologists.

The identification of rare UHP minerals (e.g. moissanite, k-cymbrite, k-wadeite) requires state-of-the-art analytical tools. Systematic data for the ages of subduction, UHP meta- morphism, and granulite facies overprinting, together with accurate P–T estimates, are essen- tial for delineating the tectonic evolution of crustal basement and lithospheric chromitite. Raman identification of submicron-size inclu- sions in domains of zircon from all litho- logies, secondary ion mass spectrometry (SIMS) analyses of in situ stable isotopes (O, C, and N), together with O and H isotope data from min- erals formed at different stages are necessary to determine the amount of recycled supracrustal materials, the source of fluids, and the extent of melt-rock interactions through subduction, mantle-plume ascent, and exhumation (e.g. Dobzhinetskaya 2012; Schulze et al. 2013). •##

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The image is of a garnet-mica schist from Brittany, France. Microtextures suggest the rock has undergone high-grade, regional metamorphism with associated polydeformation. Image courtesy of Michael Garrick.
The Realm of Ultrahigh-Pressure Metamorphism

Jane A. Gilotti*

The discovery of diamond and coesite in crustal rocks is compelling evidence that continental material has experienced pressures that can only be achieved at mantle depths. At least 20 terranes of unequivocal continental crust containing diamond or coesite are now recognized around the globe; their study constitutes a new field in petrology called ultrahigh-pressure metamorphism. The idea that continents do not subduct has given way to the notion that Earth has been sufficiently cool since the Cryogenian (~850 Ma) to allow density changes to drive continental crust into the mantle during collision. Some of this crust is exhumed to the surface. In this issue, microscopic observations, phase-equilibrium modeling, geochronology, and geodynamic modeling track the journey of crustal rocks to the mantle and back to Earth’s surface.

KEYWORDS: coesite, continental subduction, exhumation, diamond, eclogite, ultrahigh-pressure metamorphism

ULTRAHIGH-PRESSURE METAMORPHISM

The concept that buoyant continents resist subduction has slowly been eroded by the recognition of coesite and diamond in crustal rocks from mainly Phanerozoic mountain belts around the world (Fig. 1). Coesite, a high-pressure polymorph of SiO$_2$, was independently discovered in two different crustal rocks almost 30 years ago. Christian Chopin (1984) reported tiny grains of coesite as inclusions in pale pink garnet in an unusual quartzite from Dora-Maira, Italy, while David Smith (1984) identified coesite inclusions in clinopyroxene in an eclogite from Grytting, in the Western Gneiss Region of Norway. The identification of microdiamonds as abundant inclusions in garnet from eclogites, gneisses, and schists in the Kumdy Kol unit of the Kokchetav massif, Kazakhstan (Sobolev and Shatsky 1990), followed shortly after. These metamorphic diamonds are not the gem-quality diamonds brought to the surface by kimberlite pipes and coveted by society from time immemorial; rather, they are scraggly, little skeletal crystals, commonly less than 10 microns in diameter. Microdiamond and coesite in crustal rocks (Fig. 2) are relics of a journey that has taken surface material to mantle depths and back. Their discovery has fundamentally changed the way geologists view processes at convergent plate margins, from the Cryogenian to the present day.

Coesite is commonly found in eclogite—an attractive rock that is the poster child for high-pressure (HP) metamorphism because of its easily distinguished constituents, red garnet and green omphacite (Fig. 3). Basalt and gabbro transform into eclogite at high pressure when all the plagioclase has reacted with other ferromagnesian minerals to form omphacite, a dense Na-rich clinopyroxene, and garnet. The part of pressure-temperature ($P$–$T$) space that is inhabited by eclogite has long been known as the eclogite facies, but rocks of all compositions can occupy this space. The needle-in-a-haystack finds of diamond and coesite have extended known examples of eclogite facies metamorphism to even higher pressures and spawned a new field of metamorphic petrology called ultrahigh-pressure (UHP) metamorphism. Mineral assemblages with pressures above the quartz-to-coesite transition are ultrahigh-pressure metamorphic rocks by definition (e.g. Chopin 2003; Liou et al. 2009; Fig. 4). Coesite and diamond are the index minerals of UHP metamorphism, but many other minerals and microstructures point to pressures in excess of the quartz-to-coesite transition (see Schertl and O’Brien 2013 this issue). A look at $P$–$T$ space (Fig. 4) shows that eclogite facies conditions are not attained in normal continental crust but are possible when the crustal thickness doubles. Even where the crust is over 80 km thick beneath the Tibetan Plateau, the thickest crust on Earth, the rocks are still in the quartz stability field. To produce coesite, rocks must travel to mantle depths. Terminology can be confusing because very high pressures are the norm deep in the Earth’s mantle and core (see Elements, June 2008); but in this issue, the term UHP metamorphism refers to crustal rocks that have experienced mantle pressures.

We now recognize over 20 coesite and microdiamond terranes around the world (Fig. 1), which are made up of many individual localities. The majority of examples come from continental crust, but a few cases of oceanic crust are known as well. These so-called ultrahigh-pressure terranes are mainly situated in Phanerozoic continent–continent collision belts (Fig. 1)—in marked contrast to the kimberlite pipes in Precambrian cratons that host gem-quality diamonds (Harlow and Davies 2005). The most compelling evidence that rocks from the Earth’s surface have visited mantle depths comes from metamorphosed sediments. Diamond has been found in marble,
the metamorphic equivalent of limestone, while coesite and diamond are common in metasedimentary rocks with clastic depositional origins. A variety of rock types from the Triassic Dabie–Sulu UHP terrane in China still retain their premetamorphic, very negative δ18O values, which indicate exchange with heated, low-δ18O surface waters left over from Neoproterozoic glaciations (Liou et al. 2012).

Another important indication that continental crust has visited mantle depths is the presence of lenses of garnet peridotite—mantle rock composed of olivine + garnet + pyroxene—in the quartzofeldspathic UHP crust. In the majority of cases, garnet peridotites were transferred into the crust from the subcontinental lithospheric mantle wedge by tectonic processes during collision (Liou et al. 2009). The garnet peridotites demonstrate that continental crust not only reaches mantle depths but that it commonly returns with tectonically emplaced samples. Two well-known examples of garnet peridotite—Alpe Arami, Switzerland (Dobrzhinetskaya et al. 1996) and Otrøy, Norway (Spengler et al. 2006)—may have come from depths in excess of 300 km before they encountered their crustal hosts. Exhumed UHP terranes thus provide direct observations of the deeper levels of orogenic belts, subduction zones, and Earth’s mantle.

**WHAT DO UHP TERRANES LOOK LIKE?**

Field observations from the best-exposed continental UHP terranes show that the majority of the rocks are rather ordinary, gray, banded amphibolite facies gneisses. The gray gneisses are composed of common rock-forming minerals, mainly quartz, feldspar, garnet, amphibole, biotite, and white mica. In many cases they are orthogneisses (derived from an igneous parent), but they can also be paragneisses (Fig. 5a), in which case they may be interlayered with marbles and quartzites. Thin, centimeter-scale leucocratic layers formed by post-UHP partial melting are typical of the gneisses. A clue to their potential UHP heritage is the presence of easily recognizable layers and lenses of eclogite within the quartzofeldspathic gneisses. The protoliths of eclogite were original mafic components of the crust—common features such as lava flows, dikes, sills, plutons, and xenoliths—that resided in the crust prior to UHP metamorphism. During deformation, the stiffer mafic rocks were typically pulled apart to form lenses and pods, while the softer quartzofeldspathic rocks flowed around them. The example in Figure 5a shows a coesite-bearing eclogite with isoclinally folded layers of light-colored kyanite eclogite, garnet-rich eclogite, and dark green, pyroxene-rich eclogite; the compositional variation reflects the sequence’s origin as a layered gabbroic pluton. Historically, the host gneisses have been ignored in favor of the eclogites, but the discovery of diamond and coesite in zircon from such gneisses shows that large volumes of crust have seen UHP conditions. Nowhere is this better displayed than in a 5 km

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**FIGURE 1** Map of worldwide ultrahigh-pressure (UHP) terranes, modified from Liou et al. (2009), with updated diamond information from Schertl and Sobolev (2013). Solid symbols indicate confirmed coesite or diamond. Open symbols show localities where UHP metamorphism is inferred from pseudomorphs or calculated P–T conditions, or cases where index minerals have been published in abstract form but are not documented (e.g. Brazil, Sulawesi, Kontum). Only Lago di Cignana, Zambezi, and Tianshan are oceanic UHP terranes. For further information on individual localities, see online supplementary material (www.elementsmagazine.org/supplements).

**FIGURE 2** Transmitted-light photomicrographs. (A) Elliptical, intergranular coesite (at arrow) surrounded by a rim of lower-relief quartz together with omphacite (blue) and garnet (orange), from an eclogite at Yangkou beach, Sulu terrane, China (from Liou et al. 2012). (B) High-relief, cuboid diamond crystals (center) hosted by clear garnet in a biotite (brown) paragneiss from the Kokchetav massif, Kazakhstan. Photos courtesy of Ru Yuan Zhang.
diamond and coesite. The coin is 2.5 cm in diameter.

deep drill hole through the Sulu UHP terrane, China, where over 90% of the core is felsic gneiss and every lithology contains coesite (F. Liu et al. 2007). Such blocks of eclogite-bearing UHP continental crust are referred to as coherent eclogite terranes to emphasize that all crustal components share the same UHP history and to distinguish them from HP eclogite and blueschist blocks in accretionary mélanges.

The deformation state of coherent continental UHP terranes is varied. The common situation is an isoclinally folded package of high-strain rocks with subparallel, composite deformation fabrics cutting all rock types. In some cases, the eclogites retain an HP fabric at an angle to the lower-grade fabrics in the enveloping gneiss. On the other hand, remarkable pockets of low strain can remain even in highly deformed UHP terranes. Coronitic granodiorites associated with the coesite-bearing pyrope quartzite in the Brossasco-Isasca unit of the Dora-Maira massif, western Alps, retain their igneous texture. Original plagioclase in the metagranodiorite is statically replaced by a jadeitic pyroxene with ~13% Ca-Eskola molecule, a subtle sign of UHP metamorphism (Bruno et al. 2002). In a spectacular example from Yangkou beach, China (Fig. 5c), undeformed gabbro transforms to coesite-bearing eclogite (Fig. 2a) over a distance of a few meters (Zhang and Liu 1997). Low-strain regions are small but widespread in many UHP terranes, and are windows into the original character of the continental crust.

Continental UHP terranes come in assorted sizes. The largest in areal extent are the Dabie–Sulu belt, China, which is a part of the exhumed Yangtze craton (>30,000 km²), and the UHP area of the Western Gneiss Region, Norway (>5000 km²), a deeply subducted part of Baltica. Both are associated with significantly larger regions of coherent HP eclogite terranes derived from the same continental crust. A more complete estimate of size includes the thickness of the UHP terrane, but this can be difficult to determine. The Dabie–Sulu terrane must be a minimum of 10 km thick, based on exposed structural relief and the 5 km deep drill hole, while the exposed UHP Western Gneiss Region may be over 15 km thick (Kylander-Clark et al. 2012). The smaller UHP terranes are on the order of 1–50 km² and 1–3 km thick, and include the well-documented Dora-Maira and Lago di Cignana terranes in the western Alps. In most cases, size is probably underestimated because not all the diamond- or coesite-bearing rocks have been found. A current challenge is to identify individual UHP structural slices.

For example, two separate UHP units are now recognized in the Kokchetav massif, Kazakhstan (Scherli and Sobolev 2013): the diamond-bearing Kumdy Kol terrane and the coesite-bearing Kulet terrane; on the other hand, Lanari et al. (2013) proposed that the Himalayan UHP localities all belong to one terrane. Identifying individual UHP units based on structural geology and shared metamorphic history, in addition to index minerals, will lead to a better understanding of the overall tectonic evolution of UHP terranes.

WHAT CAME UP MUST HAVE GONE DOWN

The finds of coesite and diamond in rocks that today reside at the surface are direct evidence that crust was transported to mantle depths and returned as recognizable slices. Continental subduction during plate collision is the main mechanism for forming UHP terranes. The simple idea is that subduction acts like a cool conveyor belt, where the leading edge of the subducting plate starts out as oceanic crust and converts to eclogite at depth. Eclogite, being denser than the upper mantle, sinks and pulls the attached continent down to mantle depths as well. In subduction zones with geotherms around 5–8 °C/km, the crust remains cool enough to prevent melting at increasing depths. The preponderance of Phanerozoic-age continental UHP terranes (Fig. 1) also supports a subduction zone origin on a cooler Earth with well-established plate tectonics. Other mechanisms that could lead to the formation of felsic UHP terranes include subduction erosion of the overriding continental plate and

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**Figure 3** Coarse-grained eclogite with round to elliptical, glassy, pink garnet in a matrix of light green omphacite, North-East Greenland. Strong minerals such as garnet, omphacite, and zircon commonly form containers for inclusions of diamond and coesite. The coin is 2.5 cm in diameter.

**Figure 4** Pressure–temperature (P–T) space for ultrahigh-pressure (UHP) metamorphism (from Liou et al. 2012). The eclogite facies is shown in light and dark green. Metamorphic facies are delineated by thick gray lines (GS = greenschist, BS = blueschist, A = amphibolite, GR = granulite facies). UHP metamorphism is the deeper part of the eclogite facies and corresponds to the coesite stability field (dark green), while mere HP eclogites occupy the light green field. The gray region delineates a cold area below the 5 °C/km geotherm, which is sometimes called the Forbidden Zone because it is generally not found on Earth. The yellow, orange, and red lines correspond to generalized cold, tepid, and hot P–T paths for UHP rocks. The thicknesses of Tibetan and average crust are indicated.

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transport of the quartzofeldspathic crustal slices to mantle depths, or delamination of overthickened, dense crustal roots, which then sink into the mantle. Exhumation brings UHP rocks from great depths back to Earth’s surface. Exhumation mechanisms are less well understood than the processes that form UHP terranes, but ultimately they depend on body forces and the positive buoyancy of the subducted continental crust in comparison to the mantle. A variety of factors—such as size, exhumation rate, the percentage of crust actually converted to UHP assemblages, and the volume of eclogite together with garnet peridotite hitchhikers—will influence the exhumation process. Subduction zones lend themselves to exhumation because their geometry creates a complex pathway for return flow in a cool channel. Geodynamic models of continental subduction provide insight into possible mechanisms that promote exhumation (Gerya 2011).

A convenient way to describe the round-trip from Earth’s surface to the mantle and back is as a path through pressure–temperature space over time (t), or a P–T–t loop. The path is built by connecting points where the mineralogy and mineral compositions allow for a unique P and T to be determined (e.g. Massonne 2013 this issue). Time is added to the loop by the judicious application of geochronological methods to the available minerals in the rock (McClelland and Lapen 2013 this issue). U–Pb dating of multiple growth domains in zircon is a common approach. Not surprisingly, transport around the loop takes place at typical plate tectonic speeds, on the order of 1–10 cm/y. Subduction rates are approximately equal to exhumation rates for the smaller UHP terranes, which tend to take ~10–20 My to make the entire trip. Large UHP terranes may take 10–20 My to develop; they commonly return to the surface in two stages after stalling at the lower crust on their return (Zheng et al. 2009; Kylander-Clark et al. 2012).

P–T paths for HP and UHP terranes have a characteristic hairpin shape (Fig. 4), with long, steep sections that show profound increases and then decreases in pressure at relatively constant temperature. On the basis of temperature, the P–T paths can be divided into cold loops (to 600°C), tepid loops (to 800°C), and hot loops (to 1000°C). Cold loops are the hallmark of blueschist and eclogite terranes with oceanic affinities. Oceanic UHP terranes are rare, not because they fail to form but because they are too dense to be exhumed. The majority of continental UHP terranes follow a medium-T path to maximum temperatures of ~800°C (Hacker 2006). Hot UHP loops are relatively uncommon, but the three best-studied diamond-bearing terranes—the Bohemian, Kokchetav, and Rhodope massifs—fall into this category. Rocks that follow hot loops tend to melt, which decreases the chance of preserving coesite and diamond that may explain the paucity of UHP minerals in HP granulate terranes. The influence of fluids and melts during the formation and exhumation of UHP terranes is further examined by Hermann et al. (2013 this issue).

**GLOSSARY**

**Buoyancy** – the upward force exerted on the crust by the mantle; the term also refers to the difference in density between the mantle and the oceanic or continental crust because density determines the amount of displacement (floating or sinking) of the crust with respect to the mantle.

**Coesite** – a high-pressure polymorph of SiO₂. Coesite is more dense than quartz and is stable at depths greater than 90 km (P > 2.6 GPa) at 600°C. Coesite is the main index mineral of UHP metamorphism, but it can also form by shock from a meteorite impact.

**Delamination** – a process whereby rocks at the base of the crust become dense, perhaps by overthickening or gravitational instability, and sink into the mantle. These so-called mantle drips have been imaged seismically and produced in geodynamic models.

**Diamond** – a dense, high-pressure polymorph of carbon, in which each carbon atom is bonded to four other carbon atoms in a rigid tetrahedron, resulting in this cubic symmetry. Diamond is also an index mineral of UHP metamorphism.

**Eclogite** – a metamorphosed mafic rock that contains garnet and omphacite, but not plagioclase. Other common minerals in eclogite are kyanite, quartz/coesite, phengite, epidote-group minerals, magnetite, rutile, and zircon.

**Exhumation** – the movement of a buried rock towards Earth’s surface. Exhumation is distinct from uplift, which is simply the increase in elevation of the surface.

**Garnet peridotite** – an ultramafic metamorphic rock composed of garnet + olivine ± pyroxene, sometimes called orogenic peridotite because such rocks are found in collisional orogens. Garnet peridotites are commonly derived from the sublithospheric mantle, but they can also represent minor ultramafic cumulates associated with crustal mafic intrusions.

**High-pressure (HP) metamorphism** – metamorphism at pressures above the calcite to aragonite transition. Na pyroxenes are also stable in this field. HP rocks occupy the blueschist, eclogite, and HP granulate facies.

**Metamorphic facies** – the collection of mineral assemblages from rocks of all bulk compositions that crystallize at the same pressure and temperature conditions. The greenschist, blueschist, amphibolite, granulate, and eclogite facies boundaries are established based on the mineral assemblages in metamorphosed mafic rocks.

**Omphacite** – a dense, Na-rich clinopyroxene, with a minimum of 20% jadeite component. Jadeite is the pure Na pyroxene (NaAlSi₂O₆) end-member.

**Pseudomorph** – the result of the replacement of one mineral by another, where the new mineral assumes the form of the original.

**Relamination** – a process whereby continental rocks that have reached mantle depths—or their melt products—are returned to the base of the crust.

**Stishovite** – the second high-pressure polymorph of SiO₂, formed by the conversion of coesite at mantle depths in excess of 200 km (~7 GPa) at 600°C or 300 km (~10 GPa) at 1400°C. Natural stishovite has only been observed in meteorite impact structures.

**Terrane** – a crustal block with a distinct stratigraphy, structure, and geologic history. Exotic terranes are fault-bounded blocks that have a foreign origin compared to the surrounding rocks. Most UHP terranes are of known provenance and belong to a craton, although exotic UHP terranes that originated as continental arcs are also known. A **terrain** can be thought of as any physical landmass, and the term sometimes refers to topography, as in “rough terrain.”

**Ultrahigh-pressure (UHP) metamorphism** – metamorphism of crustal rocks that occurs at pressures in the coesite stability field. UHP metamorphism is identified by the presence of coesite or diamond, or by the equivalent pressure–temperature conditions calculated from thermodynamic models of mineral compositions.
The Himalayan orogen provides a conceptual framework for understanding the cycle of UHP metamorphism during continent–continent collision. The Himalayas started to form after India collided with Eurasia around 55 million years ago. The Indian subcontinent was at the leading edge of the Tethyan oceanic crust and was subducted beneath Eurasia. Two coesite-bearing localities in the western Himalayas, Kaghan Valley and Tso Morari, expose rocks belonging to the Indian margin. UHP metamorphism at Kaghan Valley is dated at 46 Ma by U–Pb spot analysis of the coesite-bearing domains of zircon (Kaneko et al. 2003), and the rocks were exhumed to the middle crust by 44 Ma (Parrish et al. 2006). The Himalayan UHP examples followed a typical tepid P–T path, with exhumation rates approximately the same as subduction rates. Even though the India–Eurasia collision is ongoing, UHP rocks have already been exposed in the exhumed core of the orogen, in a position structurally below the suture with Asia and at the top of the subducting Indian plate. The prevailing paradigm for UHP metamorphism based on the Himalayan example holds that continental subduction occurs at the leading edge of the down-going crust early in collision and that the subducted rocks follow a tepid P–T path consistent with metamorphism in a subduction channel environment. UHP terranes are assumed to be coherent crustal slices that are returned to the surface in the upper parts of subduction zones, near the base of the overriding plate. This early paradigm is already being outpaced by new results from UHP research. We are learning that some UHP terranes form late in the collision process, that some are hot, some take a long time to form, some exhumate slowly, and a few are derived from the overriding plate (Hacker et al. 2013 this issue).

**DENSITY AND THE LIMITS OF UHP METAMORPHISM**

The density contrast between metamorphosed continental crust and mantle strongly influences the maximum depth to which the crust can be subducted. Continental crust starts out with a density between 2.7 and 3.0 g/cm³ and floats on subcontinental lithospheric mantle, whose density is about 3.3 g/cm³. The density of oceanic crust is ~3.0 g/cm³ and changes to 3.5–3.6 g/cm³ as basalt converts to eclogite during subduction, allowing subducted oceanic crust to easily sink into the mantle. The density of continental crust at mantle depths cannot be directly observed but can be predicted from thermodynamic models. Calculated mineral assemblages and modes for a variety of quartzofeldspathic lithologies show that crustal rocks approach the density of the mantle at >4 GPa (Massonne et al. 2007), or ~120 km depth. For example, an average sedimentary rock at 3.5 GPa and 900 °C will consist of approximately 30% coesite, 7% garnet, 26% phengite (white mica), 26% omphacite, 10% epidote, and 1% titanite and will have a density of 3.2 g/cm³. More aluminous compositions, such as the diamond-bearing gneiss from Fjortoft (Fig. 3A), contain kyanite and 30–40% garnet, and these minerals push the density of the paragneiss to over 3.4 g/cm³, greater than mantle density. The extraction of partial melts during UHP metamorphism will lead to even higher densities in the residual rock.

If the density of continental crust exceeds that of the mantle, then there is no limiting depth for recycling quartzofeldspathic material into the mantle. The fact that UHP terranes are exhumed is perhaps more remarkable. The actual “point of no return” will depend on the specific crustal composition. How deep has continental crust been subducted and still returned to the surface? Metamorphic diamond forms at a minimum of 4 GPa at 800 °C, or the equivalent of ~130 km depth, and we know of at least nine terranes where diamonds occur in crustal rocks (Fig. 1). The reaction dolomite [CaMg(CO₃)₂] → magnesite (MgCO₃) + aragonite (CaCO₃) takes place at higher pressures than the graphite → diamond transition and has been identified in impure marbles from Dabie–Sulu, China (Proyer et al. 2013). Coesite exsolved from supersilicic titanite in marbles from Kumdyl Kol, Kokchetav massif, records pressures of 6 GPa at 1000 °C, or depths of 200 km (Ogasawara et al. 2002). The stunning interpretation of quartz + kyanite

**Figure 5** UHP terranes are commonly composed of garnet-rich quartzofeldspathic rocks and eclogites. (A) Diamond-bearing, garnet–kyanite–phengite paragneiss from the island of Fjortoft, Norway, with centimeter-size garnet. PHOTO COURTESY OF B. R. HACKER. (B) An isoclinally folded, compositionally layered, coesite-bearing eclogite block within orthogneiss (not shown), Rabbit Ears Island, North-East Greenland. The compositional layering is evidence that the protolith was a layered gabbro. The hammer is 45 cm long. (C) Map of Yangkou beach, Sulu UHP terrane, China, showing gabbros and a basalt dike in gneisses. The striped area is a zone of transition from metagabbro to UHP eclogite. The stars indicate samples with coesite (modified from Zhang and Liu 1997).
pseudomorphs after stishovite, the SiO$_2$ polymorph stable above 9 GPa, in metasedimentary rocks from the Altyrn Tagh, China, suggests that crust has been exhumed from depths exceeding 350 km (L. Liu et al. 2007). Garnet peridotites that accompany deeply subducted crust back to the surface can record extreme pressures, but this is not unexpected in mantle rocks.

**THE FATE OF UHP CRUST AT MANTLE DEPTHS**

Continental UHP terranes can be exhumed, consumed, or partially exhumed to the base of the crust. Subduction zones provide an obvious return pathway for exhumation in the form of a two-way channel; they can also form a conveyor belt for consumption by the mantle. Crustal roots that become thick and dense can delaminate from the base of the crust, founder, and sink into the mantle. As the crust reaches greater depths and temperatures, partial melting will begin. Felsic melts will separate from the denser residue, rise, and perhaps pond at the base of the crust. Such relamination of continental material to the base of the crust could be an important process of crustal growth and lead to a more felsic composition for the lower crust than currently accepted (Hacker et al. 2011).

In this issue of *Elements*, we use field geology, microscopic observations, phase-equilibrium modeling, geochronology, and geodynamic modeling to track the journey of continental crust to the mantle and back. Continental UHP terranes impact our understanding of crustal growth and recycling, mantle geochemistry, melting in subduction zones, plate tectonics through time, and collisional processes in general. The burgeoning new field of UHP metamorphism offers exciting avenues for future research and a deeper understanding of Earth’s crust.

**ACKNOWLEDGMENTS**

I thank all the contributors to this issue of *Elements* for their dedication, hard work, and patience, and John Valley and Pietrre Tremblay for their cheerful, able guidance through the editorial process. Helpful reviews from Mike Brown and Zeb Page improved this manuscript. NSF grants EAR-0208236 and EAR-1049433 have funded my research on UHP metamorphism.
Finding evidence for ultrahigh-pressure (UHP) metamorphism in crustal rocks is far from straightforward. The index minerals coesite and diamond are incredibly inconspicuous and are therefore difficult to use as UHP prospecting tools. Consequently, petrographers rely on recognizing subtle breakdown microstructures that result from pressure release during the return to the surface of the once deeply buried rock. Similarly, many other UHP minerals are first suspected on the basis of typical reaction or exsolution microstructures. Thus, the painstaking use of microscopic techniques has been fundamental to the tremendous advances in characterizing, quantifying, and understanding macroscopic-scale, deep continental subduction, rapid exhumation, and mountain-building processes.

**KEYWORDS**: ultrahigh-pressure, coesite, microdiamond, majorite, exsolution microstructures, polymorphism

**INTRODUCTION**

The spectacular discoveries of coesite and diamond in rocks of the continental crust (Chopin 1984; Smith 1984; Sobolev and Shatsky 1990) firmly established the concept that these rocks had been subducted to mantle depths, thus cementing the hypothesis of ultrahigh-pressure (UHP) metamorphism. This discovery required modification of existing geodynamic models for subduction–collision orogens, and now modern modeling techniques incorporate the changes in parameters necessary to allow deep continental subduction. Over a quarter of a century later and with at least 20 UHP terranes recognized worldwide, a variety of explicit, as well as implicit, mineralogical evidence for UHP metamorphism exists. Finding and analytically confirming the UHP index minerals coesite and microdiamond in grains only tens of microns in size is remarkably difficult. The improvement in microanalytical methods, micro-Raman spectroscopy, transmission electron microscopy (TEM), and secondary ion mass spectrometry (SIMS), for example, allows better mineral identification and assessment of composition. However, you still have to locate the right minerals under the microscope first. Importantly, the presence or former presence of key mineral phases can be inferred from characteristic microstructures resulting from partial—or even complete—transformation during exhumation, where the most critical microstructures result from polymorphic transformations.

**COMMON UHP MINERALS AND THE ROLE OF POLYMORPHISM**

Some chemical compounds adopt different crystalline structures, or polymorphs, at different physical conditions (Fig. 1). As pressure increases, the atoms adapt to their new environment by packing themselves more closely and by reducing interatomic distances. Thus, minerals transform by an increase of the coordination number (CN). The CN refers to the number of nearest neighbors of an atom or an ion in the mineral structure. The higher CN and closer-packed ions consequently lead to an increase in density of the high-pressure (HP) phases. Such features are observed in the HP and UHP indicator minerals of, for example, the SiO$_2$, C, CaCO$_3$, and TiO$_2$ systems, which are presented in Table 1. The polymorphs in these simple chemical systems are key to identifying UHP metamorphism. Confirmation of these polymorphs in natural rocks requires the determination of crystal properties—rather than mineral chemistry—of micron-sized grains in situ, and therefore the most important analytical tool in UHP petrology is laser Raman spectroscopy.

The UHP polymorphic transformations (Table 1) lead to phases with optical and physical properties clearly distinguishable from their lower-pressure counterparts and yield the simplest yet most conclusive evidence for UHP metamorphism. Thus coesite, with its higher refractive index and lower birefringence (Fig. 2a, b), and in some cases also twinning (Fig. 2c), is easily distinguishable from its breakdown product, α- or β-quartz. This newly grown quartz commonly occurs in a halo around coesite and has a radial, palisade microstructure (Fig. 2b). The phase hosting the relict coesite, a rigid container such as garnet, clinopyroxene, or zircon, usually shows radial fractures.

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**Table 1**

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<tr>
<th>Crystal System, Chemistry, and Coordination Number (CN) of Key Low- and High-Pressure Polymorphs</th>
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<tr>
<td><strong>Chemistry</strong></td>
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<td>TiO₂</td>
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is due to their occurrence as generally <10 µm, microscopically small crystals. Less easy to recognize, however, are UHP diamonds. This is due to their occurrence as generally <10 µm, microscopically small crystals.

Experimental studies on the HP behavior of TiO\(_2\) suggest that the natural occurrence of \(\alpha\)-PbO\(_2\)-type TiO\(_2\) (e.g., Withers et al. 2003) requires formation pressures that considerably exceed the graphite–diamond phase boundary (Fig. 1). Thus \(\alpha\)-PbO\(_2\)-type TiO\(_2\) can be an important indicator for formation pressures between the graphite–diamond and the stishovite fields. If an \(\alpha\)-PbO\(_2\)-type TiO\(_2\) phase is found only as nanometer-size, epitaxial slabs between twinned rutile crystals and not as true relics, caution is required before using these nanocrystals for routine geobarometry and as an unequivocal proof of ultrahigh-pressure metamorphism. Other common polymorph stability limits, such as aragonite–calcite and the boundaries of the aluminosilicates andalusite, sillimanite, and kyanite, are also shown in Figure 1 for comparison.

**THE SIGNIFICANCE OF THE DORA-MAIRA UHP ROCKS**

The discovery of the spectacular pyrope quartzite rocks from the Dora-Maira massif, western Alps (Chopin 1984), was a hallmark event in metamorphic petrology. These rocks not only increased and improved our understanding of how crustal material can be subducted to mantle depths, they also display a unique chemical composition that is essentially devoid of iron, calcium, and sodium and can be simply described by the KMASH system (K\(_2\)O–MgO–Al\(_2\)O\(_3\)–SiO\(_2\)–H\(_2\)O). As a result, the pyrope quartzites contain a variety of Mg end-member silicates that are only stable at HP and UHP conditions, even though their Fe-rich equivalents are common in “normal,” intermediate-pressure metamorphic rocks. These finds of natural Mg-rich minerals initiated numerous experimental studies aimed at defining the stability fields of such phases.
Encapsulated as inclusions within the pure pyrope (up to ~Py$_{98}$) megablasts were minerals such as magnesiostaurolite (with X$_{Mg}$ values up to 0.96) and magnesiochloritoid (X$_{Mg}$ up to 0.97) (Simon et al. 1997). Experimental studies on the stability of pyrope, magnesiostaurolite, and magnesiochloritoid document their HP and UHP nature, but they also show that magnesiochloritoid—although stable up to about 4.5 GPa—can be expected only in UHP terranes that experienced temperatures below 700 °C (Fig. 4; Fockenberg 2008; see also Table 2).

Ellenbergerite (Table 2), a hexagonal nesosilicate, is another important mineral included in pyrope megablasts of the Dora-Maira pyrope quartzite. Its structure reflects high-pressure conditions due to face-sharing AlO$_6$-, MgO$_6$-, and (Mg,Ti,Zr,$\ldots$)O$_6$-octahedra that form chains parallel to the c-axis. Ellenbergerite is often zoned and pleochroic, colorless to deep lilac (due to Fe$^{2+}$–Ti$^{4+}$ charge transfer; Fig. 5b). Whereas the stability field of ellenbergerite is restricted to very high pressures (>2.7 GPa for the Ti-, as well as the Zr-, dominant species; see Fig. 4), phosphoellenbergerite, the phosphorus end-member of a silicate–phosphate solid solution (the main substitution mechanism is Si + Al = P + Mg), is stable at much lower pressures (P > 0.5 GPa) and higher temperatures (T < 1000 °C; Brunet et al. 1998). Magnesiodumortierite (Table 2)—like ellenbergerite, with chains of face-sharing octahedra—was also described as a new species from the Dora-Maira massif. It forms inclusions in pyrope megablasts, and its textural relationship to ellenbergerite suggests that it formed at UHP metamorphic conditions. The Dora-Maira rocks were not only a trigger for an intense search for additional UHP metamorphic terranes worldwide, they also represent an ideal natural laboratory for studying crystallographic and petrological aspects of iron-free, Mg end-member silicates.

**OTHER CRUSTAL UHP MINERALS AND MINERAL ASSEMBLAGES**

Rocks of the continental crust generally contain feldspar. Reactions controlling plagioclase stability occur well below UHP conditions—that is, the albite and anorthite components yield jadeite in pyroxene and grossular in garnet,
respectively—but potassium (K) feldspar is stable at much greater pressures. Along a typical subduction geotherm, in the presence of a hydrous fluid phase, K-feldspar breaks down to produce K-cymrite (Table 2) at conditions straddling those of the quartz–coesite reaction boundary (Fig. 4). At even greater pressures, equivalent to those of the coesite–stishovite reaction boundary (Figs. 1, 4), K-cymrite transforms to KAlSi$_3$O$_8$-hollandite + water.

Another possible K-feldspar breakdown reaction, located between the K-cymrite and K-hollandite fields, produces K-wadeite ($K_2Si_4O_9$) (Yagi et al. 1994). These minerals represent the most important products of UHP metamorphism in granitoid rocks of the continental crust; but despite detailed investigation, none of these three K-bearing phases have been positively identified in natural UHP rocks, although suspected transformation products of K-cymrite have been described (Zhang et al. 2009).

The dominant potassic phase in eclogite facies rock at UHP conditions is phengite, a mixture of muscovite and celadonite (Table 2). For suitable parageneses, a high Si content in white mica is a good indicator of UHP conditions, and geobarometric formulations incorporating phengite, together with garnet and clinopyroxene, have proven successful in prospecting for UHP rocks. In addition, Auzanneau et al. (2010) showed experimentally that Ti substitutes into phengite at high P–T conditions and noted its potential for UHP geothermobarometry. Unfortunately there are no characteristic breakdown microstructures involving UHP phengite, and chemical microanalysis is required for the determination of UHP conditions. Gneissic rocks from the Kokchetav massif (Kazakhstan) contain zoned tourmalines with K-dravite cores (Shimizu and Ogasawara 2013; Table 2), where up to 59% of the X-site (Na + Ca + K + vacancy) is occupied by potassium. Because only the K-dravite cores contain inclusions of microdiamonds, they were interpreted to have formed under UHP metamorphic conditions. It appears that at very high pressures the “big” potassium atom is able to occupy the X-site of the tourmaline structure.

The mineral topaz is usually rich in fluorine, but Zhang et al. (2002) discovered hydroxyl-rich topaz ($X_{OH} = 0.4–0.55$) in the Sulu (China) UHP terrane and showed that it can act as an important carrier of water to depths exceeding 100 km. Experimental data on topaz-OH from Wunder et al. (1993) are illustrated in Figure 4 and document that the OH end-member is stable at P exceeding 5 GPa. An additional phase that potentially plays a role in the transportation of water in subduction zones, but not (yet) observed in nature, is Mg-sursassite (Fig. 4; Fockenberg 2008).
THE RETURN TO EQUILIBRIUM: BREAKDOWN AND EXSOLUTION TEXTURES DURING PRESSURE RELEASE

UHP conditions are most commonly recognized in the field in rocks of ultramafic and mafic composition, that is, garnet peridotite and eclogite, respectively. These rocks can be devoid of a free SiO$_2$ or C phase, requiring other criteria to ascertain their possible UHP origin. The most important of these indicators is related to the phases garnet and clinopyroxene. In garnet, at pressures between those of diamond and stishovite stability (Fig. 1), Si has 6-fold as well as the usual 4-fold coordination (Table 1). This change in coordination number eventually results in a tetragonal phase, majorite, replacing the lower-pressure cubic garnet phase by incorporation of a pyroxene solution component. Some garnet peridotites captured by deeply subducted crust (Van Roermund 2009) have been interpreted to have formerly contained majorite based on the presence of pyroxene exsolution lamellae, tens of microns wide by hundreds of microns long, in garnet (Fig. Sc).

Clinopyroxene is an essential component of eclogite, but its composition in basaltic rocks is strongly dependent on bulk-rock chemistry and is a poor direct indicator of UHP conditions. However, at higher-temperature conditions, clinopyroxene in UHP rocks can become supersilicic by incorporating a Ca-Eskola (C$_{60}$Si$_{60}$Al$_{12}$O$_{60}$) component and can even accept potassium in a KAl$_2$O$_6$ component sometimes called K-jadeite (Konzett et al. 2008). During decompression, such components unmix to produce needles, blebs, or lamellae of quartz (Fig. 5d) from Ca-Eskola or of K-feldspar (Fig. 5e) in the case of K-jadeite.

Unfortunately, the loss of a Ca-Eskola component is not the only possible mechanism for producing quartz lamellae in clinopyroxene (Pryer et al. 2009), thus making for a poor UHP textural indicator. Non-isochemical, open-system replacement reactions can also lead to the growth of lamellae of potassic phases (e.g. K-feldspar, kokchetavite, phengite, philogopite, amphibole) from clinopyroxene in UHP rocks (Hwang et al. 2013 and references therein). For these reasons, exsolution microstructures in clinopyroxene alone are unreliable UHP indicators.

Calcisilicate rocks and impure marbles also have a high potential for yielding diagnostic exsolution textures. The common accessory phase titanite, for instance, has been identified as a possible UHP mineral. In impure marbles from the Kokchetav massif, exsolution lamellae of both coesite (confirmed by laser Raman studies) and quartz in titanite indicate a former supersilicic composition (e.g. K-feldspar, kokchetavite, phengite, philogopite, amphibole) from clinopyroxene in UHP rocks (Hwang et al. 2013 and references therein). For these reasons, exsolution microstructures in clinopyroxene alone are unreliable UHP indicators.
REFERENCES


SUMMARY AND OUTLOOK
The discovery of UHP minerals in the extremely unusual Dora-Maira Mg-rich rocks was the trigger to start looking more closely for UHP evidence in rocks of normal basaltic, pelitic, and granitic bulk compositions. In many cases (e.g. Kockott et al. 2011), microdiamond and coesite were suddenly identified in rocks already long under investigation. Our better knowledge of phase-stability relations and access to high-precision, in situ analytical tools have undoubtedly helped in characterizing UHP phases and their conditions of formation. However, the recognition of critical transformation and exsolution microstructures in UHP minerals using the polarizing microscope, a tool disappearing from modern geoscience curricula, has been the starting point for all further investigations. Will the next revolution in geodynamics start with finding natural K-cymrite/K-wadeite/K-hollandite in subducted granites? Time will tell.

ACKNOWLEDGMENTS
Many thanks to Jane Gilotti and John Valley for the invitation to participate in this issue of Elements and for many valuable discussions. The article significantly benefited from detailed and constructive reviews by Barb Dutrow and an anonymous reviewer. We thank Yoshi Ogasawara for providing us with a photo of titanite, Hermann van Roermund for a sample of majoritic garnet from the Western Gneiss Region, Norway, and Haijun Xu for a rock sample of eclogite containing omphacite with quartz exsolution from Weihai, China.

X-W Liu et al. (2007), and the idea that this phase derives from pyrolitic mantle below about 300 km was discussed by Woodland and Angel (1997).
Constructing the Pressure–Temperature Path of Ultrahigh-Pressure Rocks

Hans-Joachim Massonne*

INTRODUCTION
By definition, the presence of coesite in metamorphic rocks assigns them to an evolution at ultrahigh pressure (UHP). However, many UHP rocks lack coesite, either because their SiO$_2$ content is too low to form a free SiO$_2$ phase or because coesite has completely transformed to quartz during exhumation (Schertl and O’Brien 2013 this issue). Fortunately, specific minerals that form solid solution series are capable of storing the information of their growth at UHP in their chemical composition. The most suitable minerals, which are also common in UHP rocks of continental affinity, are phengite and garnet. A large number of high-pressure experiments have been undertaken on the compositional relations of these phases in various mineral assemblages. Furthermore, the molar volume ($V$) of phengite and garnet has been explored as a function of composition and pressure. As a result, the thermodynamic properties of these minerals—enthalpy, entropy, and $V$ for end-member compositions, and the Margules parameters for describing the nonideal behavior of solid solution series (see Powell and Holland 2010)—are well known (e.g. for garnet, see Ganguly et al. 1996). Calculations that employ experimentally determined thermodynamic data from internally consistent data sets (e.g. Holland and Powell 2011) can determine the position of specific mineral equilibria in $P$–$T$ space. Isochemical phase-equilibrium diagrams, known as pseudosections, can also be calculated to show the modal and compositional change of minerals for a constant bulk-rock composition, for instance, in $P$–$T$ space. These calculations can be applied to a variety of lithologies containing garnet and/or phengite, which are particularly useful minerals for studying UHP metamorphism.

Keywords: thermodynamics, mineral equilibrium, phase relations, $P$–$T$ pseudosection, ultrahigh-pressure metamorphism

P–T ESTIMATES USING MINERAL EQUILIBRIA
Decades ago, the first geothermometers, based on the Fe$^{2+}$–Mg exchange between mineral pairs such as garnet and omphacite or garnet and biotite, were experimentally calibrated, opening the door for quantifying metamorphic conditions. Geobarometers followed. Early on, they were used in combination with geothermometers to estimate $P$–$T$ conditions for a single event, which was taken as the peak $P$–$T$ point of a metamorphic loop. The chemical zonation of minerals allowed the definition of a number of $P$–$T$ points, which were used to construct a metamorphic path. Such paths were derived for countless rocks from the low- to high-grade metamorphic realms. With the derivation of extended thermodynamic data sets for rock-forming minerals (e.g. Berman 1988), new geothermobarometers could be defined by mineral equilibria that were not experimentally calibrated, and previously calibrated ones could be extended to mineral compositions far from the compositions used in the experiments. Using quantitative mineral chemistry collected with the electron microprobe, these equilibria can be thermodynamically calculated within minutes with specially designed computer software (e.g. Powell et al. 1998; Brandelik and Massonne 2004), the main assumption being that the selected mineral compositions were once in equilibrium. Garnet, omphacite, and phengite, which are typically compositionally zoned (Fig. 1), are often used to calculate mineral equilibria for UHP rocks. The $P$–$T$ datum of interest is found by calculating the intersection of two independent equilibria involving end-member components in garnet (Gt), clinopyroxene (Cpx), and potassic white mica (WM). Two such equilibria are:

\[
\text{almandine (in Gt) + 3 diopside (in Cpx) = pyrope (in Gt) + 3 hedenbergite (in Cpx),} \tag{1}
\]

and

\[
3 \text{ MgAl-celadonite (in WM) + 2 grossular (in Gt) + pyrope (in Gt) = 3 muscovite (in WM) + 6 diopside (in Cpx).} \tag{2}
\]

Equilibrium (1) is a typical Fe$^{2+}$–Mg exchange thermometer, whereas equilibrium (2) is one of several phengite geobarometers. This method and its simplified version, based only on empirically calibrated geothermobarometers, have been successfully applied to UHP rocks (e.g. Hacker 2006). This kind of geothermobarometry is generally restricted to eclogites, which is probably the reason

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Coesite and diamond in metamorphic rocks point to their very deep burial, but these minerals do not allow a precise derivation of metamorphic pressure–temperature ($P$–$T$) conditions at ultrahigh pressure (UHP). Thermodynamic calculations of mineral equilibria can accomplish this task when it is possible to assign mineral compositions to a former UHP equilibrium state. Pressure–temperature pseudosections are superior, because they often permit the construction of $P$–$T$ paths to and from UHP conditions only on the basis of chemically zoned minerals such as garnet and phengite. The examples of a metapelite from Oman and an eclogite from the Erzgebirge, Germany, illustrate this method, but also demonstrate its limits. The derived paths are the basis for further geodynamic modeling and insight into tectonic processes.

Keywords: thermodynamics, mineral equilibrium, phase relations, $P$–$T$ pseudosection, ultrahigh-pressure metamorphism

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that this minor rock type in continental UHP terranes is much better investigated than the country rocks. In fact, UHP rocks of ordinary pelitic and acidic compositions should also contain the Gr–Cpx–WM assemblage, but because of the low Ca/Na ratio of their bulk composition, the Na-pyroxene is jadeite-rich and low in hedenbergite component. Unknown Fe$^{3+}$/Fe$^{2+}$ ratios in clinopyroxene and, thus, poorly defined amounts of hedenbergite component lead to high uncertainties in the P–T positions of equilibria (1) and (2). Another factor contributing to the uncertainty is the difficulty of identifying the equilibrium composition of the Gr–Cpx–WM assemblage from the metamorphic texture. A solution to this problem is to add mineral components (e.g. Fe$^2+$Al-celadonite in WM) or phases, such as kyanite and an SiO$_2$ phase (e.g. Ravna and Terry 2004), which allows the thermodynamic calculation of other independent equilibria. If all the equilibria intersect near a single P–T point, we can be fairly sure that the selected mineral compositions were once in equilibrium (see the TWQ method by Berman 1991).

**P–T PSEUDOSECTIONS**

At first glance, calculating the P–T location of multivariant mineral equilibria is the more convenient alternative to the time-consuming calculation of P–T pseudosections and their contouring using parameters such as the content of grossular in garnet (see below). But P–T pseudosections have considerable advantages for the derivation of P–T paths for UHP rocks. The detailed thermodynamic background of the method, with various examples, was recently presented by Powell and Holland (2010).

Three different software packages are commonly used for the calculation of pseudosections: THERMOCALC (Powell and Holland 1988), PERPLE_X (see Connolly 2005), and THERIAK-DOMINO (see de Capitani and Petrakakis 2010). THERMOCALC is based on the solution of a system of nonlinear equations and can directly calculate field boundaries of stable mineral assemblages (Powell and Holland 1988). PERPLE_X and THERIAK-DOMINO use the approach to equilibrium by means of Gibbs free energy minimization, for instance, to determine the stable mineral assemblage, including the mode and composition of the minerals for the fixed bulk-rock composition at specified P–T conditions. If the second approach is undertaken for a dense grid of P–T points, a P–T pseudosection can be constructed. Pseudosections obtained from different software are virtually identical when the same thermodynamic database is utilized. Differences in calculated metamorphic assemblages arise from the choice of different solid solution models (e.g. Hoschek 2004).

Two examples (see below) demonstrate the advantages and possible pitfalls of the calculation of P–T pseudosections for UHP rocks. The examples were calculated with the computer software package PERPLE_X (Connolly 2005), the thermodynamic data set by Holland and Powell (1998 and updates), and solid solution models that are compatible with this data set and given in the works cited below. As suggested by Connolly (2005), the raw data for P–T boundaries of mineral assemblages and isopleths for diverse parameters, produced by PERPLE_X, need to be redrawn and smoothed in order to optimize the P–T position of these curves and to eliminate inconsistencies of phase relations. The examples show how P–T paths can be constructed for different lithologies and temperature regimes during UHP metamorphism.

**P–T Path of a Low- to Medium-Temperature UHP Metapelite**

Minor metapelite interlayers occur in eclogite of the lower As Sifah unit, a slice of oceanic crust, located on the northeastern coast of Oman. The metapelite, originally a pelagic clay poor in SiO$_2$, is characterized by abundant phengite and millimeter-sized garnet (~25 vol%), with minor amounts of quartz, rutile, epidote, and sodic amphibole (Massonne et al. 2013). Pseudomorphs of paragonite + epidote and albite + magnetite after original lawsonite and Na-rich clinopyroxene, respectively, are enclosed in garnet. Pseudo-section modeling of the metapelite (Fig. 2) produces an abundance of diagnostic mineral assemblages and demonstrates that pelitic rocks have the same potential as basic rocks to indicate UHP conditions, even when the bulk-rock composition is too low in SiO$_2$ to produce coesite. For example, the UHP assemblage of the Oman metapelite was phengite + Na-rich clinopyroxene + chlorite + chloritoid + garnet + lawsonite + ilmenite + rutile + hematite/magnetite at around 2.75 GPa and 440°C according to the calculation, while only phengite, garnet, and oxide minerals are preserved in the rock today.

The P–T path for the Oman metapelite (Fig. 3) was mainly derived from the variable chemical composition of garnet, which exhibits prograde zoning similar to that shown in Figure 1A, using the isopleths for molar fractions of garnet components (Fig. 3A). For example, the innermost core of garnet contains about 11 mol% spessartine (Mn), 6 mol% pyrope (Mg), and 17 mol% grossular (Ca) (+ andradite) components. The corresponding isopleths intersect at about 2.5 GPa and 490°C, marking the conditions at which early garnet formed. The maximum Si content of chemically inhomogeneous phengite (Fig. 1A) is 3.6 atoms per formula unit (apfu), which places the peak P in the coesite stability field (Fig. 3A). The phengite grew in the rock before considerable quantities of garnet formed, because the mica is enclosed in garnet cores. There is a higher degree of P–T uncertainty for the late, peak-stage because of incomplete equilibration of the early-stage minerals. The discrepancy between the observed (4 vol%) and calculated (9 vol%) modal composition of amphibole at 1.3 GPa and 565°C is due to the preservation of relatively early-formed minerals. For instance, the garnet core can change the effective bulk-rock composition since it does not participate in late metamorphic reactions. This problem can be overcome by subtracting garnet cores from the bulk-rock composition in the pseudosection models to better assess a late metamorphic stage (e.g. Konrad-Schmolke et al. 2008). P–T pseudosections can also quantitatively determine the release of
Figure 2  
P–T pseudosection for an SiO2-poor metapelite from Oman (modified from Massonne et al. 2013). The bulk-rock composition (in weight %) is: SiO2 = 43.6%, TiO2 = 1.47%, Al2O3 = 21.5%, FeO = 13.74%, O2 = 0.15%, MnO = 0.17%, MgO = 2.74%, CaO = 2.36%, Na2O = 0.48%, K2O = 6.76%, H2O = 7.0%; O2 refers to some Fe being trivalent. The white P–T fields are low-variance fields, where the number of coexisting phases is equal to the number of components (here, 11 elements). The darker the P–T field, the lower is the number of phases. Labels for small P–T fields are omitted for clarity.

Figure 3  
The pseudosection in Figure 2 contoured for various parameters. (A) Garnet composition; X = molar fraction. (B) Phengite composition and modal content of garnet. (C) Weight % water in solids. The P–T path (magenta line, broken = uncertain) was derived from intersections of isopleths for molar fraction of garnet components (A) and Si content in potassic white mica (B). The calculated water content in solids (C) predicts the release of H2O during prograde metamorphism. The boundaries of P–T fields of hydrous minerals are shown in color. Abbreviations are the same as in Figure 2. Modified from Massonne et al. (2013).
water from minerals on the prograde path (Fig. 3c), which is an important motor driving metamorphism. For the Oman example, the formation of garnet above 2 GPa has released about 3 wt% H$_2$O.

**P–T Path of a High-Temperature Eclogite**

A coesite-bearing eclogite occurring close to the diamondiferous rocks of the Erzgebirge in Saxony, Germany, provides an example of UHP metamorphism at high $T$. The eclogite contains abundant inclusions of carbonate, mainly dolomite, in garnet cores, whereas very little carbonate is present in the matrix. From this observation—and because of the unusually high Mg and Ca contents in garnet—Massonne (2011) inferred a reaction at UHP that led to garnet growth at the expense of carbonate, resulting in the release and escape of CO$_2$. This change in the effective bulk-rock composition with decreasing CO$_2$ (and H$_2$O) was modeled by three $P$–$T$ pseudosections (Fig. 4): a pre-UHP stage I with a CO$_2$ content of 12 wt% in the bulk rock, a UHP stage II with CO$_2 = 4$ wt%, and a post-UHP stage III with CO$_2 = 1$ wt%. Despite the change of the original garnet core composition by intracrystalline diffusion due to the high temperatures, the $P$–$T$ conditions of stage I (Fig. 5) could be defined on the basis of the inclusion assemblage in garnet, i.e. kyanite, phengite, omphacite, (clino)zoisite,
and dolomite. Stage III conditions were derived from the matrix minerals, kyanite, biotite, and phengite, and the omphacite and garnet rim compositions, within reasonable error. The UHP stage II could not be well defined because of large fields of high-variance assemblages with little compositional variation of the solid solution minerals, such as garnet; but the result is consistent with the stability of diamond, which occurs in adjacent rocks. This example shows a low sensitivity of geothermobarometers (here, variable garnet composition) at UHP conditions and high temperatures. The shape of the derived P–T path for the coesite-bearing eclogite differs significantly from that of the Oman metapelite, suggesting that different geodynamic processes led to very deep burial and subsequent exhumation.

**CONCLUDING REMARKS**

Valuable information on the P–T evolution of UHP rocks can be obtained from both individual mineral-equilibria calculations and contoured P–T pseudosections. The P–T uncertainties in the two methods are similar because they both depend on the quality of the applied thermodynamic data. Each method suffers from a major pitfall. In the case of geothermobarometry using mineral-equilibria calculations, the main challenge is finding chemical compositions of minerals in equilibrium at a particular stage of metamorphism. Berman’s (1991) TWQ method can be used to circumvent this problem if suitable UHP equilibria assemblages exist. The assumption that the bulk-rock composition equals the effective composition for pseudosections can be violated if the inner portions of minerals,

**TYPES OF P–T PATHS FOR UHP ROCKS**

Although the number of well-constrained P–T paths in the literature for UHP rocks is fairly limited, two types of P–T loops are discernable (Fig. 6) despite large P–T errors in the corresponding estimations. A P–T path like the one determined for the Oman metapelite and similar paths for eclogites with the geochemical signature of mid-ocean ridge basalt (paths 1 and 2 of Fig. 6a) suggest an evolution starting near-atmospheric pressures at near-surface conditions, though this is not provable. This suggestion is compatible with the widespread idea that such paths reflect subduction of oceanic crust, the upper part of which can contain continental material in sediments. Portions of continental crust in the overriding plate can also be involved in the subduction process through tectonic erosion by the downgoing slab (Massonne 2012). Such crust could have experienced a P–T evolution displayed by path 3. Rocks from the subduction zone, exhumed in a subduction channel, often reached the UHP realm at close to peak pressure conditions and temperatures between 400 and 750°C in Phanerozoic times.

In contrast, some rocks experienced a common metamorphic history long before the UHP event. In this case, their P–T path starts at elevated temperature, and the burial segment of this path is characterized by a relatively steep dP/dT slope (Fig. 6b). This can be explained by the frequently invoked process of continental subduction. However, gneisses in the Erzgebirge area do not show evidence for metamorphism at UHP conditions (path 4), in contrast to diamondiferous UHP rocks, which also originated from the continental crust. The diamond-bearing rocks of the Erzgebirge crystalline complex experienced temperatures above 1000°C (path 5). Mantle delamination with crustal material involved was invoked for the UHP evolution of these rocks, including the Erzgebirge eclogite in the example above. Since very high temperatures were reached during this process (path 5), partial melts formed, which, as a result of density reduction, caused the ascent of continental material from deep mantle levels (Massonne and Fockenberg 2012).

**FIGURE 4** pseudosections of P–T paths in the literature for UHP rocks. The P–T path (Massonne 2011) is shown by the gray arrows, while the estimated uncertainties of each stage are given by the gray error ellipses. Stage I was assessed using the assemblage of pyrope and grossular fractions in garnet. The P–T conditions of stage I were mainly deduced from the fairly homogeneous garnet composition of stage I. The moderate zoning is the result of considerable cation diffusion, owing to the high temperatures reached by the rock, which erased the original garnet composition of stage I. The P–T conditions of stage II were mainly deduced from the fairly homogeneous garnet mantle. Stage III is characterized by kyanite, biotite, and phengite (Si = 3.25 apfu) of the matrix and by the outermost-rim compositions of omphacite and garnet.

**FIGURE 5** pseudosections of P–T paths in the literature for UHP rocks. The P–T path (Massonne 2011) is shown by the gray arrows, while the estimated uncertainties of each stage are given by the gray error ellipses. Stage I was assessed using the assemblage of pyrope and grossular fractions in garnet. The P–T conditions of stage I were mainly deduced from the fairly homogeneous garnet composition of stage I. The moderate zoning is the result of considerable cation diffusion, owing to the high temperatures reached by the rock, which erased the original garnet composition of stage I. The P–T conditions of stage II were mainly deduced from the fairly homogeneous garnet mantle. Stage III is characterized by kyanite, biotite, and phengite (Si = 3.25 apfu) of the matrix and by the outermost-rim compositions of omphacite and garnet.
such as garnet cores, do not equilibrate with the other minerals or if a component of the fluid phase disappears along the $P$–$T$ path. It is possible, however, to modify the bulk-rock composition by calculating a different $P$–$T$ pseudosection for each metamorphic stage, as was achieved for the Erzgebirge example. In addition, even when the well-analyzed bulk rock is the effective composition, a reasonable $O_2$ content (see caption of Fig. 4) must be deduced from the observed mineral assemblage. Due to these weaknesses, we should have in mind absolute $P$ and $T$ errors as high as 10% and 5%, respectively, for the two methods presented here.

The pseudosection method is powerful because $P$–$T$ paths can be deduced from zoning in a single mineral (e.g. garnet) using contoured $P$–$T$ pseudosections (Figs. 3, 5), if the zoning is not greatly modified by diffusion. As demonstrated above, $P$–$T$ pseudosections can also deliver information about compositional variation and modal changes in minerals of UHP assemblages, in contrast to $P$–$T$ estimates based on the TWQ method. For this reason, the author highly recommends applying $P$–$T$ pseudosections, if possible in conjunction with robust $P$–$T$ estimates for selected points along the $P$–$T$ path. Such $P$–$T$ paths contribute to our understanding of geodynamic scenarios and explain the UHP nature of some crustal rocks. $P$–$T$ paths so derived can also be tested against the paths predicted from numerical models for a better understanding of the tectonic processes that form and exhume UHP terranes.

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Figure 6 Typical $P$–$T$ paths of Phanerozoic high- to ultrahigh-pressure rocks. (A) Subduction environment: paths 1 and 2 represent the common evolution of the top of subducted oceanic crust (e.g. the Oman metapelite example) exhumed in a subduction channel; path 3 (Massonne 2012) is assigned to a rock from the continental crust involved in the subduction environment through tectonic erosion. (B) Crustal foundering: path 4 represents the common evolution of a slice of the middle to lower continental crust buried beneath an overriding continental plate during continent–continent collision; path 5 refers to a rock (e.g. the Erzgebirge eclogite example and diamondiferous rocks studied by Massonne and Fockenberg 2012) that, after burial, is delaminated and partially melted at UHP conditions.
Establishing the timing and duration of ultrahigh-pressure metamorphism (UHP) for crustal rocks subducted to mantle depths of over 100 km requires high-precision geochronology directly coupled with pressure-sensitive indicators. The best links between UHP conditions and an age estimate are inclusions of the UHP indicator minerals coesite and/or diamond in datable zircon or garnet. Lu–Hf and Sm–Nd garnet ages define the prograde and peak portions of the pressure–temperature path for cold (<700°C), fast (>1 cm/y) UHP systems. UHP metamorphism in hotter (>800°C) and slower (<1 cm/y) terranes is best dated by U–Pb analysis of coesite-bearing zircon domains coupled with Sm–Nd and Lu–Hf garnet analysis.

**Keywords:** zircon, garnet, geochronology, ultrahigh-pressure metamorphism, eclogite

**GEOCHRONOLOGY AND PRESSURE–TEMPERATURE–TIME PATHS**

The overarching goals of geochronology are to establish the absolute timing of geologic events and the tempo of geologic processes. The orogenic cycle in collision zones typically consists of burial or subduction, heating and possibly melting, and finally exhumation and cooling. Geochronology provides the timing of the different segments of the cycle, which can be graphically represented as a path in pressure–temperature–time (P–T–t) space. A comparison of paths from different orogens allows discussion of the time and rates associated with tectonic processes and the reasons for variety (Fig. 1). Geochronometers generally track variation in T rather than P because most mineralogical changes during metamorphism are more directly tied to increasing T on the prograde (increasing metamorphic intensity) path. In addition, many datable minerals exhibit open-system behavior due to diffusion at high T and only record the time of cooling below the T at which diffusion ceases, i.e. the closure temperature and cooling ages, on the retrograde (decreasing metamorphic intensity) path. The strong dependence on T presents specific challenges for establishing the time of maximum P for crustal rocks that contain microdiamond or coesite, a high-pressure polymorph of SiO₂ (Chopin 1984; Sobolev and Shatsky 1990)—that is, the time the rocks were buried to greatest depths at ultrahigh-pressure (UHP) conditions.

The difficulty in dating the time and duration of UHP metamorphism is compounded by the typically steep P–T paths for UHP terranes, most of which show a rapid increase and decrease in P relative to T. There is a considerable range in maximum P and T attained by various UHP terranes (Fig. 1). For relatively cool (<700°C) prograde P–T paths, the peak P and T can be nearly synchronous and burial and exhumation rates are fast (Fig. 2a). The conditions are more variable for hotter P–T paths where the chances that peak P occurs at nearly the same time as peak T diminish (Fig. 2a). Linking time to the P–T path for each of these examples provides essential information for understanding orogenic processes and mechanisms; for example: How quickly is crustal material subducted? What is the typical residence time for crust at mantle depths? What are the rates at which UHP terranes are returned to crustal levels? Establishing the time at which rocks are at UHP conditions is essential to exploring each of these questions.

There are several common ways to address the challenge of linking absolute chronology to P conditions, but here we distill them into two main approaches: (1) analysis of minerals that have a direct connection to the metamorphic reactions and/or P–T conditions of interest, and (2) geochronologic analysis combined with petrologic and geochemical modeling. Either compositional and growth zoning of minerals or mineral-inclusion domains can link the measured age to segments of the P–T path. The most significant pitfalls of both methods are a possible resetting of the geochronometer with changing P–T conditions and the difficulty in tying a specific age—whether it represents mineral growth or cooling—to the continuous process of metamorphism.

Several criteria must be met to successfully link a measured age to a geologic event. The precision of the date must be sufficient to statistically distinguish the particular events studied, and the measured age must be accurate in an absolute time frame. Second, the age information needs to discriminate between individual processes or events recorded in the phase(s) being analyzed (e.g. growth zones, inclusion domains). In situ analysis afford the high spatial resolution necessary to target small volumes in specific age domains. Unfortunately, as the sample volume decreases so
The timing information provided by zircon and garnet ages (Ma, million years) highlights the variability in response of the two geochronometers, largely as a function of rate and temperature. Fast terranes increase in $T$ from Dabie–Sulu (D-S) to Greenland (G). The petrogenetic grid, the phengite/melt curve, and the $P$–$T$ paths for LC, D-S, and K are from Gilotti (2013 this issue) and Hermann et al. (2013 this issue). Fields in $P$–$T$ space: HP = high-pressure metamorphism; UHP = ultrahigh-pressure metamorphism does the precision of the analysis. The competing requirements of higher precision versus smaller sample size have been addressed through advances in analytical techniques and instrumentation over the last few decades (see review by Davis et al. 2003). Microsampling of material for dissolution and analysis by thermal ionization mass spectrometry (TIMS) or multicollector inductively coupled plasma mass spectrometry (MC-ICPMS) allow high-precision age determinations in a spatial context (e.g. Pollington and Baxter 2011). Laser ablation (LA)–ICPMS and secondary ion mass spectrometry (SIMS) allow in situ multi-element geochemistry and geochronology on small sample volumes. The high spatial resolution of the SIMS and LA–ICPMS techniques has been instrumental in resolving complex zircon histories. Solution chemistry and isotope analysis by TIMS or multicollector ICPMS remain the primary method for garnet geochronology. Combining the results from in situ analytical methods with extensive textural and compositional characterization of the geochronometer and related metamorphic minerals has opened the door to more refined studies that address the need for a strong link between the dated material and the particular segment of the geologic process that the age is interpreted to represent. Establishing the time spent at UHP conditions is essential to determining rates of subduction and exhumation, constraining geodynamic models for formation of UHP terranes, and understanding processes that initiate exhumation of crustal material. Many other geochronologic systems and minerals provide valuable information on the pre-UHP and post-UHP portions of the $P$–$T$–$t$ history, but the time of UHP metamorphism provides the anchor point for rate calculations. Zircon and garnet have proven to be particularly useful minerals in overcoming the challenges of linking time with a $P$–$T$ path through UHP metamorphic conditions, in large part because they commonly contain inclusions of pressure-sensitive index minerals, such as microdiamond and coesite. Below we highlight cases where the uranium–lead (U–Pb) zircon and the samarium–neodymium (Sm–Nd) and lutetium–hafnium (Lu–Hf) garnet geochronometers have been applied in tandem to successfully date UHP metamorphism. Once the timing for UHP conditions is established, subduction and exhumation rates can be estimated by comparison with other geochronometers, including U–Pb ages from accessory minerals such as monazite and titanite and $^{40}$Ar–$^{39}$Ar cooling ages from a variety of minerals.

**THE ROLE OF ZIRCON**

Zircon has proven to be a robust geochronometer across a broad spectrum of rock types that have been subjected to a variety of metamorphic conditions, but it is particularly useful in high-$T$ environments that involve partial melting. In essence, most metamorphic zircon precipitates from zircon-saturated fluid or melt, incorporating U in its lattice during crystallization but excluding Pb. Zircon growth occurs either through subsolidus dissolution and reprecipitation of existing zircon or another zirconium (Zr)-bearing mineral, or precipitation directly from a melt or metamorphic fluid. Metamorphic zircon generally grows in response to prograde and retrograde metamorphic and melting reactions encountered along $P$–$T$ paths through amphibolite and granulite facies conditions (Fig. 1). Age information is retained by prograde zircon despite increasing $T$ because of its high closure temperature: diffusional loss of the daughter-product Pb only occurs at very high temperatures. Important exceptions to this behavior are radiation damage and zircon recrystallization that result in disturbance or resetting of the U–Pb system and subsequent loss of earlier age information. Growth versus recrystallization

| Figure 1 | Pressure–temperature diagram comparing generalized $P$–$T$ paths for the UHP terranes discussed in the text. The timing information provided by zircon and garnet ages (Ma, million years) highlights the variability in response of the two geochronometers, largely as a function of rate and temperature. Fast terranes increase in $T$ from Dabie–Sulu (D-S) to Greenland (G). The petrogenetic grid, the phengite/melt curve, and the $P$–$T$ paths for LC, D-S, and K are from Gilotti (2013 this issue) and Hermann et al. (2013 this issue). Fields in $P$–$T$ space: HP = high-pressure metamorphism; UHP = ultrahigh-pressure metamorphism. |  
| Figure 2 | Generalized pressure and temperature versus time paths for UHP rocks depicting the segments dated by garnet (Lu–Hf and Sm–Nd) and zircon (U–Pb) geochronology and cooling ages (e.g. $^{40}$Ar–$^{39}$Ar). (A) Peak $P$ is nearly synchronous with peak $T$ for terranes with burial and exhumation rates of $<1$ cm/ky. Garnet retains prograde element zoning when peak $T$ is $<$700 °C or rates are fast. The Lu–Hf age is weighted to early garnet growth, whereas the Sm–Nd age is weighted towards later garnet growth, potentially reflecting peak $P$ and $T$ conditions. Zircon typically fails to capture UHP conditions in cold settings. (B) Peak $P$ precedes peak $T$ for terranes with exhumation rates of $<1$ cm/ky. Garnet either resets or grows on the retrograde path when peak $T$ is $>$800 °C. Zircon domains may capture prograde, UHP, and retrograde metamorphism in slow and/or hot systems. |
processes can often be distinguished by textural variation observed in backscattered secondary electron or cathodoluminescence (CL) imaging (Fig. 3). An important feature of metamorphic zircon is its ability to preserve multiple domains that record metamorphic events along the P–T–t path, as well as the premetamorphic history of the protolith (Rubatto and Hermann 2007).

Zircon-forming processes at UHP conditions are the same as for high-T conditions, where the presence of a fluid and/or melt is considered essential for growth of volumetrically significant metamorphic zircon (Rubatto and Hermann 2007). The main difference in zircon growth at UHP versus other lower-P environments centers on the availability and nature of the metamorphic fluids. Continental rocks travelling along steep P–T paths to UHP conditions miss the prograde amphibolite to granulite facies reactions that lead to melting at shallower crustal levels, or do not experience them until after significant exhumation (Fig. 1). In addition, continental rocks are relatively dry by the time they reach UHP conditions. The dominant hydrous phase in subducted intermediate and felsic crustal rocks is phengite, a high-pressure (HP) white mica that is stable once phengite is approached (Figs. 1b; 275). In their crystal structure and back again occurs quickly unless the phengite is adequately protected within a robust container, such as zircon or garnet, that also grows at UHP conditions. Spectacular zircon grains that record the transition across the quartz-to-coesite transition are observed from several UHP terranes. Zircon grains from the Kaghan Valley in the Pakistani Himalaya preserve quartz inclusions in domains grown along the prograde path and coesite inclusions in outer domains that grew before the grain left the UHP field (Fig. 3; Kaneko et al. 2003). Liu and Liou (2011) document the case where zircon cores contain coesite and quartz inclusions reside in the outer rims, thus capturing the retrograde path for UHP rocks from the Dabie–Sulu belt in China. Zircon grains from UHP rocks in the Kokchetav massif, Kazakhstan, display an inner domain with coesite and diamond inclusions surrounded by outer rims with quartz, plagioclase, and chloride inclusions (Hermann et al. 2001). Compositional data from inclusion suites can be compared with matrix minerals and used to estimate P–T conditions based on mineral equilibria; however, the required condition of equilibrium among the mineral inclusions can be difficult to demonstrate (e.g. Mattinson et al. 2006).

FIGURE 3 Cathodoluminescence (CL) images of zircon from the North-East Greenland UHP terrane. (a) Igneous protolith zircon (P, dark) overgrown by eclogite facies rims (E); both are cut by domains of recrystallization (Rx) and veining. (b) Protophant zircon (P) overgrown by UHP zircon (E) with a coesite (coe) inclusion. (c) UHP zircon (within dotted line) with a coesite inclusion, overgrown by syn-exhumation rims (E). (d) Zircon from an amphibolite facies leucosome; P = protolith zircon; A1 and A2 represent two generations of rims. (e) Characteristic, chondrite-normalized rare earth element patterns from protolith zircon (P), eclogite facies and UHP overgrowths (E), and amphibolites facies zircon (A1, A2). Modified after Guiotti et al. (2013).

Changes in trace element composition define zircon growth at higher P conditions, independent of inclusions. Eclogite facies zircon formed in the presence of garnet, which preferentially sequesters heavy rare earth elements (HREEs), and the absence of plagioclase has a characteristic REE signature: a flat middle (M)REE to HREE pattern and no negative europium (Eu) anomaly (profile Figs. 3e; see Rubatto and Hermann 2007 and references therein). This signature differs from the magmatic patterns characteristic of igneous protolith zircon (profile F, Fig. 3e), and is distinct from younger zircon precipitated from melts formed on the retrograde path (profiles A1 and A2, Fig. 3e; e.g. Gilotti et al. 2013). Variation in REE patterns is useful...
for defining domains within zircon and tying observed age variations between the domains to the P–T path (e.g. Hermann et al. 2001; Mattinson et al. 2006); however, the characteristic eclogite signature can record eclogite facies conditions below the quartz–coesite transition and cannot reliably be tied to UHP conditions in the absence of inclusion data. Several studies have demonstrated that the characteristic eclogite REE signature can locally persist to lower-P amphibolite facies conditions during decompression because the HP/UHP phase assemblage is still present (e.g. Liu and Liou 2011). Nevertheless, trace elements provide a valuable tool for tracking changes in zircon composition with age.

Another tool that helps link zircon dates to the P–T path is a geothermometer based on the titanium (Ti) concentration in zircon (Ferry and Watson 2007). Although developed for igneous zircon, the initial applications to metamorphic zircon are promising (Gilotti et al. 2013). Zircon growth at UHP conditions lies well outside the experimental calibration of the thermometer, and there is a known but uncertain effect of increased P on the T estimates. As a result, obtaining reliable T estimates from UHP zircon remains challenging.

In summary, different domains within a suite of zircon grains can be defined by CL imaging and then characterized by inclusion suites, trace element and isotope chemistry, and age (Rubatto and Hermann 2007). The presence of coesite or diamond inclusions in metamorphic zircon definitively links zircon growth to UHP conditions. Dating these coesite- and diamond-bearing zircon domains by U–Pb SIMS or LA–ICPMS analysis provides the most direct link between age and residence at UHP conditions available. Isolating the UHP domain for separate analysis is critical for obtaining useful information on the time of UHP conditions. Age data from zircon domains with lower-P inclusions or trace element patterns provide additional ties to the prograde or retrograde P–T path depending on their spatial relationship to the coesite-bearing domain (e.g. Hermann et al. 2001).

**TIMING FROM GARNET**

Garnet is a common mineral in a variety of moderate- to high-grade metamorphic rocks. The element-partitioning behavior of garnet generally favors high parent/daughter ratios of Sm–Nd and Lu–Hf, making it a useful mineral for chronology. Isochron ages are determined by comparing isotopic ratios between garnet and the bulk rock or other mineral phases, assuming equilibrium during garnet growth. Garnet ages can be tied to the P–T path because garnet is an important component of several widely used geothermobarometers and is also well known for its ability to preserve UHP inclusions. Analytical advances in garnet chronology over the last few years have yielded ages with very high precision (e.g. Pollington and Baxter 2011), providing the potential to link the geothermobarometry to high-precision geochronology in many metamorphic environments.

Because subduction-related metamorphism is a protracted process, it is critical that measured ages are interpreted in the context of the correct segment of the metamorphic cycle. This is especially relevant to chronology involving garnet due to its potentially long growth history (e.g. Skora et al. 2009). Garnet generally records prograde to peak-T conditions as long as the grains are not modified by diffusion at peak temperatures. The garnet core will record early growth and the rim will represent peak conditions in the general case where growth is radial. Mineral inclusions and chemical zoning in lower-T garnet can accordingly reflect prograde growth up to UHP conditions (Fig. 5). Lutetium typically is incorporated into garnet early in the crystallization history, whereas samarium is more concentrated in the outer, later-grown portions of the grains during prograde growth (e.g. Lapen et al. 2003; Skora et al. 2009). Thus, the Lu–Hf age should record the prograde path and the Sm–Nd age should reflect growth close to peak P–T conditions for bulk garnet analysis in cooler settings (<700 ºC; Fig. 2a).

Garnet size can vary considerably, from <1mm to >30 cm, so either bulk analysis or microsampling approaches may be utilized. Bulk garnet ages, typically determined from 50 to 500 mg of material, are dramatically controlled by the core-to-rim zoning of 176Lu and 147Sm: Lu–Hf and Sm–Nd ages will be weighted to the early and late stages of garnet growth, respectively. The difference in the two ages provides a minimum estimate of the duration of garnet growth.
growth, which can be linked to a calculated prograde $P$–$T$ path. Rates of mineral growth and crystal size distribution also have profound effects on skewing the measured bulk garnet ages toward early core or later rim growth. Element profiles from central cuts across garnet and 3-D imaging of the garnet size distribution establish the dominant growth mechanism and the appropriate growth rate law for modeling of bulk Lu–Hf and Sm–Nd ages (Skora et al. 2009). Microsampling techniques can also assess the time and duration of prograde to peak metamorphism for samples with garnet grains large enough to facilitate isolating multiple core-to-rim sampling domains (e.g. Pollington and Baxter 2011). The garnet(s) chosen for analysis must represent the whole population to allow appropriate age modeling based on element zoning, mineral growth rate, and crystal size distribution. Microsampling is particularly useful for isolating the garnet rim and dating peak $P$–$T$ conditions. Garnet geochronology can often precisely document the tempo of the prograde $P$–$T$ evolution of a terrane and provide absolute timing for crustal-thickening and subduction processes.

Dating of garnet in higher-temperature (>800°C) terranes is more complicated due to diffusion. The degree of resetting for different systems is controlled both by the peak $T$ and the length of time spent at high $T$. Garnets from high-$T$ UHP terranes are often compositionally unzoned in major elements and have uniformly distributed UHP inclusions. The Sm–Nd system in garnet is reset at much lower $T$ than the Lu–Hf system, so that Lu–Hf ages provide the time at UHP conditions, whereas the Sm–Nd ages are cooling ages (Fig. 2; Schmidt et al. 2011).

Despite the problems of uncertainty in Lu and Sm distribution, diffusional resetting, and disequilibrium, garnet geochronology can precisely document the timing of the prograde metamorphic history and provide absolute ages for processes associated with the formation, and perhaps early exhumation, of UHP terranes. Although diffusion at high $T$ can cause variable resetting, Lu–Hf and Sm–Nd ages can be used to determine the time of UHP conditions and cooling during exhumation by careful linking of element profiling and inclusion suites and comparison with ages from other minerals (Kylander-Clark et al. 2008; Schmidt et al. 2011).

**LESSONS LEARNED FROM EXAMPLES**

**Cold and Fast: Lago di Cignana, Western Alps, Italy**

The rocks at Lago di Cignana represent one of the few exposed UHP terranes dominated by oceanic lithologic assemblages. Coesite and its relics are present in prograde-zoned garnet from both mafic eclogites and metasedimentary rocks (Reinecke 1998). $P$–$T$ modeling of garnet suggests a very steep prograde and retrograde path (LC in Fig. 1) with nearly synchronous peak $P$ (~2.8 to >3.2 GPa) and $T$ (~630°C) (Figs. 1, 2s; Reinecke 1998; Groppo et al. 2009). The mean U–Pb age of metamorphic zircon is 44.1 ± 0.7 Ma, but there are no inclusions in the zircon that directly link its growth to UHP conditions (Rubatto et al. 1998). A Lu–Hf bulk garnet age of 48.8 ± 2.1 Ma and a Sm–Nd bulk garnet age of 40.6 ± 2.6 Ma from the same sample aliquot represent early- and late-formed garnet (Amato et al. 1999; Lapen et al. 2003). The age difference reflects the minimum duration of garnet growth during prograde metamorphism. Given that the Sm–Nd age represents the late stage of garnet growth based on trace element distributions and growth modeling, the ~41 Ma age is the best estimate of the timing of UHP conditions (Amato et al. 1999; Lapen et al. 2003). The slightly older zircon ages suggest that metamorphic zircon growth occurred on the prograde path. The garnet ages, combined with peak $P$ estimates, provide a basis for estimating a subduction rate of ~0.45 cm/y (Lapen et al. 2003). Exhumation to shallower crustal levels is assumed to be fast (1–3 cm/y) since cooling ages are within a few million years of the peak UHP age (Amato et al. 1999). The discovery of microdiamond in garnet at Lago di Cignana (Frezzotti et al. 2011) supports peak $P$ estimates based on pseudosection modeling (Groppo et al. 2009) and provides further opportunity to link garnet geochronology to the $P$–$T$ path at UHP conditions. New age data from the diamond-bearing garnet will likely yield faster exhumation rates than previously documented.

**Warm and Fast: Dora-Maira, Western Alps, Italy**

The Dora-Maira nappe contains a mineralogically unique UHP quartzite with large coesite-bearing pyrope garnets (Chopin 1984). Diamond has not been observed, but peak $P$–$T$ estimates are 3.5–4.4 GPa and ~750°C (Schertl et al. 1991; Hermann 2003). Prograde chemical zoning is locally preserved, but most garnet is unzoned. Coesite occurs throughout the unzoned grains without preference for the core or rim; therefore, the bulk garnet ages most likely represent the time of UHP metamorphism. Age determinations of peak metamorphic conditions are 34.1 ± 1.2 Ma (Lu–Hf garnet; Duchêne et al. 1997) and 35.4 ± 1.0 Ma (U–Pb zircon; Gebauer et al. 1997). Coesite is included in both garnet and zircon, but the Lu–Hf age is most robustly linked to the age of UHP metamorphism because coesite in zircon occurs along cracks in the grains—a cautionary note that the relationship between inclusions and the dated material must be carefully documented (Gebauer et al. 1997). Additional support for the age of UHP metamorphism comes from metamorphic titanite, which is interpreted to be in equilibrium with the surrounding UHP assemblage and gives a U–Pb age of 35.1 ± 0.9 Ma (Rubatto and Hermann 2001). The UHP ages, combined with cooling ages and ages of ~32 Ma from titanite that formed during decompression, indicate fast exhumation rates of 2.0–3.4 cm/y (Gebauer et al. 1997; Rubatto and Hermann 2001). A peak $P$ of 4.4 GPa (Hermann 2003) pushes the exhumation rate to >4.5 cm/y, but there is no direct tie between the age and peak $P$ estimates at Dora-Maira yet.

**Really Hot and Fast: Kokchetav, Kazakhstan**

The Kokchetav massif records fast, hot UHP metamorphism and exhumation. Peak $P$–$T$ estimates of >4.5 GPa and 950–1000°C, coupled with abundant microdiamond and coesite inclusions, are consistent with observations of widespread melting (Sobolev and Shatsky 1990; Hermann et al. 2001). Inclusions, trace elements, and CL images of zircon delineate peak UHP and retrograde granulite to amphibolite facies domains. Phengite dehydration melting at UHP conditions is clear for the high-$T$ Kokchetav locality, since the $P$–$T$ path crosses the melting curve (Fig. 1). The presence of melt promotes zircon growth that preserves diamond and coesite inclusions, allowing the time of UHP metamorphism to be determined at 527 ± 5 Ma (Hermann et al. 2001). Zircon ages define the time of melt crystallization on the decompression path at 528 ± 8 Ma, statistically similar to the time of UHP metamorphism and suggesting that exhumation was fast, with a minimum rate of 1.8 cm/y (Hermann et al. 2001). Sm–Nd garnet ages of 535 ± 3 Ma, U–Pb UHP zircon ages as old as 537 ± 9 Ma, and cooling ages as old as ~529 Ma, coupled with $P$ estimates of >6 GPa, lend a high degree of uncertainty to estimated exhumation the rates (see review in Schertl and Sobolev 2013), but they also highlight the need for increased preci-
sion in the age information obtained at UHP and lower-P conditions in order to better estimate the rates of rapid tectonic processes.

**Hot and Slow: Dabie–Sulu, China**

The Dabie–Sulu UHP terrane offers premier examples of UHP rocks with well-preserved coesite in zircon and other HP and UHP phases (Liu and Liu 2011). Pressure-temperature estimates from a variety of lithologies define a range of 2.8–4.0 GPa and 720–870°C, and generally indicate that decompression was accompanied by heating such that peak P and peak T occur at significantly different times (Figs. 1, 2a; Liu and Liu 2011). Zircon records multiple periods of metamorphism defined by inclusion suites: ~245 Ma prograde zircon, 235–225 Ma coesite-bearing UHP zircon, and 215–208 Ma amphibolite facies retrograde zircon (Liu and Liu 2011). Compositional zoning patterns combined with Lu–Hf garnet ages of 223–215 Ma suggest that garnet in eclogites of the Dabie–Sulu terrane formed on the decompression path—perhaps recording the time of peak T (Fig. 1; Schmidt et al. 2011). The spread in ages obtained for coesite-bearing zircon demonstrates a prolonged history of UHP metamorphism in the Dabie–Sulu terrane, with residence times in the coesite stability field on the order of 15 My and relatively slow exhumation rates of 0.5 cm/y. The spread in U–Pb, Lu–Hf, and Sm–Nd ages from different localities may also be interpreted to record a series short-lived events; applying multiple dating methods at the same locality will help resolve the differing interpretations (Schmidt et al. 2011).

**Really Hot and Slow: Greenland**

Coesite-bearing exposures in the North-East Greenland eclogite province provide an example of a hot UHP terrane that formed in the overriding plate of a collisional orogen and experienced peak conditions of 3.6 GPa and 950°C, followed by slow exhumation and cooling (Gilotti et al. 2013). UHP zircons with coesite inclusions from both eclogite and quartzofeldspathic gneiss give SIMS U–Pb ages over an extended period of 365 to 350 Ma. Granulite facies retrograde metamorphism from 345 to 330 Ma and amphibolite facies metamorphism from 330 to 320 Ma are recorded by zircon from the gneisses and exhumation-related intrusions. Garnet grains from a kyanite eclogite give a Sm–Nd age of 342 ± 6 Ma, which is interpreted to record cooling through the closure temperature of garnet but may record new growth on the retrograde path. The observed ages indicate a 10 to 15 My duration of UHP metamorphism followed by exhumation to amphibolite facies conditions by 330 Ma, which gives an exhumation rate of ~4 mm/y. In this type of long-lived UHP terrane, we can begin to address the continuous versus episodic nature of metamorphic processes. In some cases, the large range of zircon ages from within an individual sample points to a continuous growth process. Age variation among closely spaced (tens to hundreds of meters) samples indicates episodic zircon growth controlled by fluid availability, mostly related to melting and retrograde reactions during exhumation (e.g. Zheng 2009). Distinct pulses of zircon growth, observed in a number of different intrusive and metamorphic lithologies, help pin timing to the retrograde P–T path. A similar protracted UHP and exhumation history is defined by SIMS analysis of coesite-bearing zircon and cooling ages in the Qaidam UHP terrane of western China (Mattinson et al. 2006). The Western Gneiss Region, Norway, also shows slow exhumation rates based on garnet, titanite, and cooling ages, but the duration of UHP metamorphism is not well constrained (Kylander-Clark et al. 2008). These long-lived UHP terranes present an opportunity to evaluate the systematics of the geochronologic methods employed and to establish the rates of slower tectonic processes.

**CHALLENGES**

State-of-the-art studies to place time limits on subduction, residence at UHP conditions, and exhumation require a multielement and multichronometer approach applied in concert with extensive compositional characterization of other phases in the host rock. We can currently resolve differences in timing for the slower processes but clearly have a long way to go for faster orogenic cycles. We often place too much emphasis on high-precision ages, which in reality represent averages of a metamorphic continuum. Analytical advances focused on coupling improved precision and accuracy with higher spatial resolution and reduced sample size will help parse the P–T path into smaller, temporal segments. Deploying additional geochronometers with specific spatial and chemical relationships to zoning within the chronometer itself or adjacent P- and/or T-sensitive minerals will provide multiple points on the P–T path for individual samples. This approach should help tease out subtle differences in the timing of metamorphic processes and distinguish between continuous versus episodic events and changes in metamorphic conditions. Additional P–T points are also necessary to define inflections in the path that reflect changes in various rates, such as the rates of subduction, exhumation, heating, cooling, and fluid influx.

A better understanding of the conditions and specific reactions that produce key mineral geochronometers is required. Currently, the only robust tie between P and time is the preservation of P-dependent phases and geobarometry using phases demonstrably in equilibrium with the geochronometer at UHP conditions. The discovery of additional high-pressure phases or exsolution textures that can be uniquely tied to geochronometers would be helpful. Improvements to techniques for demonstrating equilibrium conditions between mineral, fluid, and melt inclusion suites would be fruitful as well. Perhaps the most promising future lies in defining P-dependent reactions that produce or can be recorded by geochronometers. For example, the growth of UHP zircon in eclogites is commonly assumed to require the presence of fluid, but the origin and nature of the required fluid are not well understood (Zheng 2009). A broad approach that includes multiple chronometers combined with detailed inclusion analysis, accessory-phase composition, phase equilibria, and trace element budgets for all minerals involved in producing individual geochronometers will no doubt improve our ability to establish the time and duration of UHP metamorphism.

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Credits
1. Garnet from eclogite, Martin, Rubatto et al. submitted Chemical Geology
2. Dora Maira, Rubatto, Herrmann and Guethiez-Putallaz personal communication
3. Zircon from eclogite, Martin et al. 2011, Lithos
4. Eclogite-facies rock from Sesia-Lanzo Zone, Western Alps, courtesy D Rubatto

The SIMS for Metamorphism
Deep Fluids in Subducted Continental Crust

Jörg Hermann1, Yong-Fei Zheng2, and Daniela Rubatto1

Observations from ultrahigh-pressure metamorphic rocks combined with experimentally determined phase relations provide a framework for understanding fluid-mediated mass transfer in deeply subducted continental crust. At temperatures below 650 °C, aqueous fluids derived from dehydration reactions involving hydrous phases contain limited amounts of solutes. At temperatures of 700–800 °C, a supercritical fluid with a composition intermediate between aqueous fluid and hydrous melt might be present. The most significant mass transfer at ultrahigh-pressure conditions occurs at 800–1000 °C, where subducted crust undergoes partial melting related to the breakdown of the hydrous mineral phengite. Partial melting leads to a significant change in the composition and density of the rocks, and also affects the rheology of deeply subducted crust.

Keywords: UHP metamorphism, subduction, fluids, partial melting, zircon, phengite

Why Are Ultrahigh-Pressure Fluids Important?

Subduction zones are crucial for understanding element recycling within planet Earth because they transport oceanic basalt, seafloor sediment and fragments of continental crust to mantle depths. Subduction delivers differentiated crustal materials enriched in volatiles and incompatible trace elements to a mantle that has been depleted in these elements by partial melting over geological time. As crustal rocks are buried during subduction, they undergo high-pressure (HP) to ultrahigh-pressure (UHP) metamorphism, leading to the liberation of metamorphic fluids (i.e., aqueous fluid and hydrous silicate melt). These fluids ascend into the mantle wedge above the subduction zone, where they induce partial melting resulting in arc magmatism (Tatsumi and Eggins 1995; Zheng 2012). While some incompatible elements, like K, H2O, Ba, Rb, Sr, Pb, U and, to a lesser extent, Ce, are recycled from the subducting slab and incorporated into juvenile crust, other elements, like Y, Zr and Nb, stay behind and are subducted to the deeper mantle (Tatsumi and Eggins 1995; Zheng et al. 2011). Fluid-mediated mass transport in subducted crust affects the long-term differentiation of Earth.

If we want to understand the processes of crustal recycling, we need to study materials that were subjected to deep subduction, where the most important mass transfer occurs. Geophysical data show that subducted oceanic slabs reside at 80–170 km below volcanic arcs, corresponding to a pressure range of 2.5–5 GPa (Tatsumi and Eggins 1995). UHP metamorphic rocks record this range in pressure, and thus provide an exciting natural laboratory for studying fluid–rock interaction relevant to mass transfer in continental subduction channel (Zheng 2012). These processes also greatly influence the physical properties, such as density and rheology, of the subducted material.

The characterization of UHP fluids is complicated for several reasons. First, the fluids are fugitive and commonly leave only traces of their activity in the rock record. Second, the rocks travel a long way back to the surface, and the processes that occur during this journey can obscure the activity of UHP fluids at mantle depths. The investigation of fluids in UHP rocks requires information from advanced microanalytical techniques combined with laboratory data from experiments conducted under the appropriate pressure–temperature conditions.

Experimental Constraints

Phase Relations

The phase relations of rocks containing fluids at crustal pressures are well understood. The addition of water depresses the melting point of rocks considerably, leading to partial melting in the deeper and hotter parts of the crust. For example, a free aqueous fluid will react with a gneiss or metapelite at the wet solidus to form a hydrous melt at a temperature of ~650 °C at the base of a 35 km thick continental crust (~1.0 GPa). The water content of a water-saturated melt is about 12 wt%, whereas the solute content of the aqueous fluid that triggered melting is less than 2 wt% (Fig. 1). At higher pressure, the amount of solute increases in the aqueous fluid and decreases in the hydrous melt, while dissolved water in the hydrous melt increases (Fig. 1). At high pressure and temperature, the physical properties of aqueous fluid and hydrous melt approach each other until they are identical at the termination of the wet solidus. This point is called the second critical...
in minerals and fluids can be used to distinguish between H$_2$O derived from a variety of geological environments (Zheng 2009).

The minerals present and the metamorphic conditions will determine how much material is dissolved during the liberation of the fluid phase (Manning 2004). Table 1 summarizes the experimentally determined solubilities of major and key trace elements in felsic crustal rocks at UHP conditions (Hermann and Spandler 2008; Hermann and Rubatto 2009 and references therein). Hydrous melts are granitic in composition, since they are dominated by SiO$_2$, Al$_2$O$_3$ and alkalis. The large variation in SiO$_2$ is mainly related to the variable amount of water in the melt (Fig. 1). The Si/Al and (Na+K)/Al molar ratios plot in a very restricted field and are consistent with a dominant melting reaction in which phengite + jadeite + coesite + water react to produce a melt (Fig. 2). Both ratios decrease with increasing temperature. The solubility of mafic components is very low, such that MgO + FeO < 3 wt%. The concentrations of Zr, Ti and Ce each increase by a factor of 5–10 with temperature increasing from 750°C to 1050°C. Aqueous fluids have at least 5–10 times lower concentrations in major and trace elements than hydrous melts. The solubility of Al is significantly lower with respect to Na+K and Si in aqueous fluids compared to hydrous melts (Fig. 2). Wohlers et al. (2011) observed a decrease of Na/Al and Si/Al in HP aqueous fluids coexisting with albite/jadeite + paragonite + quartz with increasing amounts of solutes, and they related this feature to a higher amount of polymerized Na–Al–Si-bearing species in the solution. The composition of intermediate supercritical fluids in basalt + H$_2$O experiments (Kessel et al. 2005) plots between the fields of aqueous fluid and hydrous melt (Fig. 2). Although data are scarce, supercritical fluids appear to have major and trace element compositions that fall between those of aqueous fluids and hydrous melts (Table 1).

**Figure 1** Phase diagram of metapelites and granitic rocks in the presence of H$_2$O (modified from Hermann and Rubatto 2013). The H$_2$O content of rock-buffered fluids changes as a function of the pressure–temperature conditions. The wet solidus terminates at the second critical endpoint (CP). The fine black lines show the approximate wt% H$_2$O in the fluid phase. For high water contents the fluid phase is called an “aqueous fluid” (blue field), whereas for low water and high solute contents, the fluid phase is a “hydrous melt” (light and dark tan fields). Supercritical fluids are present above the CP; their water contents are transitional between those of aqueous fluid and hydrous melt. The grey lines mark melting reactions (Schmidt et al. 2004; Auzanneau et al. 2006; Hermann and Spandler 2008) that consume phengite, the most important hydrous phase in felsic UHP crust. Three P–T trajectories are shown for UHP rocks: Lago di Cignana (LC), Dabie–Sulu (DS) and Kokchetav massif (Ko). Abbreviations: als = aluminosilicate, bt = biotite, coe = coesite, cpx = clinopyroxene, grt = garnet, kfs = K-feldspar, m = melt, phe = phengite, pl = plagioclase, qtz = quartz.

**Figure 2** The Si/Al and (Na+K)/Al molar ratios can be used to distinguish among experimental aqueous fluids, intermediate supercritical fluids and hydrous melts. The positions of key minerals are shown. Arrows indicate trends of fluid compositions with increasing temperature and increasing solute content (given in wt%); the aqueous fluid trend is likely related to increasing polymerization. Circles: Wohlers et al. (2011); diamonds: Kessel et al. (2005); squares: Hermann and Spandler (2008).

**Fluid Composition**

Water is a primary constituent of crustal fluids. During progressive metamorphism, water is liberated from the breakdown of hydrous minerals (Schmidt and Poli 1998) and from the exsolution of structural and molecular water in nominally anhydrous minerals (Zheng 2009). The quantification of H$_2$O in different forms in UHP minerals is essential for understanding the storage capacity of water in subducted UHP slabs (Zheng 2009). The stable isotope signature of water itself provides another exceptional tracer for the origin of the fluids. Because natural waters of various origins exhibit systematic differences in their H and O isotope compositions, H and O isotopes trapped endpoint. For metapelitic and granitic compositions, the second critical endpoint is situated at ~3–3.5 GPa and ~750°C (Hermann et al. 2006; Zheng et al. 2011). Above the second critical endpoint, aqueous fluid and hydrous melt exhibit complete miscibility. The amount of solutes in the fluid is still constrained by the pressure and temperature of the system and increases gradually with increasing temperature (Fig. 1). The disappearance of the solidus at the P–T conditions recorded in UHP rocks makes these rocks highly relevant for understanding the nature and composition of the fluid phase in subducted crust (Zheng et al. 2011; Hermann and Rubatto 2013).

**Elements**
TABLE 1 COMPOSITIONAL RANGE OF AQUEOUS FLUID AT 2.5–4.5 GPA AND 600–700°C AND OF HYDROS MELT AT 2.5–4.5 GPA AND 750–1050°C in subducted felsic crustal rocks, based on experimental data reported by Hermann and Spandler (2008) and Hermann and Rubatto (2009).

<table>
<thead>
<tr>
<th>Major elements (wt%)</th>
<th>Aqueous fluid</th>
<th>Hydros melt</th>
</tr>
</thead>
<tbody>
<tr>
<td>SiO₂</td>
<td>5–15</td>
<td>55–75</td>
</tr>
<tr>
<td>Al₂O₃</td>
<td>0.5–2</td>
<td>10–15</td>
</tr>
<tr>
<td>Na₂O</td>
<td>0.5–2</td>
<td>3–6</td>
</tr>
<tr>
<td>K₂O</td>
<td>0.1–0.2</td>
<td>2–10</td>
</tr>
<tr>
<td>H₂O</td>
<td>80–95</td>
<td>5–30</td>
</tr>
<tr>
<td>CaO</td>
<td>0.1–0.2</td>
<td>1–2</td>
</tr>
<tr>
<td>FeO</td>
<td>0.1–0.2</td>
<td>0.5–1</td>
</tr>
<tr>
<td>MgO</td>
<td>0.1–0.2</td>
<td>0.5–1.5</td>
</tr>
</tbody>
</table>

| Trace elements (ppm) | | |
|----------------------| | |
| Ti                   | 10–100        | 1000–10000  |
| Rb                   | 1–5           | 100–200     |
| Sr                   | 3–30          | 200–1000    |
| Zr                   | 0.1–5         | 50–350      |
| Ce                   | 0.1–5         | 50–500      |

APPLICATION OF EXPERIMENTAL RESULTS TO UHP TERRANES

Three examples highlight how an experimental framework can be used to understand UHP fluids. (1) The Lago di Cignana unit (Western Alps, Italy) consists of a metabasalt–sediment sequence that constitutes a rare example of UHP metamorphism in altered oceanic crust. As shown experimentally, during subduction and prograde metamorphism from greenschist to blueschist to eclogite facies, the gradual breakdown of hydrous phases such as chlorite, amphibole, and lawsonite liberates a fluid phase (Schmidt and Poli 1998). The prograde, peak, and retrograde evolution of the Lago di Cignana rocks all occurred at conditions where an aqueous fluid was stable. Peak temperatures of ~620°C were too low to form partial melts; therefore, at any stage where a dehydration reaction occurred, an aqueous fluid was produced. This fluid might have contained other components, such as Cl and CO₂, but the amount of solutes was in a range that is characteristic of an aqueous fluid.

(2) A significant part of the P–T path of the Dabie–Sulu UHP rocks (China) was at conditions above the wet solidus (Zheng et al. 2011). Because no free aqueous fluid was available during peak metamorphic conditions, partial melting was restricted to the breakdown of hydrous phases. Experimental studies have shown that phengite, the stable white mica at ultrahigh pressure, is the most important hydrous phase in felsic UHP rocks (Schmidt et al. 2004; Hermann and Spandler 2008). Two melting reactions involving phengite (Fig. 1) were crossed during decompression and concomitant heating of the Dabie–Sulu UHP rocks, resulting in a major melting event during exhumation (Hermann et al. 2006; Zheng et al. 2011).

(3) The Kokchetav gneisses (Kazakhstan) record subduction to extreme UHP conditions where \( P \geq 5 \) GPa and \( T \approx 1000°C \). These very high temperatures resulted in the breakdown of phengite close to peak pressure, and most of the retrograde path passes within the field where melt was probably present (Fig. 1).

MACROSCOPIC ROCK RECORD OF UHP FLUIDS

Inferences on the nature and composition of the fluid phase can be made from traces of fluid left behind in UHP rocks. The simplest, but least conclusive, way of characterizing UHP fluids is by studying reaction products that involved a fluid phase. For example, the formation of giant garnet crystals (Fig. 3a) in the classic whiteschists (phengite-quartzites) of the Dora-Maira massif (Western Alps, Italy) can be related to the breakdown of chlorite during prograde conditions of 2–3 GPa and 600–650°C. Smaller, millimeter-sized garnets and coesite were produced from kyanite and talc close to the peak metamorphic conditions at ~4 GPa and 720°C. Thus, garnet formation is related to the breakdown of hydrous phases such as chlorite and talc, which results in the liberation of a fluid phase. The trace element

![Figure 3](https://example.com/figure3.png)

**Figure 3** Macroscopic and microscopic rock record of fluid interaction at UHP conditions. (A) Pyrope-rich garnet (Grt) megablasts in whiteschist (phengite quartzite) from the Dora-Maira massif originate from a prograde dehydration reaction during subduction. (B) Thin section photomicrograph of a vein containing kyanite (Ky), zoisite (Zo), garnet, omphacite (Omp) and quartz (Qtz) in a UHP eclogite from the Dabie–Sulu terrane, related to the breakdown of lawsonite (Li et al. 2004). (C) Vein of phengite (Phe) and quartz in a UHP eclogite from the Dabie–Sulu terrane, formed by a retrograde dehydration reaction during exhumation (Chen et al. 2012). (D) Garnet- and quartz-rich restite from a migmatitic metasediment, Kokchetav massif (photo courtesy of A. Stepnov).
composition of different garnet domains contains information on the nature and composition of the fluid phase present during garnet growth (Ferrando et al. 2009). The trace element composition of whiteschists is surprisingly similar to the country rock orthogneiss, from which the whiteschists evolved. Hence, dehydration reactions that produce an aqueous fluid containing a relatively low amount of solutes do not result in a significant change in the composition of the host rock and lead to only limited mass transfer (Hermann and Rubatto 2013).

Metamorphic veins in UHP rocks display discordant textures and large minerals, providing strong evidence for solution–precipitation reactions in the presence of a fluid phase. For this reason, many studies have targeted veins in UHP rocks (Zhang et al. 2008). A vein in an eclogite from Dabie–Sulu consists of kyanite + zoisite + quartz (Fig. 3a) and is interpreted as having precipitated from a fluid produced during the breakdown of the hydrous phase lawsonite close to peak pressure (Li et al. 2004). In contrast, quartz–phengite veins in the Dabie–Sulu eclogites formed during a dehydration event related to exhumation (Fig. 3c). The composition of the vein does not directly reflect the composition of the fluid phase but rather what is left behind (Hermann et al. 2006; Chen et al. 2012). Careful study of the trace element and isotope compositions of vein minerals can discriminate between fluid generated internally due to dehydration reactions (Zheng 2009) and fluid infiltration from an external source (John et al. 2012). Significant mass transfer can occur in vein systems, especially if they are related to a large amount of fluid flow.

A few UHP terranes, such as the Kokchetav massif and the Erzgebirge (Bohemian massif, central Europe), reached peak temperatures that resulted in partial melting of the felsic rocks (Fig. 1). Thus, migmatites and garnet-rich restites (Fig. 3d) are common in these UHP terranes. Extraction of partial melts leads to a change in bulk composition. This chemical signature is largely preserved through later re-equilibration and can be used to constrain the composition of the hydrous melt that left the rocks. The Kokchetav restites are characterized by enrichment in FeO and depletion in K$_2$O and Ce (Hermann and Rubatto 2013), which is consistent with the extraction of a K$_2$O-rich granitic melt (Table 1). Partial melting is the most effective way to produce a large transfer of mass from subducted crust to the mantle (Hermann and Spandler 2008; Zheng et al. 2011).

The study of mass transfer at contacts between felsic and ultramafic rocks serves as a natural laboratory for processes occurring at the slab–mantle interface during deep subduction. In UHP ultramafic rocks from Dabie–Sulu, hydrous granitic melts that were generated within subducted gneisses reacted with olivine to form new orthopyroxene, garnet and phlogopite (Malaspina et al. 2006). During this process the majority of dissolved elements in the hydrous melts, such as Si, Al and to some extent K, precipitated to form the new minerals, resulting in a residual aqueous fluid that had fewer solutes but that still retained a characteristic crustal trace element signature, with elevated Ba, Sr and Pb abundances.

When the nature and composition of deep fluids is deduced from residues, it is crucial to demonstrate that the minerals retain their major, trace element and isotopic composition at the time of fluid–rock interaction. For relatively low metamorphic temperatures, such as documented in the Dora-Maira massif, this is likely the case; however, many UHP terranes reach peak temperature after peak pressure, resulting in recrystallization. The recrystallized minerals may not provide a faithful record of fluid–rock interactions at UHP conditions.

**MICROSCOPIC RECORD OF UHP FLUIDS**

While macroscopic features mainly represent the material that is left behind by fluid–rock interactions, on rare occasions, the UHP fluids themselves can be trapped as microscopic fluid inclusions. The challenge is to determine the timing of inclusion entrapment and to demonstrate that their composition has not been significantly modified during exhumation. During decompression, the host mineral and the fluid inclusion expand at different rates, and thus the fluid inclusions commonly burst. However, tiny fluid inclusions 10–20 µm in size included in very robust container minerals, such as garnet, kyanite and zircon, are able to survive. Such rare fluid inclusions may exhibit negative crystal shapes within the host mineral. The analysis of these tiny inclusions is challenging and methods are still under development, but the inclusions yield direct information about fluid composition. Using a few examples, we illustrate below how the appearance and composition of inclusions can vary with changing P–T conditions.

Primary fluid inclusions are hosted in garnet from a UHP, Mn-rich quartzite from Lago di Cignana (Fig. 4a). The inclusions contain an aqueous fluid, a vapour bubble and solids dominated by carbonate, along with minor amounts of other minerals and diamond (Frezzotti et al. 2011). This finding provides evidence that the fluids were trapped at diamond-facies conditions. The reconstructed composition is that of an aqueous fluid with dissolved carbonate and with minor amounts of other elements in solution—in agreement with the phase relations shown in Figure 1.

We have already shown that garnet in the Dora-Maira whiteschists records prograde to peak growth related to fluid-producing reactions. Detailed fluid inclusion studies demonstrate that in the core region of the garnet, aqueous fluids with dissolved chlorine predominate, whereas garnet rims contain inclusions with higher amounts of daughter minerals, indicating a greater concentration of solutes in the fluid (Fig. 4a). Laser ablation ICP–MS analysis of major and trace elements in inclusions in garnet rims shows that the fluids are characterized by elevated contents of lithophile elements, such as Rb, Ba, Pb and Sr (Ferrando et al. 2009).

Minerals from veins in a Dabie–Sulu eclogite that formed at ~760 °C and ~3 GPa contain fluid inclusions as well as solid inclusions of anhydrite, siderite, magnetite and paragonite (Zhang et al. 2008; Fig. 4c). The higher proportion of solids with respect to liquids trapped in the inclusions suggests that the original UHP fluid had a greater concentration of solutes. The general interpretation is that during decompression and cooling, the solutes in the UHP fluid precipitated as minerals. The presence of paragonite [NaAl$_2$Si$_2$O$_{10}$(OH)$_2$] as a main solid inclusion highlights one of the ambiguities in the interpretation of such inclusions. While it provides evidence that Na and Si were enriched in the fluid phase, the Na/Al and Si/Al ratios of paragonite do not overlap with experimental fluid compositions (Fig. 2). This indicates that some of the Al may have been derived from interaction of the fluid phase with the host kyanite (Al$_2$SiO$_3$). The presence of anhydrite suggests that sulfur was present in the oxidized form in the UHP fluid, in agreement with the presence of magnetite (Zhang et al. 2008).
The appearance of fluid inclusions changes drastically when temperatures approach 1000 °C at ~5 GPa, such as in the UHP gneisses of Kokchetav and Erzgebirge. The inclusions have a much higher proportion of minerals and only small amounts of void space that was occupied by the aqueous fluid. However, they share similarities with aqueous fluid inclusions, such as negative crystal shape and constant proportions of infilling minerals (Fig. 4d). The mineral assemblage in the polyphase inclusion trapped in garnet shown in Figure 4d consists of phengite, phlogopite, paragonite, quartz and diamond (Stöckhert et al. 2001). The average bulk composition of these inclusions approaches that of a hydrous granitic melt (Table 1), providing evidence that hydrous melt was trapped under diamond-facies conditions. Subsequently, the melt must have crystallized during exhumation because paragonite is not stable at UHP conditions. Similar multiphase solid inclusions, consisting of an irregular intergrowth of K-feldspar and quartz (Fig. 4e), were found in garnet within eclogite from Dabie–Sulu (Gao et al. 2011). These inclusions were interpreted as crystallization products of hydrous melts that formed by the breakdown of phengite during decompression (see Figure 1).

**ACCESSORY PHASES AS FLUID MONITORS**

Subducted continental crust contains trace element–rich rock types that favour the formation of accessory minerals during metamorphism. Monazite, apatite, allanite, rutile and zircon are common accessory phases in UHP rocks; these minerals are important hosts for key trace elements, such as rare earth elements (REEs), Th, U, P, Ti, Nb, Ta, Zr and Hf. Therefore, the release or retention of these elements during dehydration and melting at UHP conditions is governed by the behaviour of accessory phases (Hermann and Rubatto 2009). Many of these elements are essential structural components of minerals, for example, Th and Ce in monazite and allanite, P in apatite and monazite, Ti in rutile and Zr in zircon. Thus, the concentration of these elements in the fluid phase (Table 1) is controlled by the solubility of the host minerals (Hermann and Rubatto 2009; Zheng et al. 2011). In many cases, UHP rocks recrystallized extensively during their way back to the surface, making it difficult to extract information about the nature and composition of the fluids at UHP conditions. Refractory accessory phases are commonly less affected by retrograde metamorphism and thus are better able to retain information about UHP fluids.

Among the accessory minerals, zircon has attracted a lot of attention as a potential monitor for fluid-related processes (Rubatto and Hermann 2007; Zheng 2009). Zircon is a very refractory mineral that is reluctant to participate in metamorphic reactions and is essentially inert in the absence of fluids. However, when fluid phases are present, zircon undergoes varying degrees of metamorphic recrystallization via the mechanisms of dissolution–recrystallization and replacement alteration along fractures and crystal boundaries (Chen et al. 2010). Either metamorphic or metamorphosed zircons can serve as a monitor of fluid–rock interaction during subduction zone processes (Zheng 2012). Zircon can trap mineral inclusions as it grows; in many gneisses, inclusions within zircon are the...
only evidence that the rocks were once at UHP conditions (Liu and Liou 2011). The great advantage of zircon as a fluid monitor is that it can be accurately dated by the U–Pb radiometric method, thus providing an absolute age for the fluid activity (Zheng 2009; Chen et al. 2012). Figure 5 displays a compilation of zircon images from the Dabie–Sulu UHP area. Solid inclusions composed of the UHP assemblage coesite, garnet, jadeite and phengite and fluid inclusions consisting of CO$_2$ + H$_2$O are present in the metamorphic zircon domain of Triassic age (Liu and Xu 2004). In situ zircon analyses show systematic differences in trace element patterns, U–Pb ages and O isotope ratios between inherited cores and newly grown rims (Chen et al. 2011). The inherited cores exhibit increasing heavy-REE patterns, Neoproterozoic U–Pb ages and positive $\delta^{18}$O values. In contrast, the metamorphic domains exhibit flat heavy-REE patterns, Triassic U–Pb ages and negative $\delta^{18}$O values. This $\delta^{18}$O difference indicates that the UHP metamorphic fluid was derived from the dehydration of Neoproterozoic rocks that were hydrothermally altered by meteoric fluid at high temperatures, before the subduction. The Hf isotopes in relict zircon cores provide important information on the genesis of the protolith for the UHP rocks (Chen et al. 2010, 2011). Metamorphic zircon domains commonly exhibit elevated Hf isotope ratios but decreased Lu/Hf isotope ratios relative to the relict protolith cores, suggesting involvement of metamorphic fluids that were related to the dissolution and precipitation of garnet (Zheng et al. 2005).

With the advent of microbeam in situ analytical techniques, a comprehensive study of accessory phases such as zircon, monazite, titanite and rutile can provide a wealth of information on the formation and evolution of crustal fluids in UHP rocks. Fluid evolution can be added to the pressure–temperature–time path of UHP rocks (McClelland and Lapen 2013 this issue) to describe more completely deep subduction of continental crust.

**IMPLICATIONS**

The combined data from UHP rocks and laboratory experiments demonstrate that the most significant mass transfer in continental subduction zones occurs at T > 700°C by means of hydrous melts. Such melts are broadly granitic in composition, and accessory phases play an important role in controlling trace elements such as Th, Ce and Zr. Melting is related to the breakdown of phengite, the most common hydrous phase in felsic UHP rocks. The scarcity of a free fluid phase in subducted continental crust at UHP conditions (Zheng 2009) is a limiting factor for extensive melting. This is the most important difference compared to subducted oceanic crust, where abundant aqueous fluids are available. Accordingly, mass transfer in subducted continental crust is less significant than in subducted oceanic crust.

The extraction of deep fluids from UHP crust has implications not only for the recycling of elements in subduction zones but also for the physical properties of deeply subducted crust. The presence of UHP fluids will influence...
the rheology of the rocks at mantle depths and during exhumation. This is particularly apparent when rocks undergo partial melting, which greatly reduces the strength of the rocks. Therefore, partial melting in hot UHP terranes, such as the Bohemian and Kokchetav massifs, might be an important trigger for initiating exhumation. In other areas, such as Dabie-Sulu, significant partial melting occurs during an advanced stage of exhumation, and thus processes at the slab-mantle interface may be responsible for the switch from subduction to exhumation. In either case, melt-peridotite interaction may result in crustal metasomatism of the mantle wedge overlying the continental subduction zone (Zheng 2012). If a significant amount of partial melt is extracted from UHP rocks, the residue can become refractory, with enrichment in minerals such as garnet and kyanite. Such restites may reach a density as high as that of eclogite, and thus are able to sink into deeper parts of the mantle where they will create chemical and isotopic anomalies.

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Formation and Exhumation of Ultrahigh-Pressure Terranes

Bradley R. Hacker1, Taras V. Gerya2, and Jane A. Gilotti3

The reignig paradigm for the formation and exhumation of continental ultrahigh-pressure (UHP) terranes is the subduction of crust to mantle depths and the return of crustal slices within the subduction channel—all at plate tectonic rates. Additional processes beyond the paradigm are needed to explain the diversity of geological observations gathered from the growing study of UHP terranes—for example, variations in the size, degree of deformation, petrologic evolution, timing of UHP metamorphism, and exhumation rates. Numerical models that evaluate physical parameters in time and space have produced new insights into the formation and exhumation of UHP terranes.

KEYWORDS: ultrahigh pressure, exhumation, channel flow, exudation, diapir

INTRODUCTION

The two discoverers of coesite in regional metamorphic rocks, Chopin (1984) and Smith (1984), immediately deduced that subduction of continental crust was responsible for the formation of this unusual high-pressure form of SiO2. This led naturally to the conclusion that continental ultrahigh-pressure (UHP) terranes form from the subduction of continental margins. Exhumation of continental UHP terranes has typically been ascribed to positive buoyancy of these dominantly quartzofeldspathic rocks with respect to the mantle, and one of the earliest ideas for the mechanism of exhumation—detachment of a crustal slice (Fig. 1)—held sway for many years. The preservation of metamorphic coesite was originally judged to be so rare that it was assumed that unusual processes were critical to its preservation. This led to the prevailing assumption that UHP terranes had to be exhumed at plate tectonic rates and that exhumation without overprinting is an unusual process.

Challenges to understanding the formation and exhumation processes involved in UHP metamorphism arise because structures formed at mantle depths are commonly overprinted or excised by younger structures. Numerical models help explore possible scenarios because they can predict rock behavior for a range of boundary conditions and forces. Here we review a blossoming of observations and ideas showing that some UHP terranes are large and some are small; some were exhumed at plate tectonic rates and some more slowly; some were exhumed with almost no melting, whereas others were exhumed with vast amounts of melt; and others were never exhumed at all. This variety implies that UHP terranes formed and were exhumed via a wide array of mechanisms, some of which have not yet been imagined.

RAPID SUBDUCTION AND EXHUMATION OF A CONTINENTAL SLIVER: THE REIGNING PARADIGM

The earliest models for UHP tectonism assumed that it occurs during subduction of a continental margin because the metamorphic pressure–temperature (P–T) conditions of UHP rocks are typical of subduction zones and not of overthickened continental collision zones, such as the Tibetan Plateau. A second point in favor of a subduction zone model is that a subduction zone can provide a pathway for conveying crustal rocks back to Earth’s surface without exceeding the moderate temperatures (<800°C) observed in most continental UHP terranes. The need for such cool temperatures to be maintained by either continued, deeper-level subduction refrigeration or rapid, near-adiabatic exhumation has led to the general dominance of a single model. In this model, a relatively thin slice of UHP continental crust becomes detached from the subducting lithosphere at a depth of ~100 km and is rapidly exhumed up the subduction zone during continued convergence (Fig. 1). The requirement to have continental rocks reach mantle depths has led to the assumption that most UHP terranes formed where continental margins were subducted at the end of ocean closure. The presence of UHP rocks in continent collision zones has caused most workers to assume that the upper plate of the subduction zone was continental. The subduction of a continent is assumed to eventually cause the downgoing slab to break off (Davies and von Blanckenburg 1995), triggering a range of specific tectonic processes such as volcanism and uplift. To many observers, this overall paradigm of rapid continental-margin subduction during the early stages of continental collision satisfies most of the geologic constraints teased from UHP occurrences. The dominance of this paradigm has been further solidified by an imaginative and evocative series of analog experiments by Chemenda and coworkers (1995), which demonstrated that large, coherent slices of crust—bounded by a thrust below and a normal fault above—could be exhumed in one piece (Fig. 1). The exhumation of a crustal slice, or the Chemenda model as it has come to be known, remains a popular model for the exhumation of some UHP terranes.
FORMULATION OF UHP TERRANES: NUMERICAL MODELS

Numerical and physical analog models are tools that can be used to understand the formation and exhumation of UHP terranes. These models use estimates of rheology, density, plate-convergence rates, and physical conditions to produce realistic scenarios for a large range of conditions and tectonic settings. Numerical models in particular can portray the changing geodynamic situation over time, and they can follow single rocks from near Earth’s surface to mantle depths and back, tracking their pressure–temperature–time (P–T–t) history.

Forces and Controls

The main forces that operate during the formation and exhumation of UHP rocks—that is, global tectonic forces transmitted by plate motions and local body forces derived from the buoyancy of subducted rocks—are well understood and can be modeled quantitatively (see overviews in Warren et al. 2008; Duretz et al. 2012; Sizova et al. 2012). Tectonic forces are typically responsible for the subduction of UHP-rock precursors, whereas local body forces often (but not always) drive various styles of exhumation. At the most rudimentary level, why UHP continental crust is exhumed to the continental Moho—or to Earth’s surface in oceanic settings—is not difficult to understand: although mafic eclogite is denser than peridotite, eclogite facies continental crust is positively buoyant with respect to the uppermost mantle, and former eclogite facies continental crust is positively buoyant with respect to oceanic crust. Buoyancy is affected by composition and phase transformations (so-called “chemical” buoyancy), pressure, and temperature. Melting is a particularly important type of phase transformation in that whether the melt remains with, or separates from, the solid may significantly change the buoyancy. Body forces are not the only relevant controls on exhumation: surface tractions, pressure gradients, rheology, and local tectonic plate motions also play a role. For both buoyancy and rheology, radiogenic, conductive, and viscous heating may play determinative roles. Transformational weakening—that is, weakening associated with phase transformations—may be especially important to the formation and exhumation of UHP terranes because the large pressure variations and high temperatures accentuate the roles of phase transformations, including melting.

Models of UHP-terrane exhumation are fundamental to constraining exhumation mechanisms. To be most meaningful, such models must produce deformation–pressure–temperature–time–space predictions that can be tested by integrated structural geology, petrology, and geochronology field studies. Characteristic features of interest include the rate of burial and how it varied spatially; magnitudes, distributions, ages, and durations of peak temperatures and pressures and their spatial variations during subduction and exhumation; magnitudes, kinematics, ages, durations, and spatial variations in deformation during subduction and exhumation; types and volumes of igneous activity during subduction and exhumation; and tectonic relationships with respect to surrounding tectonic units, such as lower-pressure rocks and volcanoplutonic arcs.

Numerical thermomechanical models of the exhumation of UHP rocks deal naturally with this testability requirement, although three-dimensionality, high resolution, and self-consistent plate motions remain as challenges. On the other hand, three-dimensional analog models cannot do an adequate job of representing time-dependent changes in temperature, temperature-dependent rheology (including melting), and pressure-induced changes in density. These models are only relevant in situations where the conductive length scale is large and phase transformations are minor.

A Numerical Scenario for the Formation and Exhumation of UHP Rocks

Numerical investigations of UHP-rock formation and exhumation processes are based on conducting systematic calculations that explore the effects of variations in major physical parameters, such as external and internal forces, boundary conditions, plate structures, and rock properties. Based on these experiments, the physical parameters for different UHP formation and exhumation scenarios are defined.

Figure 2 illustrates the results of a numerical investigation that produced exhumation via Chemenda-style, large-scale crustal stacking (Fig. 1). The model (Sizova et al. 2012) simulates subduction of a continental plate following closure of an ocean basin (Fig. 2a). The incoming continental passive margin subducts in a coherent manner, reaching depths of 100–150 km within 5.8 My (Fig. 2a). Buoyancy of the deeply subducted continental crust creates large deviatoric stresses that trigger brittle or plastic failure along the subducted continental Moho. A large, coherent, crustal-scale block of continental crust then separates from the subducting plate and is thrust back over the subducting plate along a major shear zone; the exhumation of the UHP rocks is extremely rapid, occurring within 0.2 My (Fig. 2c). Shortly after, subduction is terminated by slab breakoff in the continental part of the subducting plate at a depth of ~300 km.

To exemplify the P–T–t evolution of subducted crustal rocks during this UHP tectonism, three distinct rock markers within the upper part of the incoming continental crust are traced in Figure 2 with colored squares. The orange marker is located closest to the margin at shallow depth within the sedimentary cover; these sedimentary cover rocks (orange line) are rapidly subducted to diamond-stable depths of >150 km, where they are scraped off the top of the crust, heated by the overlying asthenospheric mantle to temperatures up to 750 °C, and rise rapidly in a relatively thin subduction channel (Fig. 2a). When the first large crustal segment detaches from the slab, it rapidly exhumes these subducted sedimentary rocks to lower-middle crustal levels (Fig. 2c). The green marker, initially located farther from the margin below the sedimentary cover, has a distinctly different evolution. It is part of a small segment of the continental margin that stays attached to the oceanic slab even after the slab breaks; thus, even positively buoyant continental rocks can be recycled into the mantle during subduction. The purple upper-crustal marker is initially located farthest from the margin. This rock reaches coesite-
stable depths but is thermally isolated from the wedge asthenosphere, thus reaching a peak pressure of 3 GPa and a peak temperature of 400°C before being exhumed as part of the first crustal block. This numerical model demonstrates that the P–T–t paths of UHP rocks in the same metamorphic complex may be dramatically different. Consequently, a proper understanding of the geodynamic scenarios that form different UHP complexes requires parallel, mutually informed, and systematic modeling and geologic investigations.

**UHP TERRANES: GEOLOGICAL OBSERVATIONS AND ALTERNATIVE MODELS**

The reigning paradigm (Figs. 1, 2) does seem to provide a reasonable explanation for some UHP terranes—for example, the small UHP terranes exposed in the Kaghan Valley, Pakistan, and at Tso Morari, India. Both of these Himalayan localities consist of chiefly quartzofeldspathic rocks from the leading edge of the Indian plate, are in the footwall of the India–Asia suture, and yet are now being thrust over the downgoing Indian footwall (Massonne and O’Brien 2003), which is still subducting northward. UHP metamorphism at Kaghan and Tso Morari occurred at ~46 Ma, not long after continental collision began at ~55–50 Ma. The UHP rocks were exhumed rapidly to crustal levels at ~44 Ma (Parrish et al. 2006).

**Channel Flow**

An alternative explanation for exhumation of the Himalayan UHP terranes is by ductile return flow in a subduction channel (Fig. 3), as suggested by the numerical models of Warren et al. (2008) and Beaumont et al. (2009). Whether these localities are better explained by exhumation of relatively coherent slabs (Figs. 1, 2) or ductile return flow (Fig. 3) hinges on the internal deformation of the UHP terrane; field study of the Tso Morari and Kaghan UHP terranes could resolve this question. Ductile return flow in a subduction channel is a plausible explanation for many of the smaller UHP terranes.

**“Eduction”**

Another major challenge to the fast-subduction and fast-exhumation aspect of the Chemenda model has arisen with the burgeoning data sets suggesting slow subduction and exhumation of at least two UHP terranes: the Dabie–Sulu of eastern China and the Western Gneiss Region of Norway. Not only did these two UHP terranes apparently undergo slow subduction and exhumation over tens of millions of years, they are also large—tens of kilometers thick and tens of thousands of square kilometers in area (including related HP eclogites). Kylander-Clark et al. (2012) have drawn attention to the possibility that UHP terranes might be divided into two main types: big terranes formed and exhumed slowly and small terranes formed and exhumed quickly.

The Western Gneiss Region (WGR) consists chiefly of orthogneisses of the Baltic craton. The UHP–HP portion of the WGR is inferred to have formed by Silurian subduction of the western edge of the Baltic craton beneath Laurentia, prior to the final stages of the Baltic–Laurentia collision. The preservation of a tectonostratigraphy, the general coherence of peak pressures, and the preservation of pre-UHP structures indicate that this giant UHP terrane was exhumed without strong deformation except in its highest P–T portions (Hacker et al. 2010). An extensive database of dates obtained via a range of methods and isotopic systems indicates that subduction was underway by 425 Ma and ended around 400 Ma, and that exhumation of the deepest rocks to crustal levels was complete no sooner than ~390 Ma (Kylander-Clark 2008). In other words, the entire cycle was much slower than the rapid subduction–exhumation cycle proven for Tso Morari and Kaghan and inherent to the Chemenda-type model.

**FIGURE 2** A numerical model of the formation and exhumation of UHP rocks during continent–continent collision (after Sizova et al. 2012). Cross sections (colors same as in Figure 1, except as noted) show that 5.8 My after the beginning of continent subduction (B), a relatively coherent block of continental crust abruptly detaches from the downgoing slab and rises to crustal levels in <1 My (C). P–T diagrams show that UHP rocks with dramatically different P–T paths are juxtaposed by the end of the orogeny. Colored squares link P–T conditions to the corresponding positions in the cross sections. The continental crust is divided into upper and lower parts. See text for further explanation. UHPM = ultrahigh-pressure metamorphism.

**FIGURE 3** A numerical model of the formation and exhumation of UHP rocks in a subduction channel about 7 My after the beginning of continental subduction. Thickening of the subduction channel leads to instability, and a slice of UHP continental crust detaches from the downgoing slab and rises as a strongly deformed plume to crustal levels in ~1 My. After Beaumont et al. (2009). Colors as in previous figures.
How the Western Gneiss Region was subducted and exhumed slowly and with relatively little internal deformation remains a mystery because slow isothermal processes demand large conductive length scales. The inability to identify a contractional structure carrying the WGR eastward over the Baltic foreland led Andersen et al. (1991) to propose one of the first alternatives to the Chemenda model: wholesale extraction of the Baltic crust from beneath Laurentia by reversal of relative motion between the two plates (Fig. 4). Andersen and coauthors applied the term *eduction* to this process. Numerical models show that eduction is feasible once the subducted slab has failed by necking (Duret et al. 2012). Other workers in the WGR have long maintained that contractional structures placed the UHP–HP rocks over lower-pressure rocks (Tucker et al. 2004), which would invalidate a pure eduction model. Assessing whether such a basal thrust exists in the Scandinavian Caledonides will allow differentiation between these exhumation hypotheses.

The Dabie–Sulu terrane is dominated by crustal rock inferred from its isotopic signatures and tectonostratigraphy to represent the northern margin of the South China Block (Liou et al. 2012). It is thought to have formed by northward Permo-Triassic subduction beneath the North China Block. Like the WGR, an extensive database of dates indicates that subduction was underway by 245 Ma and that exhumation of the deepest rocks to crustal levels was complete no sooner than ~220 Ma (Hacker et al. 2000). The specific exhumation mechanism of this giant UHP terrane is obscured by significant Jurassic–Cretaceous igneous and structural reworking (Ratschbacher et al. 2000). An along-strike gradient in peak pressures and a differential orientation of retrograde stretching lineations suggest rotation of the UHP–HP terrane during exhumation from mantle depths, but crustal-slice models have been suggested as well. The degree of internal deformation was sufficient to form kilometer-scale folds but not so severe as to destroy a presubduction tectonostratigraphy or delicate, local igneous textures (Schmid et al. 2003). Limited exposures and strong deformation within the foreland south of the orogen preclude assessing whether the UHP–HP rocks were extruded over the foreland or whether the entire lower plate was extracted by eduction.

**Trans-mantle Diapirs**

An enigmatic and intriguing small UHP terrane is exposed in a series of eclogite-bearing gneiss domes in the D’Entrecasteaux Islands of Papua New Guinea (PNG) (Baldwin et al. 2008). The enigmatic nature of this terrane stems from the fact that the UHP eclogite formed at ~8 Ma, and yet the most recent subduction event in the region was the subduction of the Australia–New Guinea continental margin at 35–30 Ma. Possible solutions to this conundrum include subduction of the protolith shortly before 8 Ma along an unknown subduction zone that is not currently active, or subduction of the protolith at ~30 Ma and transformation to eclogite at ~8 Ma (Little et al. 2011).

Zircon U–Pb data indicate that the gneiss was derived chiefly from Cretaceous or younger rock (Zirakparvar et al. 2013), but whether that material was seafloor sediment or Australian-margin sedimentary rock is unclear. The PNG terrane might also be the best-known example of UHP rocks formed by subduction beneath an oceanic hanging wall, perhaps similar to the modern-day subduction of the Australian plate beneath the Banda arc. The PNG terrane is unusual in one other respect: it is composed of ~30–40% plutonic rocks that formed during exhumation-related melting at 3.5–2.5 Ma (Gordon et al. 2012). The combination of a >20 My gap between the last-known subduction event and the eclogite date, and the presence of extensive exhumation-related 3.5–2.5 Ma plutonic rocks has led to the suggestion that the PNG terrane may have been exhumed through the mantle as a diapir (Fig. 5) (Little et al. 2011).

The idea that UHP terranes might be exhumed as aggregates of diapirs (Fig. 5) that rose through the mantle was originally suggested for the UHP rocks of the Alps (Gerya and Stöckhert 2006). The idea may seem outrageous at first blush, but Currie et al. (2007) and Yin et al. (2007) have shown that subducted crustal rocks may rise diapirically through the mantle wedge without melting or being assimilated into the wedge. Sediment subduction is ongoing beneath arcs around the world (Clift and Vannucchi 2004; Scholl and von Huene 2007), and while these authors suggested that most of this crustal material is recycled in the mantle, it is equally likely that much of this material may reaminate the base of the upper plate, perhaps after undergoing significant changes in chemical and physical properties (Hacker et al. 2011). If the D’Entrecasteaux Islands terrane was derived from seafloor sediment, it could perhaps represent the first recognized occurrence of large-scale continental relamination, now exhumed.

**UHP Metamorphism in the Overriding Plate**

Not all UHP terranes need be derived from the subducting slab. Most active subduction zones are erosional (Scholl and von Huene 2007), meaning that pieces of the overriding plate are being plucked from the hanging wall and subducted to unknown depth. Xenoliths of Asian crust erupted in the southern Pamir from near-UHP mantle depths may be direct evidence of tectonic erosion of Asia by the downgoing Indian plate (Hacker et al. 2005). Wholesale subduction and UHP metamorphism of the overriding plate is also possible. Intracontinental subduction is a plausible explanation for the UHP terrane in North-East Greenland (Gilotti and McClelland 2011), where Laurentian crust in...
the overriding plate of the Caledonides experienced UHP metamorphism late in the collision and far from the suture with Baltica, in a setting not unlike the Tibetan Plateau today. Deep subduction of material from the overriding plate demonstrates that HP and UHP rocks alone are not conclusive evidence for the polarity of subduction.

**FUTURE WORK**

The diversity of observations from UHP terranes has led to the realization that there must have been a variety of processes of formation and exhumation, and attempts have been made to address these differences through geodynamic modeling. The diversity of models of UHP terranes has expanded the range of formation and exhumation scenarios being tested through field geology.

For the future, we see the following tasks as exciting and relevant: (1) Understanding why there are so many Phanerozoic UHP terranes, but few older. (2) Producing geodynamic models that replicate as closely as possible the geologic data from well-studied UHP terranes (for example, the very long timescales for subduction and exhumation of the giant UHP terranes). (3) Acquiring field and laboratory data that test the predictions of the latest geodynamic models. (4) Imaging actively exhumin UHP terranes (e.g. PNG). (5) Identifying more UHP material that originated in the overriding plate. (6) Assessing the fluxes of continental material returned to the mantle, exhumed to Earth’s surface, and remobilized to the base of continents.

**ACKNOWLEDGMENTS**

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**REFERENCES**


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Innovation with Integrity
MORASKO: THE LARGEST IRON METEORITE SHOWER IN CENTRAL EUROPE*

The Morasko meteorite, discovered in 1914, is one of the most famous iron meteorites (IAB-MG). It is well known for its large strewn field and its particular chemical composition and mineralogy. It attracts much attention from scientists, a growing number of meteorite collectors, and the general public. During the last two decades, many new finds of Morasko have been reported, inspiring new scientific investigations. The recent state of knowledge of the Morasko iron is outlined in the monograph Morasko: The Largest Meteorite Shower in Central Europe, edited by A. Muszyński, R. Kryza, Ł. Karwowski, A.S. Pilski, and J. Muszyńska, and coauthored by P. Drożdżewski, M. Dworzyńska, A. Gurdziel, K. Helios, R. Jakiela, M. Nowak, A. Pack, M. Raith, E. Słaby, and W. Stankowski. The monograph, nicely produced by Bogucki Wydawnictwo Naukowe, Poznań, is an overview of recent studies carried out as part of a research project of the Ministry of Science and Higher Education of Poland: Morasko, Przełęcy, Jankowo Dolne – a meteorite shower, NN 307 3533/33, 2007-2012. The project was carried out by a team of scientists from several Polish and foreign scientific institutions and was coordinated by Andrzej Muszyński of Adam Mickiewicz University, Poznań.

The book does not present systematically all detailed results of recent investigations of Morasko published as extensive research papers. Rather, it presents, in an easily read format, the most important achievements and interpretations of recent studies that have been (or are being prepared to be) published as separate, regular papers.

The first two chapters of the monograph, the Introduction and Historical Notes, provide interesting details about the discovery of Morasko and the three similar, and probably related, irons of Przełęcy (Seelaßen), Jankowo Dolne, and Tabarz (Fig. 1). Chapter 3, Iron Meteorite Shower Morasko, Przełęcy, Jankowo Dolne, outlines the geological setting and provides field observations on the Morasko craters and the reconstructed strewn field. It also reviews ideas concerning the fall, including the favored hypothesis of a single, large iron meteorite shower. The following four chapters summarize the geochemistry, petrology, mineralogy, and Raman spectroscopy and isotopic data on Morasko and the paired irons. Two additional chapters are devoted to micrometeorites and weathering of the meteorites. Chapter 30 is a short report on recent meteorite prospecting and new discoveries in the Morasko meteorite reserve. The monograph is completed by an extensive photo gallery, which documents historical and recent finds of the Morasko, Przełęcy, and Jankowo Dolne irons, as well as meteorite prospecting and technical works.

Several important conclusions can be derived from the new data overviewed in the Morasko monograph:

1. Morasko and the similar irons of Przełęcy, Jankowo Dolne, and possibly Tabarz represent a single, large meteorite shower (the total mass of all finds is estimated at over 1500 kg) that occurred at around 5000 BP. These conclusions are based on the size and shape of the strewn field ellipse, field evidence, petrology, mineralogy, chemistry, and geochronological data.

2. Morasko and the paired irons show unique chemical features, for example, low Ir and Cu concentrations; these features assign them to a special group within the IAB-MG irons. They also have an extraordinary mineralogy; in particular, frequent graphite–troilite nodules; these contain many accessory minerals, such as rare phosphates, a few of which display compositions that have not yet been reported either from the Earth or from extraterrestrial rocks.

The monograph was printed soon after the discovery of the new main mass of Morasko (Fig. 2; see Elements, volume 9, 2013, page 152) by meteorite prospectors Magda Skirzewska and Łukasz Smuła on October 8, 2012. The excavation works were coordinated by Andrzej Muszyński and assisted by Pierre Rochette and a group of Polish scientists and meteorite hunters. This mass, named Memorss (from Meteorite Morasko), is an oriented meteorite, 261.2 kg in weight after cleaning, and the largest meteorite ever found in Poland (and, apparently, the fourth-largest iron in Europe).

The new record find and several other large masses discovered in the past decade have increased the general public’s interest in meteoritics. Many reports have been published in the mass media, and two films have been produced by the film studio of AMU Poznań and one as part of the series Meteorite Men of Discovery Science (Steve Arnold and Geoffrey Notkin). The Morasko research team received an award from National Geographic Traveler as the scientific discovery of the year 2012 in Poland.

The Morasko monograph has been technically edited with care. The text is presented in two parallel columns, in Polish and English. Many high-quality photographs and diagrams provide valuable documentation of the meteorites. Specific scientific points are explained in special boxes inserted into the main text. These editorial features should make reading the book easy and pleasurable. The book will appeal to all those interested in meteorites, but especially to meteorite collectors. It will also be useful to scientists working on meteorites, although to get more detailed data from recent studies on the Morasko iron shower, they would need to access regular research papers.

Stanisław Lorenc

Adam Mickiewicz University, Poznań


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**Figure 1** Location of the Morasko and paired irons in Central Europe (modified after Czajka 2005)

**Figure 2** The new main mass of Morasko: Memorss meteorite, 261.2 kg (21 × 30 cm), found on October 8, 2012
PRESIDENT’S LETTER

American Mineralogist and the Mineralogical Society of America

Although the Mineralogical Society of America is involved in many activities, the Society is perhaps best known for its publications in the fields of mineralogy, crystallography, petrology, and geochemistry. At the recent spring Council meeting, various aspects of the MSA publishing enterprise were discussed in detail, including changes in the editorship of American Mineralogist; those discussions allow me to highlight the Society’s journal.

The most visible activity of the Society is certainly the publication of American Mineralogist, which began in 1916. The journal has been published continuously for nearly a century, under the guiding hands of many able editors and associate editors and an outstanding professional editorial office. The editorship model has evolved from that of a single editor to three editors, and a call was made earlier this year for a replacement for one of the current editors. Although we received expressions of interest from several excellent candidates, Council decided to reduce the number of editors from three to two, reverting to an earlier model. Thus the new structure will consist of one editor (Keith Putirka, California State University, Fresno) who will handle all regular submissions to the journal and a second editor (Ian Swainson, National Research Council of Canada, Ontario) who will be responsible for all letters to the journal. I am very grateful to them for selflessly contributing their time. They will, of course, be aided by a large staff of outstanding associate editors, who carry much of the responsibility for the scientific content of the journal. They will also be helped by the members of our editorial office, based at the Society offices in Chantilly and led by Managing Editor Rachel Russell. We are fortunate to have such a talented team working to create the journal. The current editorial staff is making many positive changes to the journal, and I urge you to keep an eye out for those changes. One change that I believe is very positive is the request to all authors to conclude their submissions with a summary of its implications.

Since the American Mineralogist was first published in 1916, it has risen to preeminence in the discipline. Today, the journal is ranked #3 in “journal influence” in the field of mineralogy by Journal-ranking.com (interestingly, the Society’s RIMG volumes are #2), and it is in the top 10% of all journals in the Earth and planetary sciences for total citations. American Mineralogist abstracts receive over 350,000 hits per year, attesting to their relevancy and impact.

I am pleased to have on my bookshelves every number of every issue of American Mineralogist ever published, at least until January 2013. This year I decided to subscribe to the journal electronically, but I find I miss receiving the paper copy. So I will be resubscribing in order to receive the back issues of the paper version and complete my collection of issues from 1916 to 2013; my collection will eventually be donated to the Society.

I urge you all to consider submitting your best work to the Society’s journal as it approaches its centennial. Plans are already underway to celebrate the journal’s milestone.

John M. Hughes (jm Hughes@uvm.edu)
2013 MSA President

NOTES FROM CHANTILLY

- At its meeting in May, MSA Council voted to increase the 2014 dues for regular and student members by $10 per year, to $80 and $20, respectively. Dues were last increased by $5 to $70 for regular members in 2011 for 2012. Student dues were last increased in 2006 from $5 to $10. As a compensating benefit for these increases, which are necessary to meet the rising cost of society operations, all members will be given electronic access to the American Mineralogist. This will also allow all members easy access to the journal and thus to see the changes that the editors are making. Senior fellow and member dues are $0. Sustaining membership will remain at $150 + regular dues.

- Member subscription rates to the print version of the 2014 American Mineralogist will differentiate between domestic and foreign destinations to reflect mailing costs and to share with institutional subscribers the cost of producing print copies. The US member subscription price (paper and electronic) will be $105 (currently $100), and the foreign member subscription price will be set at $115 (currently $110). Member electronic-only subscriptions will be included as part of the dues and no longer sold separately. The US institutional price (paper and electronic) will increase to $1000 (from $975), and foreign institutional subscriptions will be raised to $1025 (from $1000). Institutional electronic-only subscriptions will remain at $900. These prices represent increases of 3–5%. Included with the institutional subscription are all the current-year issues of Reviews in Mineralogy and Geochemistry, Elements, and access to the electronic journal on the MSA website. GeoScienceWorld institutional subscriber prices for archival print copies of American Mineralogist and the Reviews remain at $150 and $125, respectively.

- MSA 2013 membership renewals will start by October. Membership renewal notices will be sent electronically, followed by electronic reminders; a paper copy will be sent to those who do not renew online by the end of October.

- Members and Fellows who are in the senior, honorary, and life categories are sent renewal notices. They need not pay dues, but they are sent notices as the best way to prompt an update of membership information, particularly mail and e-mail addresses.

- If you subscribe to other journals through MSA—Gems & Gemology, Journal of Petrology, Mineral News, Physics and Chemistry of Minerals, or Rocks & Minerals—please renew early. MSA needs to forward your renewal to the respective publishers before your subscription runs out.

- An agreement was signed by Springer and MSA for MSA members to subscribe to Mineralogy and Petrology at a reduced rate of $60 for the print and electronic edition and $20 for the electronic edition starting with the 2014 volume. If interested, you can subscribe when renewing for 2014.

- The plan to domesticate the MSA Corporation to Virginia and the restated MSA Articles of Incorporation and Bylaws were overwhelmingly passed by the members in the February balloting. The District Government granted MSA a Certificate of Domestication, and an application to domesticate has been filed with Virginia.

- MSA’s ninety-fourth Annual Meeting will be held in Denver, Colorado, USA, on 27–30 October 2013. The MSA Awards Banquet will be on Tuesday, 29 October, when the Roebling Medal will be presented to Frank C. Hawthorne, the MSA Award to Wendy Li-Wen Mao, and the Distinguished Public Service Medal to Pierrette Tremblay. The 2012–2013 MSA Distinguished Lecturers will also be recognized: Julia A. Baldwin, Matthew J. Kohn, and Hans-Peter Schertl. The MSA awards lectures, annual business meeting, and presidential address will be on Tuesday, 29 October, at the Denver Convention Center. Frank C. Hawthorne will give the Roebling Lecture: “Toward a Theoretical Basis for Mineralogy”; Wendy Li-Wen Mao will give the MSA Award Lecture: “Space, Energy, Time: A Closer Look at Minerals at Extreme Conditions”; and John M. Hughes will follow with his MSA Presidential Address: “The Many Facets of Apatite.” The MSA/GS/MGFPV Joint Reception will follow, from 5:45 to 7:30 pm.

J. Alex Speer (jaspeer@minsocam.org)
MSA Executive Director
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, 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 wish to consider contributing at the next opportunity. Here we want to extend our gratitude to the individuals and organizations that have made contributions to MSA between 1 July 2012 and 30 June 2013. These contributors are listed on the MSA website and can be found by selecting “Contributions to MSA” on the MSA home page (www.minsocam.org), under “The Society.”

Geochemistry of Geologic CO₂ Sequestration
7–8 December 2013 (prior to 2013 Fall AGU)
Berkeley, California, USA

Convenors
Donald J. DePaolo, Lawrence Berkeley National Laboratory
David R. Cole, The Ohio State University
Alexandra Navrotsky, University of California-Davis
Ian C. Bourg, Lawrence Berkeley National Laboratory

Geological formations, such as oil and gas fields, coal beds, and brine aquifers, are likely to provide the first large-scale opportunity for testing the geological sequestration of CO₂, with the goal of developing a method to moderate the rapid increase in the concentration of atmospheric CO₂ and mitigate global warming. The geochemical and mineralogical processes encountered in the subsurface during storage of CO₂ will play an important role in facilitating the isolation of anthropogenic CO₂ in the subsurface. This timely course will be a discussion of the underlying geochemical and mineralogical processes associated with gas–water–mineral interactions encountered during sequestration of CO₂. It will consider the nature of fluid properties and the chemical, thermal, mechanical, and biological interactions between fluids and the surrounding geologic formations over broad ranges of temperature, pressure, fluid composition, and spatial and temporal scales to determine how the subsurface will perform as a storage container, both rapidly as the stored material is emplaced underground and gradually over hundreds to thousands of years.

Information and registration: www.minsocam.org

MINERALOGICAL SOCIETY OF AMERICA AND GEOCHEMICAL SOCIETY
SHORT COURSE ANNOUNCEMENTS

MINERALOGICAL SOCIETY OF AMERICA AND GEOCHEMICAL SOCIETY
DEEP EARTH PUBLICATIONS

2013–2014 MSA DISTINGUISHED LECTURERS

The Mineralogical Society of America is pleased to announce its Distinguished Lecturers and their lecture titles for 2013–2014:
Nita Sahai, Department of Polymer Science, University of Akron, Akron, Ohio, USA. (1) “Silicate Mineral Implants Direct Stem Cells to Promote New Bone Formation” and (2) “Did Mineral Surface Chemistry Drive Evolution of Bacterial Extracellular Polymeric Substances?”
Richard Wirth, Helmholtz Centre Potsdam, GFZ German Research Centre for Geosciences, Potsdam, Germany. (1) “Nanoinclusions in Minerals and Rocks: Small Particles Tell Big Stories” and (2) “FIB-TEM: Exploring Earth Materials with Ions and Electrons.”

For more description, tables of contents, and online ordering of these books, visit www.minsocam.org or contact Mineralogical Society of America, 3635 Concorde Pkwy Ste 500, Chantilly, VA 20151-1110, USA; phone: +1 (703) 9950 • fax: +1 (703) 652-9951 • e-mail: business@minsocam.org

IN MEMORIAM

Donald A. Brust – senior fellow 1950
PRESIDENT’S CORNER

Geochemical Cooperation

This issue of Elements arrives near the time of the Goldschmidt Conference. For the Florence conference, the European Association of Geochemistry (EAG) marshaled a large number of people who spent countless hours developing a scientific program that will have attracted about 4000 attendees and organized the program so that participants could see all they wanted under the most pleasant conditions possible. Our thanks go out to the many volunteers who contributed to make the meeting a success. Next year, the Geochemical Society (GS) will return the favor, inviting all geochemists to attend the California Goldschmidt Conference from June 8 to 13. Along with the major effort and attention to detail provided by Cambridge Publications, the professional meeting organizer for Goldschmidt Conferences, making the Goldschmidt Conference a reality involves a very large amount of mostly volunteer labor. Volunteers and cooperation between professional societies is critical to a number of activities undertaken by the GS to help unite the geochemistry community and promote the field of geochemistry. Elements involves 17 participating societies (each with a member on the Executive Committee), 4 editors, and an advisory board of 20 members. Geochimica et Cosmochimica Acta relies on 92 volunteer associate editors and advice from the 6-member Joint Publications Committee appointed by the Geochemical Society and the Meteoritical Society, in addition to the dedicated services of Executive Editor Marc Norman and the publisher, Elsevier.

I could go on, but the point I’m trying to make is that support of the field of geochemistry involves a good deal of cooperation. Building working, cooperative agreements is a delicate process, whose goal is to expand the benefits to each cooperating society without imposing restrictions on its ability to follow new pursuits. The GS partners with EAG through the Goldschmidt Forum to oversee Goldschmidt Conference management, the Meteoritical Society through the Joint Publications Committee to assist with GCA, and the Mineralogical Society of America (MSA) to decide on topics for the Reviews in Mineralogy and Geochemistry book series published by MSA. The GS is working to build more such cooperative efforts, for example, with the Geochemical Society of Japan, who will help host the 2016 Goldschmidt Conference in Yokohama. The GS also is seeking to strengthen and extend its long-running relationship with the American Geophysical Union (AGU) to provide member benefits, such as an enhanced geochemical presence at the AGU Fall meeting and particularly the Meeting of the Americas, the latter to better engage our South American colleagues. You may have noticed that links to new papers appearing in the AGU journal G-cubed are now listed in the GS’s weekly newsletter, Geochemical News.

Seeking and expanding such collaborative efforts is an important and ongoing task for the GS. Through these collaborations, we hope to be able to provide to the GS membership access to, and knowledge of, the geochemically relevant activities of other professional geoscience organizations and thereby expand the influence, impact, and interest in geochemistry in the broad international geoscience and planetary science community.

Richard Carlson, GS President

THANK YOU VOLUNTEERS!

What we do at GS day after day to deliver on our mission to impact the direction of geochemistry at a global level is only possible through the Herculean efforts of our volunteers. Thank you! The following volunteers completed terms at the end of June 2013; an asterisk denotes committee chair. Visit www.geochemsoc.org/society/committeesandpersonnel/ for full committee rosters.

2013 Program Committee
Elizabeth Cottrell* (National Museum of Natural History, USA)
Jeff Vervoort (Washington State University, USA)

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2014 AWARD NOMINATIONS

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

Make a nomination at www.geochemsoc.org/awards/makeanomination.htm

DEADLINE: OCTOBER 15, 2013

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I warmly invite you and other geoscientists from around the world to attend the 24th V. M. Goldschmidt Conference, to be held June 8-14, 2014 in Sacramento, California. Sacramento is the Capital of the “Golden State” of California, so named both for the weather and for the gold deposits discovered in the mid-nineteenth century only 75 km from Sacramento. Nestled at the confluence of the Sacramento and American Rivers, the city is a gateway to many of California’s natural wonders including majestic Yosemite National Park in the Sierra Nevada Batholith. The abundance of diverse geological features nearby, from ophiolites to batholiths to arc volcanoes to the classic Franciscan subduction complex, as well as mining activity and its environmental legacies, presents outstanding opportunities for field trips which will be a hallmark of the conference. Also nearby are the renowned Napa Valley, Sonoma Valley and Sierra Foothills wine regions and myriad other opportunities for cultural excursions. This venue offers excellent options for combining a high-level conference with a family vacation.

As the capital of a state with the world’s ninth largest economy and significant production of agricultural and natural resources, Sacramento is a nexus of activity in these areas. The venue is thus uniquely opportune for topics such as energy, resources and environment wherein policy needs to be informed by science. As at previous Goldschmidt conferences, societally relevant topics such as these will be combined with the latest developments in all areas of geochemistry, cosmochemistry, and related fields. A Science Program comprising 25 themes has been developed by the International Program Committee, and can be viewed on the conference website goldschmidt.info/2014. A call for additional session suggestions is planned to be open on this website between September 15 and October 31, 2013. Please make sure to submit your abstract by February 1 and plan to join us in California next summer.

I look forward to welcoming you to Goldschmidt 2014!

Paul Renne, President, Local Organizing Committee, 24th V. M. Goldschmidt Conference
THE SHAPE OF THINGS TO COME – HORIZON 2020

The European Union’s 7th Framework funding programme (FP7) is at an end – long live Horizon 2020! This new programme is the 80-billion-euro successor to FP7, which will start in January 2014 and run until 2020. Details of H2020 are now widely available, and although many of the funding programmes, such as ERC grants and Marie Curie Actions (now Marie Skłodowska-Curie Actions) will be very similar, there are notable changes in structure and strategy, in addition to a simpler and less bureaucratic implementation. One major strategy change will be the opening up of international collaboration by including countries that are not EU members or associated states. Here we examine some of these changes and put the new strategies into perspective by examining a collaborative project from the end of FP7 with many of the characteristics that the EU will be looking for in the future.

The EU sets out clear goals for its new research and innovation programme. This new programme will respond to the economic crisis through investment in growth-building research and development (R&D), will address societal concerns in health and the environment, and will strengthen the EU’s global position in research and innovation. Many of the measures in H2020 are aimed at strengthening the EU’s highly valued small- and medium-sized enterprises (SMEs) – small companies responsible for much of Europe’s R&D-driven growth. The EU has listened and learned from FP7, and is playing to its strengths.

Rather than the 4 programmes of FP7, H2020 will have just 3 main sections: (1) Excellent Science, with funding of around 24 billion euros (€), comprises Marie Skłodowska-Curie training and mobility actions, improvement of research infrastructures, a new action on future and emerging technologies, and the European Research Council (ERC), which will receive over half the funds; (2) Industrial Leadership, with 18 G€, will invest in innovation in SMEs and attract more private investment into R&D; and (3) Societal Challenges, with 31 G€, will fund research addressing concerns such as health, food security and climate change. Research in health and food security, as well as in energy and (smart, green) transport, will account for most of these funds; however, 3 G€ are earmarked for research into climate change and resources.

Perhaps one of the biggest changes with respect to FP7 is that non-European countries will be able to take part in many actions. Such international cooperation was already worked into specific funding calls of FP7, but in H2020 the aim is to broaden this to include international collaboration across a range of programmes. The target here is not to integrate European cooperation into the research landscape of established economies, like those of the US or Japan, but rather into countries such as the BRICS nations – Brazil, Russia, India, China and South Africa – which account for a rapidly increasing share of the world’s R&D expenditures.

Many of the continuing funding initiatives that will now come under the Excellent Science programme have become key features of European research over the years. The H2020 boost in funding for the ERC, for example, recognizes how well received and regarded this programme has become. But with such a large chunk of the budget going into research on societal challenges and with a general emphasis on international cooperation, it is important to consider what shape geochemical projects in this programme might take.

One project recently funded under the International Collaboration action of the FP7 Capacities programme ticks many of the boxes that H2020 reviewing panels might be considering in the future.

CLIM-AMAZON is a joint European–Brazilian cooperation termed Amazon, Climate Change and Geochemistry. The Amazon basin is almost the size of Europe, and it supplies more than 15% of the total freshwater input to the world’s oceans. It is well recognised that deforestation, agriculture, mining and urbanization have put the region under anthropogenic stress, affecting, for example, regional climate, CO₂ balance, biodiversity, river discharge and sediment load. The damage has been hard to assess, however, as access to the region for detailed scientific research has in the past been difficult. CLIM-AMAZON is designed to provide access to one of the world’s largest and most delicate fields. The principal goal is to jointly investigate global transport and sedimentation processes in the Amazon basin, which plays a key role in global climate regulation and sediment supply to the Atlantic Ocean. In addition to Fundação Universidade de Brasilia, the consortium includes research groups from France, Germany, the UK and the Netherlands.

Research goals call on key expertise from the participating groups. A team from Royal NIOZ Texel (Netherlands) will assess the paleohydrological and palaeotemperature changes in the Amazon River using lipid biomarkers. Scientists from the University of Amsterdam will perform an integrated palynological study to gain new insights into the evolution of the Amazon drainage basin and its effects on algal blooms along the Brazilian Atlantic coast. Researchers from Imperial College London (UK) will test present and past atmospheric transport and deposition of mineral dust, particulate matter and trace elements in the Amazon basin, and they will estimate the implications for climate change and anthropogenic forcing. A team from the GeoForschungsZentrum Potsdam (Germany) will estimate changes in sediment loads during the past 5 million years in the lower Amazon basin using the cosmogenic isotopes ⁰⁹Be and ⁰⁸⁶Al. A research group from Jacobs University Bremen (Germany) will investigate the distribution and behaviour of high-technology metals, such as rare earth elements, yttrium, zirconium and tantalum, in large sediment particles, nanoparticles and waters from the Amazon River and its major tributaries.

Geochemistry is of course a broad discipline, which is reflected in the diverse interests of EAG members. However, it is a key field in the understanding and potential resolution of many societal challenges, such as global warming, water scarcity, pollution, energy shortages and mineral resources. Horizon 2020 should, therefore, be full of important opportunities for the geochemical community.

For more information on CLIM-AMAZON, go to www.clim-amazon.eu or contact Michael Bau (m.bau@jacobs-university.de) or Lucieth Vieira (lucieth@gmail.com).

Michael Bau (Jacobs University Bremen) and Daniel Frost (University of Bayreuth)
The EAG invites nominations for the Urey Award, the Houtermans Award, the Science Innovation Award and the GS/EAG Geochemical Fellows Award. Your nomination can make a difference by ensuring the recognition of deserving scientists from all generations. Below is a short description of these awards. The nomination process is simple.

The **Urey Award** recognizes outstanding contributions advancing geochemistry over a career.

The **Houtermans Award** is given to a scientist no more than 35 years old or within 6 years of their PhD for a single exceptional contribution to geochemistry, published as a single paper or as a series of papers on a single topic.

The **Science Innovation Award** subject area differs every year according to a five-year cycle. In 2013, the award will be named in honour of Samuel Epstein for his work in isotope geochemistry. This award is conferred for important and innovative breakthroughs in geochemistry, and the recipient must be between 35 and 55 years of age.

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

Please submit your nominations **before 15 October 2013** for the GS/EAG Geochemical Fellows Award and **before 15 November 2013** for all other awards. The web page [www.eag.eu.com/awards/nomination/](http://www.eag.eu.com/awards/nomination/) provides details.

### DISTINGUISHED LECTURE TOUR 2013

The third edition of the EAG Distinguished Lecture tour will take Thomas Röckmann (Utrecht University, Netherlands), a leading specialist in the development and application of isotope techniques to atmospheric research, to three institutions in Eastern Europe:

- Institute of Geography and Earth Sciences, Eotvos University, Budapest, Hungary (25 November)
- Faculty of Environmental Science and Engineering, Babes-Bolyai University of Cluj-Napoca, Romania (27 November)
- Faculty of Physics and Applied Computer Science, University of Science and Technology, Kraków, Poland (29 November)

Thomas Röckmann, whose research covers a wide field of applications using isotopes (e.g. global trace-gas budgets, detailed kinetic isotope effects, impact of anthropogenic activities on the atmosphere or stratosphere–troposphere exchange, will present the following lectures:

- “Oxygen isotope anomalies in the atmosphere”
- “Reconstructing changes in atmospheric trace gases in the industrial era from isotope measurements on air extracted from polar firm”
- “The isotopic composition of long-lived trace gases in the stratosphere”

Details are available at [www.eag.eu.com/education/dlp](http://www.eag.eu.com/education/dlp), and videos of the lectures will be made available after the tour.

### JOURNAL OF MINERALOGICAL AND PETROLOGICAL SCIENCES

Vol. 108, no. 2, April 2013

**ORIGINAL ARTICLES**

**Steady-state luminescence measurement for qualitative identification of rare earth ions in minerals** Maria Barbara CZAJA, Sabina BODYL-GAJOWSKA, and Zbigniew MAZURAK

Petrology, geochemistry, and origin of metamorphosed mafic rocks of the Trans Vietnam Orogenic Belt, Southeast Asia Kazuhiro YONEMURA, Yasuhiro OSANAI, Nobuhiro NAKANO, Masaaki OWADA, and Sotaro BABA

Texture of lutecite Toshiro NAGASE, Koichi MOMMA, Takahiro KURIBAYASHI, and Masahiko TANAKA

**LETTERS**

Makovickyite and cupromakovickite from the Obari mine, Yamagata Prefecture, Japan Yuya IZUMINO, Kazuo NAKASHIMA, and Mariko NAGASHIMA

Water molecules in the channel-like cavities of osmiumite Nozomi SOGAWA, Keiji SHINODA, and Norimasa SHIMOBAYASHI

Namibite and hechtsbergite from the Nagata mine, Fukuoka Prefecture, Japan Seicho UEHARA and Yohei SHIROSE

The structure of hydrated copper-silicate gels, an analogue compound for natural chrysocolla Tsuyoshi HARIU, Hiroshi ARIMA, and Kazumasa SUGIYAMA

Talmessite from the Uriya deposit at the Kiura mining area, Oita Prefecture, Japan Masayuki OHNISHI, Norimasa SHIMOBAYASHI, Shigetomo KISHI, Mitsuo TANABE, and Shoichi KOBAYASHI

The Japan Geoscience Union (JpGU) 2013 annual meeting was held from May 19 to 24, 2013, at Makuhari Messe, Chiba, Japan. The meeting featured more than 40 international sessions, and many non-Japanese researchers attended the events.

Atsushi Kamei, associate professor at Shimane University, Japan, staffing the JAMS booth at the 2013 JpGU annual meeting, with a poster of *Elements* and back issues stacked in a rack.

The Japan Association of Mineralogical Sciences (JAMS) installed a booth at the venue to exhibit our journals—*Journal of Mineralogical and Petrological Sciences* and *Ganseki Koubutsu Kagaku*—as well as books authored by our members. In addition, some back issues of *Elements* were also exhibited. All copies of *Elements* were soon distributed among the participants, demonstrating the popularity and strong public interest in the magazine. We welcome your participation in the JpGU Meeting 2014, which will be held in Yokohama (April 28–May 2, 2014).
IAGC AWARDS FOR 2013

The International Association of GeoChemistry is pleased to announce its award winners for 2013. Congratulations to all the recipients, and thank you for your service to the IAGC and the geochemical community!

Distinguished Service Award – Ron Fuge, University of Aberystwyth (UK)

IAGC member Dr. Ron Fuge receives the Distinguished Service Award for excellence and dedication as executive editor of the IAGC’s journal, Applied Geochemistry, from 1994 to 2012. During these 19 years, Ron exhibited total dedication and selflessness in carrying out this responsibility. As a consequence, the journal has flourished under Ron’s leadership and editorial excellence. The annual number of published papers has increased steadily during his tenure, and the journal’s impact factor has risen continually throughout the past decade, so that today Applied Geochemistry is held in high regard by the geochemistry community.

IAGC Fellow – Heinrich Wänke, Max Planck Institute, Mainz (Germany)

The first IAGC Fellow distinction for 2013 has been awarded to IAGC’s Past President Heinrich Wänke for outstanding research contributions in applying the principles and techniques of geochemistry to the study of the extraterrestrial domain. Prof. Wänke is a prominent German geochemist who pioneered the application of the tools and approaches of geochemistry to the study of the formation history of the Solar System and its inner planets. As documented in more than 200 research publications, he has applied geochemistry to the analysis of samples of Solar System objects, producing diagnostic tools for the geochemical study of meteorites. These studies have led to a better understanding of the history of irradiation processes and cosmic rays in the Solar System and to the determination of important constraints on the identification of the parent bodies of meteorites. His research has also contributed to the understanding of the formation of the Moon and the accretionary history of the terrestrial planets. Through his personal work and as director of the Cosmochemistry Division of the Max Planck Institute for Chemistry in Mainz from 1967 to 1996, he made major contributions to the development of geochemical techniques for the in situ analysis of planetary surfaces, especially the surface of Mars, via space missions. He also played a major role in the development and implementation of the European planetary exploration program at ESA. Prof. Wänke is a member of the Academia Europaea and the International Academy of Astronautics. He is also a member or an associate member of several national academies of science and was president of IAGC from 1988 to 1992. He has received many awards and honors, including the Jean-Dominique Cassini Union Medal of the EGU in 2005 and the EGS Runcorn-Florensky Medal in 1999.

IAGC Fellow – Michael Hochella, Virginia Tech (USA)

The second IAGC Fellow honor for 2013 is awarded to Dr. Michael Hochella, University Distinguished Professor at Virginia Tech, for outstanding research contributions in applying the theory and techniques of geochemistry to the study of the nanoscale domain and creating the field of nanobiogeochemistry. He received his PhD from Stanford University in 1981 and over the past 23 years has been a faculty member at Stanford and Virginia Tech. Prof. Hochella’s research interests include elucidating the roles that nanoscience and mineral-surface geochemistry/biogeochemistry play in major aspects of the Earth sciences. His research involves environmental issues and the biogeochemical cycling of the elements; studying mineral–microbe interactions from both geochemical and biochemical perspectives; understanding the behavior of nutrients and toxic elements in the environment and their mobility; characterizing aqueous partitioning reactions at oxide and silicate surfaces; and understanding interactions between mineral surfaces and species in solution, with applications to aqueous-system transport. He was a pioneer in the emerging field of nanobiogeochemistry and was the first in his field to use atomic-force, scanning-tunneling, and high-resolution transmission electron microscopy to study surface properties of nanomaterials of geological interest at the atomic level. Prof. Hochella has been a Fulbright Scholar, a Humboldt Award winner, and Virginia Scientist of the Year. He is a fellow of six international scientific societies, a Dana Medal winner (Mineralogical Society of America), and a former president of the Geochemical Society. He has also won the Brindley Lecture Award (Clay Minerals Society) and the Distinguished Service Medal of the Geochemical Society. He has served on high-level advisory boards of the National Science Foundation and the Department of Energy, including a current appointment to the Basic Energy Sciences Advisory Committee of the US Department of Energy.

Certificates of Recognition

Dr. Gwendolyn Macpherson is an associate professor of geochemistry at the University of Kansas in Lawrence, Kansas (USA), and director of the university’s Plasma Analytical Laboratory. Her primary research interest is in weathering and the consequences of global climate change on groundwater chemistry in continental-interior grasslands. Gwen incentivized a team of students in her department at KU to create the IAGC Facebook page and has been instrumental in helping the Association to reach out to students and its young members.

The IAGC also awards a Certificate of Recognition to our outgoing Council members. Thank you for your hard work serving the Society for the last four years!

Dr. Zhonghe Pang is a faculty member in the Institute of Geology and Geophysics of the Chinese Academy of Sciences.

Dr. Haruc Masuda is the chair of the Department of Geosciences at Osaka City University, Japan.

Dr. Nancy Hinman is a professor in the Department of Geosciences at the University of Montana, USA.

Dr. Rona Donahoe is a professor of environmental geochemistry and director of the Geochemistry Analytical Lab at the University of Alabama, USA.
GAC-MAC FREDERICTON 2014

We invite you to attend the next joint annual meeting of the Mineralogical Association of Canada and the Geological Association of Canada, which will be held on May 21–23, 2014, on the Fredericton campus of the University of New Brunswick.

Fredericton, the provincial capital of New Brunswick, is within easy reach of major centres in eastern Canada and the northeastern United States and a short hop from Halifax, Nova Scotia. The region has a long history of Earth science education and exploration, beginning with Abraham Gesner, who was appointed government geologist for New Brunswick from 1838 to 1842, the first such position in Canada. The 2014 GAC-MAC slogan reflects in part the 175 years of geoscience in the region, inspired by Gesner and his discoveries.

Fredericton is located a short distance from the world’s richest Pb–Zn–Ag deposits in the Bathurst mining camp, rare-metal intrusion-related deposits such as Sisson Brook and Mt. Pleasant, and spectacular exposures of hydrocarbon-bearing Carboniferous Bathurst basin sediments, and several field trips will take advantage of this proximity.

The local organizing committee has developed an outstanding scientific program. Here are some of the symposia and special sessions that will be of special interest to Elements readers. Check the website for the full list: www.unb.ca/conferences/gacmac2014/

Symposia

Applied aspects of mineralogy: A tribute to John Leslie Jambor
Bob Martin, David Blowes, Tom Al

Shock processes in natural and synthetic materials: A key to understanding planetary evolution
John Spray, Neil Bourne, Falko Langenhorst

Gold deposits: A holistic review
Dan Kontak, Richard Goldfarb, Gema Olivo, Bruno Lafrance, Benoit Dubé, Craig Hart, Bob Linnen, Robert Creaser

Precambrian supercontinent cycles: Geodynamics and its influence on mineralization
Luke Ootes, Bruce Eglington, Kevin Ansdell, Toby Rivers, Sally Pehrson

Special Sessions

Mineralogy of plutonic rocks: From magmas to ores – A special session in honor of André E. Lalonde
Keiko Hattori, Robert Linnen

Metalliferous black shales: Resolving among various metal sources
Andrey Bekker, Clint Scott, Dave Lentz

Discovering the next generation of porphyry deposits: Advancements in locating and understanding hidden intrusion-related mineralization
Neil Rogers, Bob Anderson, John Chapman, Dawn Kellett, Beth McClennaghan, Alain Plouffe

Granites and crustal evolution: Acadian–Caledonian connections
Dave Gibson, Mike Dorais, Martin Feely

Uranium ore genesis and exploration at depth
Eric Potter, Dave Quirt, Kurt Kyser

Conventional and unconventional petroleum systems of eastern North America
Grant Wach, Denis Lavoie, Robert Milici

Environmental aspects of resource development
Heather Jamieson, Michael Parsons

The age of the Earth revisited: High-precision U–Th–Pb geochronology of igneous, metamorphic, and sedimentary processes
Sandra Kamo, Mike Hamilton, Larry Heaman, Paul Sylvester

Linking metamorphic processes with large-scale geodynamics
Dave Pattison, Fred Gailey, Dong Tinkham

High-temperature metasomatic processes recorded by trace element and isotopic systematics in major and accessory minerals
Chris McFarlane, Richard Cox

Alkaline magmatism and associated mineralizations
Anne Sylvie André-Mayer, Michel Jébrak, Daniel Ohnenstetter, Anthony Williams-Jones

Environmental and economic significance of gossans associated with mineralization in rifts and LIPs
Marie-Claude Williamson, Jeff Harris, Cole Kingsbury

Cathodoluminescence and Its Application to Geoscience

Mineralogical Association of Canada Short Course
Fredericton, May 18–20

Organizers: Ian M. Coulson (University of Regina; ian.coulson@uregina.ca) and Michael Robertson (Acadia University; michael.robertson@acadiau.ca)

This short course, which will be held just before GAC-MAC2014, will address both the theory behind the phenomenon of cathodoluminescence (CL) and the application of this microscopic technique to all fields of geoscience investigation. Aimed at the graduate student, researcher, and practicing professional, the short course modules will cover the basics of theory, the causes of cathodoluminescence in minerals and materials, instrumentation, recent advances in cathodoluminescence imaging and spectroscopy data collection, and the interpretation of spectral responses. Case studies relating to sedimentological, petrological, mineralogical, petroleum geology, and economic geology fields will be included. The University of New Brunswick has excellent analytical facilities in house, and we have been offered access to this instrumentation (i.e. cold CL and Chroma SEM/CL) for demonstrations during the short course. Confirmed topics and speakers include:

Theory and methodology of CL; spectroscopy of CL (also hands-on demonstrations using a portable optical CL) – Michael Robertson (Acadia University)

CL as a petrological tool applied to the study of zoning phenomena in minerals, especially apatite – Ian M. Coulson (University of Regina)

CL as a tool in exploration geology – Anthony N. Mariano and Anthony Mariano, Jr. (consultants)

Physics background to CL and the effects of heating on luminescence signals – Roger Mason (Memorial University of Newfoundland)

CL in sodalite and alkaline rocks; fluid interaction – Melanie Kaliwoda (University of Munich, Germany)

Hyperspectral CL data collection – Martin Lee (University of Glasgow, Scotland)

The application of cathodoluminescence to chemical sedimentary rocks – Peir Pufahl (Acadia University)

Applications of CL in sedimentary geology – Melody Beachberger (Industry, USA)

CL in apatite and feldspar – Roger Mitchell (Lakehead University)

The acquisition and analysis of cathodoluminescence hyperspectral image data – Paul Edwards (University of Strathclyde, Scotland)

Cathodoluminescence and trace elements in quartz: Insights into geologic processes – Brian Rusk (Western Washington University, USA)
FROM THE PRESIDENT

Mark on your calendars the 26th International Applied Geochemistry Symposium (IAGS), to be held on 18–21 November 2013 in Rotorua, New Zealand. This extraordinary venue will host an excellent technical program, a variety of workshops, and some amazing field trip opportunities. Current information for the symposium is at www.gns.cri.nz/iags/.

I announce with pleasure the 2013 Gold and Silver medallists of the Association of Applied Geochemists. This year we have two Gold Medal recipients, Clemens Reimann and Eric Hoffman, and one Silver Medal winner, Gwendy Hall. The medals will be presented at the 26th IAGS conference dinner.

The Gold Medal is awarded for outstanding scientific accomplishments in the field of applied geochemistry. This year’s recipients boast accomplishments at both ends of the academia–industry continuum that defines the field of applied geochemistry.

Clemens Reimann (Geological Survey of Norway) has had an outstanding scientific career on the academic side of this continuum. During more than 30 years of work in government and academia, Clemens gained international recognition as a leader in the fields of environmental geochemistry, geostatistics, and geochemical mapping at scales ranging from local to continental. His prolific publication record includes numerous journal articles and book authorships. Clemens led regional geochemistry projects in Europe across geographic and political boundaries, and his work has influenced the formulation of regional surveys worldwide. His service to professional organizations has included acting as an AAG distinguished lecturer and regional councillor and as president and vice president of the International Association of Geochemistry. He has served on the editorial boards of Applied Geochemistry, our own Geochemistry: Exploration, Environment, Analysis, and Science of the Total Environment.

Eric Hoffman is recognized for his career as an industry leader in bringing novel analytical techniques to commercial fruition. Through his company, ActLabs, Eric has repeatedly been at the forefront in bringing techniques developed by research laboratories to commercial use by applied geochemists worldwide. He has anticipated the evolving needs of the applied geochemist through technique design and instrument modification for a variety of sample media. This has been particularly important as exploration has moved into progressively more difficult, concealed terrains. Eric has published consistently throughout his career, but equally important, he is always in attendance at scientific meetings to present and promote the latest in techniques and instrumentation.

The Silver Medal is awarded for outstanding service to our Association. Gwendy Hall is highly deserving of this award, having served as AAG president, vice president, councillor, committee member, and treasurer over the last 17 years. In all these roles, Gwendy has ensured that our organization thrived. The creation and success of our journal, Geochemistry: Exploration, Environment, Analysis, can be firmly credited to Gwendy as editor. Her spirit of volunteerism towards AAG is a model to emulate. As a now-retired scientist from the Geological Survey of Canada, Gwendy’s scientific contributions to applied geochemistry have also been prolific in terms of method development, publications, committee participation, and scientific review. These contributions led to her being awarded an AAG Gold Medal in 2005.

Bob Eppinger (eppinger@usgs.gov)
U.S. Geological Survey, AAG President

RECENT ARTICLE PUBLISHED IN EXPLORE


Small gold particles (<2 µm) in regolith have recently been observed but not quantified. Determining micro- (<2 µm) and nanoparticulate (<0.2 µm) gold in soils and regolith may provide an effective strategy for gold exploration. A method to quantify gold in the micro- and nanoparticulate fractions was tested using wet sieving and centrifugation of fourteen soil samples from Western Australia. Five fractions were separated and subjected to aqua regia digestion and analysis by ICP–MS. Although the soils tend to be dominated by the coarse (>250 µm), quartz-rich soil fraction in these transported soils, the analysis of all the size fractions shows that the majority of the gold is small and hosted in the <53 µm fraction. The gold associated with the bulk, coarse fraction-dominated materials is less than 2%. Analysing the nanoparticulate gold fractions via particle size separation demonstrates that gold concentrations span three orders of magnitude (<1 to 1000s ppb). The micro- and nanoparticulate fractions of gold are different within individual samples, with no single sample showing anomalously larger contents in both these fractions compared to the other samples, i.e. one soil sample is not consistently anomalous across grain size fractions. In this study, the authors developed a method to quantify gold in these very small size fractions and demonstrated it to be nuggety at all scales, down to the <0.2 µm fraction. Future research requires a more rigorous assessment of the method along with orientation surveys to determine if significant benefit exists in analysing the micro- and nanoparticulate fractions of soils for gold exploration, a process that is not conducted currently by industry.

Ryan Noble (ryan.noble@csiro.au)
CSIRO Perth
In this book, Editors F. Nieto and K. J. T. Livi have gathered reviews of past and current studies of mineral groups that have played important roles in geology, environmental science and health science. The various chapters cover the application of TEM and related techniques to mineral groups in which TEM investigations have been crucial to the understanding of their mineralogy. These groups are the pyriboles, serpentines, clays, micas and other metamorphic phyllosilicates, oxides and oxyhydroxides, sulfides and carbonates.

Some research fields in which TEM is particularly suitable and which have produced significant advances are inclusions and traces, extraterrestrial material, deformation processes, non-stoichiometry and superstructures, and biominerals.

Nowadays, we are witnessing a push for the improvement of detectors for imaging (direct detection of electrons) and X-rays (silicon drift detectors and annular high solid-angle of collection detectors), the development of new support materials (e.g. graphene) and liquid cells for imaging (direct detection of electrons) and X-rays (silicon drift detectors and annular high solid-angle of collection detectors).

Topics for the workshop will include: Archaean mantle geochemistry, craton development and evolution of the subcontinental lithospheric keel, deep cratonic structure and its potential impact on the distribution of mineralisation, strategies for targeted exploration, and current and future exploration targets within the NAC. We aim to include a wide variety of commodities and deposit types, including the ‘critical metals’, which are of ever-increasing importance to our society.

Themes:
- Archaean craton geology, mineralogy and geochemistry
- Mantle keel and subcontinental lithospheric mantle geochemistry
- Cratonisation processes and cratonic deep structure – regional controls on mineralisation (Archaean to Palaeogene)
- NAC regional metallogenesis and mineral potential (e.g. REE-Nb-Ta-Zr, Ni-Cu-PGE, base metals, Au, diamonds, gemstones)
- Temporal and spatial variation of mineral deposit types
- NAC breakup – effects of the opening of the Atlantic Ocean and Labrador Sea
- Case studies, including examples from Canada, Greenland, Scotland and beyond
- Current and future NAC exploration

This event is being organised by the Cardiff University and St. Andrews University chapters of the Society of Economic Geologists and the Applied Mineralogy Group of the Mineralogical Society of Great Britain & Ireland, in conjunction with the British Geological Survey and the Geological Survey of Denmark and Greenland.

**Euroclay 2015**

University of Edinburgh, UK

5–10 July 2015

www.euroclay2015.org


The scientific program of EUROCLAY 2015 will bring together, in an exciting, leading-edge programme, specialists from different disciplines related to clays and clay minerals. It will consist of technical sessions of both oral and poster presentations, with a generous quota of invited speakers who are the leaders in their respective fields. Pre-meeting workshops and mid-meeting field excursions will be integral parts of the scientific programme.

A key aim of this conference is to integrate industrial and academic workers by means of sessions which cover both areas. A visit to Edinburgh is one of life’s ‘must-do’ items. As Scotland’s capital city, it is the home of geology and is littered with places of interest for the delegate and accompanying person alike.
The Clay Minerals Society

THE PRESIDENT’S CORNER

The 50th anniversary annual meeting of the CMS, commemorating its establishment as a scientific society, will be held on October 6–10 at the University of Illinois in Urbana-Champaign, Illinois, USA. As mentioned in the previous President’s Corner, the CMS website (www.clays.org/CMS%20ORGANIZATION/CMShistory.html) provides basic information on the founding of the society. To provide our members and other readers of Elements with more details, the CMS has started publishing a series of short contributions on our history, which will appear on our society page in the remaining Elements issues in 2013. The second installment, like the first, was prepared by Dr. Duane (Dewey) Moore, previously at the Illinois State Geological Survey in Urbana and currently at the University of New Mexico.

Peter Komadel (peter.komadel@savba.sk)
President, The Clay Minerals Society

HOW THE CLAY MINERALS SOCIETY GOT STARTED, PART II

Interest in clays was developing around the globe. This trend was interrupted by the beginning of World War II. Scheduled before the U.S. became involved, a symposium was held at the University of Chicago in February 1942, during which Professor Ralph Grim delivered a long paper titled “Modern Concepts of Clay Materials”, along with four other papers about clay scientists from other disciplines. This symposium was a manifestation of interest in clays from many points of view: agriculture, engineering, geology, and the ceramic, rubber, paper, petroleum, paint, fiberglass, and many other industries. Grim’s exhaustive, 50-page review of what was known about clays and clay minerals almost certainly was the precursor of his book Clay Mineralogy, first published in 1953. Grim’s review, and the other four papers in the same volume, had the effect of inspiring a group of people from several disciplines to plan a symposium, “Problems of Clay and Laterite Genesis,” to be held in association with the 1951 meeting of the American Institute of Mining and Metallurgical Engineers in St. Louis.

The original suggestion for this symposium came from John J. Collins, who remained involved but transferred major responsibilities for its organization to A. F. Frederickson, then at Washington University; at this institution, Frederickson directed the thesis studies of both Bob Reynolds and John Hower. The participants, including Thomas Bates, John Burst, Ralph Grim, Walter Keller, Georges Millot, and Rustum Roy, thought that their symposium was such a success that they charged Ralph Grim with the task of seeking the sponsorship of the National Research Council, through its Clay Mineral Committee, for an annual meeting. Grim’s success made this 1951 meeting the precursor of The Clay Minerals Society.

The Clay Minerals Society was founded in 1952, and this institution published the first Proceedings. The National Research Council supported publication of the succeeding Proceedings until the Clay Minerals Society was officially incorporated in 1963, when the society assumed the publishing responsibility. In 1968, the publication was changed to a journal format, and Clays and Clay Minerals was born.

Duane Moore
University of New Mexico


CMS NEWS FROM THE 2012 GSA MEETING

The Clay Minerals Society is an “associated society” of the Geological Society of America (GSA). Representatives of the CMS attend meetings of all the associated societies each year at the annual GSA meeting.

The “umbrella” role played by organizations like GSA and the American Geosciences Institute (AGI) becomes clear at these meetings. Small societies, including CMS, together with these larger organizations are better positioned to lobby government and funding agencies and to represent our science on a national and international stage. The meetings provide a great opportunity to discuss matters of mutual interest and concern. At last fall’s meeting, Howard Harper of SEPM (the Society for Sedimentary Geology) gave a very interesting presentation about trends in membership of geoscience societies. While many smaller societies are suffering from reductions in their memberships, larger societies are growing. Future, more in-depth analysis of these trends will help us to understand if this is because younger scientists are opting for just one membership (rather than the several societies joined by their senior colleagues) or if some subject areas are no longer as attractive as they once were. Your views are welcome!

Kevin Murphy
Managing Editor, Clays and Clay Minerals

STUDENT RESEARCH SPOTLIGHT

Congratulations to Jacob Thacker for winning a CMS Student Research Grant Award. Jacob is currently pursuing an MS degree in Earth sciences and geology at Montana State University with David Lageson and other advisors. His research is on fault zone behavior as influenced by factors such as mineralogy and permeability.

Jacob Thacker
University of New Mexico
Endowment Fund can be utilized to promote the goals of the Society. Support that helps to strengthen our international community. We made as part of annual membership renewal. Thirty-one members will come from two sources—the General Endowment and our initial travel to the Meteoritical Society meeting in Edmonton. The money 2012. This year we will support scientists from low-income countries participate in the Meteoritical Society meeting in Cairns in August 2012 (June 2013). Endowment funds were also used to support the travel expenses of four professional members from low-income countries to Utrecht). The General Endowment Fund supports a variety of outreach projects. Over the last year, General Endowment funds were used to support students traveling to the Lunar Highlands Workshop (June 2013) and the Gordon Conference on the Origins of Solar Systems (June 2013). Endowment funds were also used to support the travel expenses of four professional members from low-income countries to participate in the Meteoritical Society meeting in Cairns in August 2012. This year we will support scientists from low-income countries traveling to the Meteoritical Society meeting in Edmonton. The money will come from two sources—the General Endowment and our initiative to raise money for this purpose directly through contributions made as part of annual membership renewal. Thirty-one members responded to this request this year. Your contributions provide direct support that helps to strengthen our international community. We always welcome suggestions and ideas for ways in which the General Endowment Fund can be utilized to promote the goals of the Society.

2013 MEMBERSHIP REPORT
As of May 2013, the Meteoritical Society is made up of 689 regular members, 105 student members, 155 retired members, 19 life members, and 4 members from developing countries, for a total of 972 members.

The following countries have one member at this time: Algeria, Botswana, Estonia, Holy See (Vatican City State), Ireland, Luxembourg, Malaysia, Morocco, New Zealand, Norway, Oman, Romania, Slovakia, Taiwan, and Uruguay.

The winner of the 2013 Pellas-Ryder Award is Christoph Burkhardt of the Institute of Geochemistry and Petrology at ETH Zürich (now at the University of Chicago). Dr. Burkhardt’s paper, “Origin of isotopic heterogeneity in the solar nebula by thermal processing and mixing of nebular dust,” published in 2012 in Earth and Planetary Science Letters, presents Mo and W isotope compositions in acid leachates and insoluble residue from the Murchison carbonaceous chondrite. Christoph and coauthors T. Kleine, N. Dauphas, and R. Wieler suggest that mixing or thermal processing in the solar nebula caused isotopic heterogeneity of Mo, while refractory elements such as Os and W were not affected and remain isotopically homogenous.

PAUL PELLAS–GRAHAM RYDER AWARD WINNER
The Pellas-Ryder Award for the best student paper in planetary sciences is jointly sponsored by the Meteoritical Society and the Planetary Geology Division of the Geological Society of America. It is awarded to an undergraduate or graduate student who is first author of the best planetary science paper published in a peer-reviewed scientific journal during the year prior to the award. The award has been given since 2001 and honors the memories of meteoriticist Paul Pellas and lunar scientist Graham Ryder.

Rhian Jones
TOWARDS GEO-GOGGLES:
AN IMA COMMISSION ON APPLIED MINERALOGY WORKSHOP ON QUANTITATIVE MINERALOGY,
LIÈGE, BELGIUM, 23 MAY 2013

Every one of us would dream of having geo-goggles to painlessly identify rock-forming minerals, and we would be definitely addicted if this technology could offer an estimate of mineral proportions. Although this is still science fiction (sorry), more and more technologies that deliver (semi-)quantitative mineralogical information in both the field and the lab have become available in recent years. This is particularly important in geological exploration and also in mineral processing, where a clear understanding of geometallurgical attributes is a decisive advantage for process optimization.

The Commission on Applied Mineralogy (CAM) of the International Mineralogical Association recently sponsored a one-day event entitled Quantitative Mineralogy at the University of Liège to demonstrate state-of-the-art technologies in this field. Hosted by the GeMMe (Génie Minéral, Matériaux & Environnement) Department, this event attracted more than sixty participants from all corners of Europe and beyond (Nancy, Liège, Aachen, Luxembourg, Amsterdam).

After a general introduction by CAM’s president, Prof. Eric Pirard, under the title “Reinventing Docimasy,” Dr Erick Ramanaidou (CSIRO, Perth) spoke about recent advances in a very exciting lecture titled “Using VNIR-SWIR-Raman spectroscopy in exploration.” In a talk entitled “X-ray diffraction spectra,” Qmineral’s director, Dr Gilles Mertens (KU Leuven), presented a comprehensive review of the possibilities and limits of the method. The second part of the workshop was dedicated to microscope imaging techniques. A lecture by Dr Alan Butcher, FEI’s principal petrologist, was on the subject “Quantitative mineralogy and petrography using automated SEM-EDS technology.” This lecture highlighted recent case studies using automated mineralogy to support operations in oil and gas as well as in mining. The last lecture of the day was given by Ing. Laura Perez-Barnuevo (UP Madrid), during which she demonstrated the benefits of multispectral microscopy and presented a series of new textural indices aimed at supporting a geometallurgical description of individual particles.

A general conclusion from the workshop is that sampling and sample preparation are still very critical steps. Innovation in sample preparation is needed to shorten the response time of microscopy-based techniques while at the same time allowing an increase in the representativeness of the measured surface. On the other hand, there is little doubt that other breakthroughs will occur in the near future in terms of fast and accurate mineral-mapping techniques, whether using Raman spectroscopy, hyperspectral imaging, or LIBS (laser-induced breakdown spectroscopy)-based instruments. CAM’s president reiterated his intention to set up a round-robin test in quantitative mineralogy and invited interested labs to send suggestions, or simply statements of intention to participate, to CAM’s secretary, Dr Megan Becker. The final event of the workshop was also the most rewarding: the traditional Belgian beer tasting. It certainly smoothed the networking among participants and facilitated the elaboration of future cooperative projects.

As a follow-up, CAM will hold a series of sessions on archaeometallurgy, X-ray CT and remote mineral mapping at IMA’s upcoming 21st general meeting. We look forward to meeting more passionate mineralogists in Johannesburg in 2014.
When I first arrived in research-led science, I was skeptical of the benefits of giving a poster. It seemed to me like an escape for those who are afraid of standing up and giving an oral presentation. I was, of course, naïve and overconfident in my relative ability. Over the course of my graduate degree, my opinion has changed. Now I think the two options are of equal importance.

It would be nice if all abstracts were judged solely on their scientific merit, but in reality, I think that many conference conveners believe that researchers with big reputations will deliver a quality talk. In contrast, they probably think that abstracts by researchers establishing themselves in a field have smaller track records and so may be viewed as “risky” for a talk. Talks are traditionally viewed as giving a researcher more exposure. Many early-career researchers are given, or apply for, posters. In theory, a poster should give you the same amount of exposure, or even more, if supervisors and mentors introduce you to the big names and make sure that relevant researchers come to your poster. But this is not much use if you attend a conference with no senior champion from your institution or home country.

How do early-career researchers make their name? How can they make their voice and their science heard in the cacophony of noise that characterizes the average conference venue? Does a presentation or a poster provide a bigger hit?

**My Early Experience**

My first scientific presentation was at a relatively small conference. My talk was somewhat shaky, and a researcher who thought almost exactly the opposite of me summarily took me down. I’m sure there were other esteemed scientists there who would have easily torn me to shreds had they not shown mercy on my new scientist’s soul. But I was still green and giddy with excitement at being involved in scientific research, and I got encouraging words from many a good scientist: a big tick for the oral-presentation format.

After a few small conferences, I finally went to a large international meeting two years ago. I was anticipating a big international audience. Unfortunately, although I realized there would be 16 or so parallel sessions, I had not counted on being scheduled against a superstar keynote lecture in my field. My own talk had an attendance of around eight people. I am sure that we all wished we were seeing Dr. Superstar instead!

In the end, I got a couple of quick questions, along with a few congratulations at the end of the session, and maybe fifteen minutes of discussion with a couple of interested parties. I couldn’t help but feel slightly deflated. I had done my job, given my talk, but it wasn’t enough. The poster sessions were excellent, and I felt like I had made the wrong choice.

**Lessons Learned**

Last year, I was determined not to make the same mistake and headed off for a smaller international conference, armed with my very first poster. It was my pride and joy, having spent nearly a month honing the figures and working out what I wanted to show and say.

The poster session was one of the best scientific events I have been to yet. Best of all, it was held outdoors, on a lawn under palm trees, next to the beach (photo). I think the conference had the perfect number of delegates (400 in total) for a poster session. It was small enough that almost everyone read all the poster titles, but large and specialized enough that there were lots of interested people there.

The poster session was one of the most tiring two hours I’ve ever spent. I had an almost constant stream of people coming and asking questions. Probing and inquiring: What have I done? What do my data show? Did I think about this? Why didn’t I do that? Have I considered the possibility of being completely wrong? It is exhausting to have to stand there and defend your poster and your work as academic after academic comes over and tries to pick holes in it all. It felt like being a lawyer in court, standing up and arguing for the defendant (my PhD) in the face of a barrage of questions. But it was fun! Bar a couple of people who seemed to instantly dismiss my research field, most were enthusiastic about what I had done and were certainly keen on seeing the record published. I talked to some great academics, both established and up and coming. It was exhausting, yes, especially being out in the hot sun, but it was quite an experience.

The overall reach of a poster is probably less, but in terms of communicating with those who matter, those who are interested, then a poster is far more penetrating. It certainly beat my experience of giving a talk.

**A Dependency on the Conference Itself**

My opinion of the quality of poster sessions largely correlates with the adequacy of the air conditioning. I have been to three cramped, hot poster sessions, and have tended to escape very quickly. This is in stark contrast to two light and airy sessions where I feasted on new scientific knowledge.

The reach of an average early-career scientist’s presentation has a lot to do with the size of the conference. At a small conference with only a couple of parallel sessions, a talk will almost always have good attendance. At a larger conference, there are so many talks that you can easily get lost in the noise and a poster will stand out more. But is there a point at which there are so many posters that, once again, your tree fades into the woods?

Which leads me to my current situation. By the end of the successful poster session, I had been offered a postdoctoral position... to work with one of the researchers who attended my poorly attended, but successful, talk a year earlier. So, I am pleased that two presentations on my PhD topic were enough to convince a potential employer to offer me a job. Was it the poster, the oral presentation, a combination of the two, or none of these that got me the job offer? I guess I’ll never know, but at least now I am happy with both approaches to conference presentations.

**Getting Your Point Across**

- AGU poster guidelines
  http://fallmeeting.agu.org/2012/scientific-program/poster-session-presenter-guidelines
- Visual communication
  http://elementsmagazine.org/processIP.lasso?number=e3_2&filename=dutrow.pdf
- Making effective presentations
  www.geosociety.org/graphics/seo/Effective_Presentations.pdf
- Giving good talks
  www.geol.wvu.edu/rjmitch/stoning.pdf
- Designing conference posters
  http://colinpurrington.com/tips/academic/posterdesign
- A letter to poster-session organizers
  http://colinpurrington.com/2012/open-letter-to-poster-session-organizers

Nick Scroxton, Research School of Earth Sciences
Australian National University
Cements and concretes are among the most widely used materials, and they have had a significant impact on modern human activities and the environment. Ordinary Portland cement is the essential binder in modern concrete, and together with other cement types, it represents a fundamental and cheap commodity for the development of society’s infrastructure around the world. Concrete is second only to water in terms of the total volume of raw material consumed annually. It is well known that cement production generates a substantial amount of CO₂, such that the cement industry produces approximately 5% of current, global, man-made CO₂ emissions. It is expected that the increasing global population, the economic growth of developing countries, and a need for climate change mitigation and adaptation measures will boost the future demand for cement. The lack of a real alternative to concrete as a major construction material at a global scale is a challenging issue for the whole planet. Therefore, it is appropriate that the geosciences, and specifically mineralogy and geochemistry, provide a conceptual framework for understanding the problems involved and propose possible solutions. The need for replacing Portland cement–based concrete by alternative formulations with acceptable engineering performance, long-term durability, environmental compatibility, and sustainable production ought to be a fundamental driving force in geoscience research. Given these premises, a volume devoted to the mineralogy of building materials fills an existing gap in the Reviews in Mineralogy & Geochemistry (RiMG) series.

Based on a project conceived in 2006 and approved by MSA Council in 2009, RiMG volume 74 is the product of the short course entitled Applied Mineralogy of Cement and Concrete, which was sponsored by the Mineralogical Society of America and the Geochemical Society and held in Trondheim, Norway, in July 2011, prior to the 10th International Congress for Applied Mineralogy, and again in June 2012, after the International Congress on the Durability of Concrete. The short courses were organized by the editors of RiMG volume 74, Maarten A. T. M. Broekmans, Geological Survey of Norway, Trondheim, Norway, and Herbert Pöllmann, Martin Luther Universität, Halle (Saale), Germany.

Chapter 1, by Herbert Pöllmann, provides an in-depth description of calcium aluminate cements (CAC), including their manufacture, phase diagrams, hydration reactions, and the effects of admixtures and impurities. The wide variety of phase compositions and crystal structures possibly occurring in CACs and their hydration products are listed and depicted. Notwithstanding the fact that CACs are only used in small-scale, specialized applications due to their relatively high cost (H. Justnes, the same volume), the extensive and authoritative review by Pöllmann stands as a state-of-the-art reference for a readership ranging from students to the advanced researcher.

In chapter 2, Harald Justnes presents a critical overview of low-CO₂ calcium oxide sources alternative to calcium carbonate currently used in the production of Portland cement. The pressure to make the production of concrete more sustainable, or “greener,” is considerable and increasing. Pure Portland cement will have to be replaced by more complex binary, tertiary, or even quaternary binders, including other types of cementitious materials. This short contribution by the chief scientist at a large independent research organization in Scandinavia has the merit of providing a realistic Earth sciences viewpoint on the sustainability of concrete production.

Paul Stutzman of NIST has long contributed to the development of optical and electron microscopy techniques and standards for studying and quantifying clinker phases in Portland cements. The practical advice in chapter 3 is the result of his long experience in the field. Newer and promising X-ray computed tomography methods aimed at investigating undisturbed sample volumes are briefly mentioned.

Chapter 4, by Roger Meier, Jennifer Anderson, and Sabine Verryn, reflects the great attention given nowadays by manufacturers of analytical equipment, in particular X-ray diffraction instrumentation, to the cement industry. Automated XRD measurements and Rietveld analysis have been successfully applied to the online, continuous monitoring of the cement production workflow.

In chapter 5, Miguel Aranda, Ángeles de la Torre, and Laura León-Reina provide a complete and authoritative introduction to Rietveld quantitative phase analysis as applied to ordinary Portland cements and their hydration processes. Tables 1 to 3, listing the most common phases occurring in ordinary Portland cements, along with their ICSD and PDF codes, make a very useful and reliable reference for beginners in the Rietveld analysis of cement materials. The chapter is bound to be a reliable and important reference in the future.

The comprehensive and in-depth review of supplementary cementitious materials compiled by Ruben Snellings, Gilles Mertens, and Jan Elsen in chapter 6 complements chapter 2 in convincingly showing that the performance, durability, and sustainability of concrete can be improved by mastering the wide assortment of geological and by-product materials that can be blended with Portland cements. The subject is well covered and thoroughly discussed.

The book closes with chapter 7, by Maarten Broekmans. It treats deleterious reactions of aggregate with alkalis in concrete and deals with several topics possibly related to the main subject. A merit of this chapter is that it shows that the recognition of deleterious processes in concrete requires a combination of techniques.

As pointed out in the volume preface, the applied mineralogy of cements and concrete is a steadily growing field. The selection of a limited number of topics to be covered in a single volume is therefore unavoidable. Unlike a comprehensive textbook, RiMG volume 74 provides a collection of contributions from a competent group of authors. Any reader acquainted with the basics of cements and concrete will find most of the chapters very useful in terms of the depth of coverage and the extensively cited literature. However, in the absence of general guidelines and an appropriate introduction, the beginner might find it difficult to place the chapters in an appropriate context. For example, the notation of cement’s chemistry is formally given on page 84 even though it is used earlier. Ordinary Portland cement is properly introduced only in chapter 3, although a discussion of this universally used material could have been given in an introductory chapter. Furthermore, modern methods used in cement and concrete research, such as advanced imaging techniques and computer modeling, are almost completely ignored, apart from a few sparse citations (end of chapter 3); they deserve a more complete coverage.

“Applied Mineralogy of Cement and Concrete” will be a useful reference for a wide readership in cementing materials. Some of the chapters, especially chapters 1, 5, and 6, will be comprehensive and authoritative sources for those interested in the specific topics. RiMG volume 74 maintains the tradition and standard of the Reviews in Mineralogy & Geochemistry series.

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In 2010, after more than 25 years of study and a $10-billion investment, the Yucca Mountain site in Nevada was shelved by the Obama Administration as a potential repository for high-level nuclear waste. This leaves the United States with no plan for the disposal of its high-level radioactive waste—derived from power plants and weapons manufacturing—currently scattered across 121 sites in 39 states. This story is put into its political, social, and scientific context by William M. Alley and Rosemarie Alley, a husband-and-wife team. William Alley watched the story unfold at close quarters, as he was chief of the Office of Groundwater at the USGS and oversaw the Yucca Mountain project (from 2002 to 2010). Rosemarie Alley is a literary specialist who used her talents to make sure the book delivers what it promises: “an engaging and authoritative account of the controversies and possibilities surrounding disposal of nuclear waste in the US.” The focus of the book is on the United States, but examples from other countries are woven throughout. In 2012 there were 440 nuclear power plants in 31 countries, and no country had an operating high-level waste disposal facility.

As in so many matters, historical perspectives illuminate the issue at hand. In order to put the Yucca Mountain decision in context, in the first half of the book, Alley and Alley trace the history of nuclear development in the United States, starting with the Manhattan Project, which was mostly carried out at 3 secret locations: the Oak Ridge Reservation, where uranium was enriched, the Hanford Reservation, where plutonium was created, and the Los Alamos National Laboratory, where weapons were manufactured. Electricity from nuclear power was first generated in Idaho in 1951 (this is also where the first meltdown of a nuclear reactor occurred), and construction of the first nuclear plant in the US started in 1954 in Shippingport, Pennsylvania. During the Cold War, the Savannah River site in South Carolina produced plutonium and tritium for nuclear weapons. At the end of the Cold War, 30,000 nuclear warheads were dismantled. The 100 tons of plutonium contained in these weapons are now nuclear waste that has to be dealt with.

Robert Oppenheimer, scientific director of the Manhattan Project and a fervent believer in the peaceful use of the atom, dismissed the waste problem as “unimportant.” He was not alone in thinking this way. Most researchers and politicians involved in the early years were confident that the problem of waste disposal would be an easy fix. In 1949, the chair of the Atomic Energy Commission stated that dealing with waste was just a matter of “learning to live with radioactivity.” The authors review in several chapters how thinking about dealing with waste has evolved: from dumping it in the ocean to more esoteric solutions, like ice-sheet disposal and disposal in space. There is now a worldwide consensus that a geologic repository is the best way to deal with waste; and Alley and Alley examine the main geological environments that have been considered as potential repositories, including salt beds and domes, which were studied extensively, and the thick unsaturated zone in a desert environment. The Yucca Mountain site belongs to the latter.

The second half of the book is devoted to Yucca Mountain: how Yucca Mountain became the sole candidate for a repository in 1985, the obstacles that were encountered, and the enormous amount of science that was done to characterize the site. In June 2008, in spite of many setbacks, the Department of Energy (DOE) submitted a license application to construct a nuclear waste repository at Yucca Mountain to the Nuclear Regulatory Commission (NRC) for review. The application weighed 50 kg, totaled 8600 pages, and included the results of hundreds of studies. The application was under review by the NRC when the Obama Administration decided to cancel the project.

The terms NIMBY and NIMS figure prominently throughout the book: “Not in my state” and “Not in my back yard” pretty much summarize the main stumbling blocks. Nobody wants a repository of high-level nuclear waste in his backyard. In the instances where groups or locales were interested, the states used all their legal powers to stop the projects. The authors point out that it is perhaps not accidental that the two countries most advanced in developing a repository—Sweden and Finland—are countries with only a central government and no state or provincial governments. The coup de grâce, however, was the requirement to demonstrate that Yucca Mountain could be safe for 1 million years. The authors look back at the last million years of the geological record to demonstrate how impossible a task this was.

In the wake of shelving the Yucca Mountain site, the Obama Administration created a Blue Ribbon Commission in 2010 to advise on the path forward. Members of the commission submitted their final report in January 2012 (http://energy.gov/ne/downloads/blue-ribbon-commission-americas-nuclear-future-report-secretary-energy). Alley and Alley stress that even if the world were to stop using nuclear energy tomorrow morning, we would still have to deal with the waste accumulated since 1945. Moreover, nuclear energy is one of the proposed solutions to address global warming. A realistic starting point to move forward is to acknowledge that any course chosen will be an imperfect solution: the problem is too big and too complex. The authors acknowledge that “the technical characteristics of nuclear waste make the disposal problem difficult, but it is the human factors that have made it intractable.” Taking the human elements into account is key to avoid past failings.

I encourage anyone remotely interested in the topic to buy a copy. At US$29.95, this is a very affordable book. The authors have done a remarkable job of making the scientific information accessible to lay persons. I certainly learned much about national laboratories, the role of the DOE, the National Academy of Sciences, and the amazing and complex ramifications of politics. Woven in are biographies of scientists and lots of side science stories, from ocean currents to the origin of Monte Carlo simulations. Treatment is fair: you get the sense that the authors tried hard to present the facts and all sides of the story. This book would be ideal for using in a seminar class. Overall a fascinating read!

In the “100 mineralogical questions” exercise, which was summarized in the previous issue of Elements, two questions deal with radioactive waste:

- 82. What are the dissolution reactions that lead to the breakdown of nuclear waste materials in deep geological disposal facilities, and what might be the long-term impact of nuclear waste dissolution?
- 83. What is the long-term fate of man-made actinides, mainly plutonium, in the environment?

After reading this book, I would argue that they are the two most urgent and pressing problems to attend to.

Pierrette Tremblay, Managing Editor Elements magazine
The EMU School “Minerals at the Nanoscale” was held in the Centro de Instrumentación Científica (CIC) of the University of Granada (Spain) from June 3 to 6, 2013. It was organized by Fernando Nieto and Fernando Gervilla and included both classical lectures and practical sessions. Lecturers explained the structures and microstructures of sulfides, oxides, carbonates, clay and serpentine minerals, metamorphic phyllosilicates, pyrobites, extraterrestrial minerals and biominerals studied under HR-TEM. The contents of the lectures are compiled in volume 14 of the EMU Notes on Mineralogy series, and participants used this book during the school. It is available now from the Mineralogical Society’s online bookshop (www.minsoc.org) and through the online bookshops of the Geological Society (www.geolsoc.org.uk) and the Mineralogical Society of America (www.minsocam.org).

Four practical sessions covered: (1) the preparation of samples, including extraction of a sample from a thin section, ion milling, powder sampled on a grid, embedding with resin and cutting with a microtome; (2) the acquisition of diffraction data (SAED) and conventional TEM images, and EDX chemical analysis using a CM-20 apparatus; (3) the orientation of a sample, the acquisition of atomic-resolution images, HAADF, EDX compositional maps and analysis using the new Titan apparatus, recently purchased by the CIC; and (4) the acquisition of EELS spectra and the interpretation of data. These practical sessions were conducted by Isabel Abad, Javier Cifuentes, María del Mar Abad-Ortega and Antonio Sánchez-Navas.

The school was made possible by the participation of postgraduate students and senior researchers from 8 different European countries. The maximum number of participants (40) was reached well before the registration deadline. This limit allowed a maximum of 10 participants in each of the four practical sessions. The school benefited from the financial support of the University of Granada (especially the Department of Mineralogy and Petrology and the Faculty of Sciences), the Spanish Mineralogical Society (SEM), FEI, the Andalusian Institute of Earth Sciences (IACT) and the German Mineralogical Society (DMG). In addition, 15 students attended the school with help from several scientific societies: the Spanish Mineralogical Society, the Commission on Inorganic and Mineral Structures (CIMS) of the International Union of Crystallography (IUCr), the French Society of Mineralogy and Crystallography (SFMC), the Spanish Clay Minerals Society (SEA), the Italian Association for the Study of Clay Minerals (AISA), the Italian Society of Mineralogy and Petrology (SIMP), and the PhD program in Earth sciences at the University of Granada.

The EMU School 2013 ended in the gardens of the Carmen de La Victoria (http://carmendelavictoria.ugr.es/) in front of the Alhambra castle, where participants and teachers enjoyed a cocktail and experienced the magic of a spring evening in Granada.

**Fernando Nieto and Fernando Gervilla**
Department of Mineralogy and Petrology, University of Granada

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**SFMC STUDENT SPONSORSHIP**

Romain Lafay (PhD student at ISTerre, University of Grenoble) and Guillaume Bellino (PhD student at UMET, University of Lille) received grants from the Société Française de Minéralogie et de Cristallographie to help them attend the EMU school “Minerals at the Nanoscale.”

**Report from Romain Lafay and Guillaume Bellino**

The EMU school gave us the opportunity to deal in depth with the possibilities offered by transmission electron microscopy (TEM). During the mornings, well-qualified professors gave us interesting lectures on various subjects and the types of characterization offered by TEM, including technical aspects and traps to avoid. The afternoons were dedicated to practical work, such as sample preparation and the interpretation of data. The various topics covered by the school corresponded well to the needs and expectations of the 40 participants from various countries and backgrounds. It was an opportunity for us to get answers to several questions that have arisen in our own research and, above all, to get a better understanding of this accurate tool. Indeed, we intend to perform measurements with TEM in the near future to accurately characterize our samples.

The school was well organized, and we were warmly welcomed in this beautiful World Heritage–listed city. On top of that, a closing dinner with tapas was held in a typical Spanish house (called Carmen) with a wonderful view of the famous Alhambra de Granada.

The two PhD students sponsored by the SFMC with the EMU school’s organizers. From left to right: Romain Lafay (U. Grenoble), Fernando Nieto (U. Granada), Fernando Gervilla (U. Granada) and Guillaume Bellino (U. Lille).

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**THE SEM AT THE EMU SCHOOL “MINERALS AT THE NANOSCALE”**

The Spanish Mineralogical Society (SEM) participated in the EMU school “Minerals at the Nanoscale” (www.ugr.es/~emuschool2013). SEM members Fernando Nieto and Fernando Gervilla organized this interesting school. It covered a wide range of topics related to the application of high-resolution transmission electron microscopy in the investigation of minerals at the nanoscale. The school included practical work using a Philips CM-20 and an FEI Titan at the Centro de Investigación Científica of the University of Granada. The practical work also included preparation of samples and interpretation of data. SEM members Carlos Rodríguez-Navarro, Encarnación Ruiz-Agudo, Blanca Bauluz, Isabel Abad and Antonio Sánchez-Navas gave lectures and practical sessions. Three students were able to attend the school because they received grants from the SEM to cover registration fees and travel and accommodation costs.
The 6th International Symposium on Granitic Pegmatites was held in New Hampshire and Maine from May 26 to June 2, 2013. The meeting was organized by Skip Simmons, Karen Webber, Al Falster, Bob Whitmore, and others, and was comprised of two parts. The technical part, with talks and poster presentations, was held at the Attitash Grand Summit Hotel in Bartlett, New Hampshire, from May 26 to 30. This involved three days of technical sessions and a one-day mid-meeting field trip to the phosphate-rich Palermo pegmatites of Grafton, New Hampshire. Special exhibits of New England pegmatite minerals were displayed by local collectors, miners, and museums, including Don Dallaire, Gary and Mary Freeman, Gordon Jackson, Jeff Morrison, Bob and Edna Whitmore, the Maine Mineral and Gem Museum, and the Capital Mineral Club of New Hampshire. It was a pleasure to view beautiful local minerals, and the displays were a great source of inspiration for scientific discussion. A total of 105 persons from 19 different countries participated, and most attendees gave presentations. The Attitash Grand Summit Hotel was a wonderful venue for the meeting, and catering by the hotel was outstanding. The first part of the meeting culminated with a banquet and dancing by the Four Winds Native American dance ensemble.

The second part of the meeting consisted of a three-day field trip to gem-bearing, rare-element pegmatites in Oxford and Androscoggin counties, Maine. While in Maine the group stayed at the Poland Spring Resort in Poland. Sites visited during the trip were the Bennett, Emmons, Hawy, Mt. Mica, and Waisanen (sometimes referred to as the Tamminen-Waisanen) pegmatites. The trip started with a visit to the new Maine Mineral and Gem Museum in Bethel (www.mainemineralmuseum.org/). Although the museum was still under construction, the group was given a guided tour and allowed to view many of the specimens scheduled for display.

During the field trips, lunches were elegantly prepared by Appetites Catering of Bangor, Maine. Proprietor and Chef Michael O’Neal is also a geologist and pegmatite miner. It was a real treat to be served gourmet meals (e.g. lobster rolls, grilled vegetables, and homemade pies with ice cream) while studying the pegmatites and digging for specimens. We were also provided fresh exposures at many of the mines. Gary and Mary Freeman sandblasted a portion of the underground mine walls at Mt. Mica so that the zoned mineralization could be seen more clearly, and Frank Perham made several fresh blasts at the Waisanen quarry, one while participants were watching from a safe distance. Many interesting discussions arose during the technical sessions and field trips, and most of the symposium participants joined in a semiformal conversation on reevaluating pegmatite nomenclature.

This symposium is held every two years, and this was the first time it was held in the United States. The next meeting will be convened in Poland in 2015.

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ARSENIC – THE GREAT POISONER REVISITED

D. J. Vaughan* and D. A. Polya*

In 2006, *Elements* magazine published an issue on the subject of arsenic, an issue to which we both contributed (Vaughan 2006; Charlet and Polya 2006). Topics covered in this now widely cited publication included the mineralogy, chemistry and geomicrobiology of arsenic, along with the environmental and human health impacts of arsenic contamination of soils and waters from both anthropogenic and natural sources. A particular concern highlighted in these papers was the arsenic contamination of drinking water over large parts of southern Asia, a contamination that has led to the premature deaths of many thousands, possibly millions, of people and to a situation that the leading epidemiologist A. H. Smith has described as “the largest poisoning of a population in history”.

Since 2006, over 3000 articles concerned with this arsenic poisoning have been published in the scientific literature, and numerous others in the popular press. The present article is the first in what is hoped will be a series in *Elements* under the title ‘Mineralogy Matters’. The series will address the question as to whether research in mineralogy (broadly defined to include petrology and geochemistry) has made an impact, in this case on a pressing human health problem. Has, in fact, mineralogy ‘mattered’ in this case?

In recent decades we have learnt a lot about the geochemistry of arsenic; for example, in understanding the speciation of arsenic in sulfide- or carbonate-containing solutions (Helz et al. 1995; Neuberger and Helz 2005; Helz and Tossell 2008), or the interaction of arsenic in solution with mineral surfaces (Farquhar et al. 2002), and its incorporation into minerals such as iron oxyhydroxides and oxyhydroxy-sulfates (Cutting et al. 2012). In such studies, advanced analytical, imaging, spectroscopic and computer-modelling methods have been used to considerable effect. They have been applied both to ‘model’ laboratory systems and to ‘real world’ systems such as arsenic-contaminated industrial site (Cancés et al. 2008), where the speciation of As in soils is critical for determining the bioavailability of the toxin and, hence, for a proper risk assessment.

Regarding the great contemporary problem of arsenic contamination of drinking (and irrigation) water in countries including India, Bangladesh and Vietnam, recent overviews emphasise that the original source of the arsenic is almost certainly largely rocks containing sulfide minerals in the rapidly eroding Himalayas (Polya and Charlet 2009; Fendorf et al. 2010). The breakdown products of these primary minerals include iron (oxyhydr) oxides, which can transport arsenic incorporated in their structures or sorbed to their surfaces. Following transport in this form via great rivers such as the Ganges, this material is deposited on their floodplains and contributes to the sediments hosting the aquifers that are now accessed by shallow wells from which the drinking water used by many millions of people is extracted. Release of the arsenic into the drinking water is envisaged as being particularly associated with microbial reduction of solid phase Fe(III) and of As(V) to the sometimes more labile As(III) (Islam et al. 2004). In all these processes, mineralogy plays a key role, including the possibility of controlling the distribution of As(III) versus As(V) between different biomineral species (Coker et al. 2006). As microbial reduction of Fe(III) and As(V) both require the presence of an electron donor, notably labile organic carbon, the organic geochemistry is also an important part of the story (Rowland et al. 2007; Neumann et al. 2010).

The studies mentioned above help in understanding the origins of the problem, and also inform the approaches that might be taken to remediation, both in situ and ex situ. The geology and hydrology are important here, as well as mineralogy. One approach has involved extracting water from deeper, uncontaminated aquifers, although a major concern here is the potential contamination of these aquifers by the shallower groundwaters as a consequence of extraction (Burgess et al. 2010; Winkel et al. 2011). This, and the possibility of exhausting the deeper sources, has led to calls for the use of deeper waters only for drinking rather than for less critical uses such as irrigation (Fendorf et al. 2010). The mineralogical and geochemical aspects of remediation strategies centre on both in situ and ex situ approaches. For example, it may be possible to manipulate the carbon loading in an aquifer so as to control microbial activity, or modify both chemistry and microbial activity so as to immobilise the arsenic as a highly insoluble phase, such as a sulfide (Héry et al. 2010; Omoregie et al. 2013). Such in situ approaches are still highly speculative and require rigorous testing before any widespread use, given the dangers of creating new problems. The ex situ remediation of water at the well head or at the point-of-use, for example in households, is much more established and has a distinctly mineralogical aspect. The iron oxyhydroxides produced by the aqueous oxidation of metallic iron filings, including nano-scale zero-valent iron (NZI) particles (Kanel et al. 2005), can be used to take up arsenic from the water prior to domestic use. The decrease in the efficiency of such systems as a result of clogging with Fe-bearing precipitates and other factors, however, remains a significant practical concern (Hossain et al. 2005). Also, many chemical remediation technologies involve an oxidation step, taking advantage of the often stronger sorption of As(V) as compared to As(III), although this has now been shown not always to be the case (Dixit and Hering 2003).

When we consider more generally the poisonous nature of arsenic, it is worth noting that its toxicity and bioavailability are strongly linked to its chemical speciation. For example, it is the trioxide that has been the form commonly used by murderers and assassins since ancient times, whereas compounds such as the arsenosugars are widely thought to be essentially non-toxic. Three historical examples of accidental poisonings of communities are illustrative of three major Goldschmidt-style types of geochemical behaviour that arsenic follows. In the first case, in an incident in the 1950s, many children in western Japan were poisoned through drinking milk from a commercial supplier. Here, arsenic in the form of arsenate substituting for phosphate entered the food chain when non-pharmaceutical-grade phosphate was used to stabilise the powdered milk product (Yorifuji et al. 2011). A second example illustrates why rice is particularly susceptible to arsenic contamination when irrigated with arsenic-bearing groundwaters and grown in paddy fields under reducing conditions. Under such conditions in near neutral waters, the predominant aqueous arsenic species is $\text{H}_2\text{AsO}_3$, which is of a charge (zero) and size very similar to that of $\text{H}_2\text{SiO}_3$ and, accordingly, follows an influx pathway for $\text{H}_2\text{SiO}_3$ through aquaporins (proteins forming cell
membrane pores that control the water content of cells) into the rice plant (Ma et al. 2008). The third example has arsenic in a more familiar geochemical role – as a chalcophile element. In 1900, several thousand people in Manchester, England, were struck down by poisoned beer. The poison was arsenic introduced through the use of impure sulfuric acid in the brewing process; the sulfuric acid was contaminated by the As-bearing pyrite employed to make it. This is a story where mineralogy very clearly did matter.

REFERENCES


Ma JF and 6 coauthors (2008) Transporters of arsenite in rice and their role in arsenic accumulation in rice grain. Proceedings of the National Academy of Sciences 105: 9931-9935


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PARTING SHOTS

TROUBLE WITH TELECOMMS

My little Parting Shots articles start their journey to your desk (or, I hope, your sofa) from my house in the West Highlands of Scotland. At the click of a mouse, they start their journey down a copper cable sheathed in grey plastic. For the first 200 m or so the cable runs under a field, but then it reaches a road. This is a very wet part of the world. The mountains a few kilometres to the west sometimes get 3 m of rain in a year, so the narrow roads are edged by deep ditches. The grey cables are simply dropped into these ditches, and you can see them snaking along, among the reeds and tadpoles and empty whisky bottles. About 5 km to the east, the cable abruptly turns north and runs for about a kilometre under an arm of the sea, emerging somewhere near the local telephone exchange, where the technology goes up a notch and we join the national fibre-optic network.

I expect my broadband to be slow, but a couple of weeks ago, when I was thinking about this article, it became Maddeningly erratic, and voices over the telephone became strangely muffled, which I ascribed to my advancing years. A man was sent by my telecomms provider, and he spent a whole day replacing what he called ‘wet joints’ between my house and the exchange. My broadband is now completely reliable and I feel years younger. To test this great technological leap forward, I serendipitously decided to go to the Mineralogical Society’s archive and have a look at the very first paper published in Mineralogical Magazine. By a strange coincidence I found myself back in a world dogged by telecomms problems.

The opening lines of issue 1, volume 1, of Mineralogical Magazine, August 1876, the first words of the world’s first properly scientific mineralogical journal, are reproduced nearby. The new journal was followed in March 1878 by what was then called Bulletin de la Société minéralogique de France, now subsumed in European Journal of Mineralogy. The Min Mag article by Marshall Hall is unexpectedly interesting. It relates how the cable-laying steamship Faraday is in the Mid-Atlantic, at latitude 50°30’ N, longitude 24°46’ W, ‘grappling for the broken telegraph cable’. The broken cable is clearly world news, so no further explanation is needed. The grapple brings up a 9.5 kg lump of black basalt, which is passed to a Mr J. Clifton Ward who makes a thin section, which he views using polarized light. Min Mag provides illustrations in colour, something that has become commonplace only in the last decade and for which we are still charged extra by some journals! It was only in 1849 that Henry Clifton Sorby had introduced the use of thin sections, and microscopes fitted with Nicol prisms, to geology, so the Min Mag article was state-of-the-art petrography. Ward identifies augite and olivine (see his drawing) and white needles of plagioclase showing longitudinal banding when more highly magnified. The section seems to have been on the thick side.

Ward suggests that ‘as it is possible that the mass of basalt from which the specimen was chipped had been floated southwards on ice, the microscopic examination of some of the northern basaltic tracts might indicate the parent rock’. I fear that all the techniques of chemical and isotopic analysis available today might well fail in that task! To establish whether it is feasible for ice to have carried it to the position from which it was collected, Marshall Hall consults a Dr John Rae. Rae responds that ‘he is not aware of icebergs having been seen about that spot, but that such an occurrence is not impossible’. Hall and Rae agree that the basalt is most likely to have been ‘wrenched off some submarine peak’. The discovery of basalt on the ocean floor causes consternation. Ward suggests that ‘it is possible that the mass of basalt from which the specimen was chipped had been floated southwards on ice, the microscopic examination of some of the northern basaltic tracts might indicate the parent rock’. I fear that all the techniques of chemical and isotopic analysis available today might well fail in that task! To establish whether it is feasible for ice to have carried it to the position from which it was collected, Marshall Hall consults a Dr John Rae. Rae responds that ‘he is not aware of icebergs having been seen about that spot, but that such an occurrence is not impossible’. Hall and Rae agree that the basalt is most likely to have been ‘wrenched off some submarine peak’.

Canadian and Scottish readers will know about John Rae. He is my greatest hero, a relatively unknown traveller whose explorations of northern Canada far outshine the Arctic exploits of Peary and Amundsen. Born in 1813 in the tiny village of Orphir in the Orkney Isles, off the north-eastern tip of mainland Scotland, Rae graduated as a surgeon from Edinburgh University in 1833. His father, also John, was made the Orkney agent of the Hudson’s Bay Company in 1819. The company’s supply ships would call there before crossing the Atlantic. Rae junior signed on for a single season as surgeon on an HBC ship heading for James Bay, at the southern end of Hudson Bay, but as luck would have it, the sea ice came early and Rae had to winter on bleak Charlton Island. He enjoyed it so much that he remained at Moose Factory on James Bay for ten years! He learned the hunting and survival skills of the local Inuit people, for whom he had great respect, and dressed like them. On behalf of the HBC he undertook a number of extraordinary journeys of exploration in the enormous wilderness of northern Canada and its Arctic islands, travelling in small parties and living off the land. In 1844–1845 he walked 1200 miles (1930 km) in two months, earning the nickname ‘Agloqua’ – ‘he who takes long strides’ – from the Inuit. He was involved in the search for the Franklin expedition and was condemned by the British establishment for suggesting that members of Her Majesty’s Royal Navy had resorted to cannibalism.

Telecomms entered Rae’s life again in 1860 when the Atlantic cable failed (again). A new route was sought through Faroe, Iceland and Greenland, and he was sent to assess the landward part of the route. Then, in 1884, aged 71, he was involved in a project to investigate the possibility of a telegraph route through British Columbia to Siberia, and explored a great length of the mighty Fraser River, without a guide, using a dugout canoe. This great man died in London in 1893, in his 80th year. His only memorial is a statue in St Magnus Cathedral in Kirkwall, Orkney, showing him lying down as in the open, wearing his Arctic travelling clothes, a gun at his side.

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The images above show a sample from a high pressure experiment. It was conducted with a multianvil press in order to investigate how deformation textures are affected by phase transformations. An EBSD phase map (raw data), an EBSD orientation map (IPF-X, only aragonite selected) and an EDS map of the same area are shown from left to right. Both EBSD datasets overlay the pattern quality map. The simultaneous EDS and EBSD measurement ensures conclusive results (calcite and aragonite can only be distinguished using EBSD).

Sample courtesy of Dr. Florian Heidelbach, Bayerisches Geoinstitut, Universität Bayreuth.

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