Thermodynamics of Earth Systems

PASCAL RICHET, GRANT S. HENDERSON, and DANIEL R. NEUVILLE, Guest Editors

Thermodynamics in a Nutshell
Processes in the Moist Atmosphere
Effects of Ocean Acidification
Water–Rock Interaction
Equilibrium in Metamorphic Rocks
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Thermodynamics of Earth Systems
Guest Editors: Pascal Richet, Grant S. Henderson, and Daniel R. Neuville

Thermodynamics: The Oldest Branch of Earth Sciences?
Pascal Richet, Grant S. Henderson, and Daniel R. Neuville

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Andreas Bott

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About the Cover:
From the atmosphere to the mantle and core, Earth systems are strictly controlled by thermodynamic principles. Hurricanes, such as Katrina shown on the front cover, result from strong interactions between the ocean and atmosphere and are powered by the thermal energy stored in warm oceanic waters. AVHRR (Advanced Very High Resolution Radiometer) 3-channel color composite daytime image showing the eye of hurricane Katrina on August 28, 2005, just before it hit New Orleans. Courtesy of Steven Barn and Ray Sterner of the Johns Hopkins University Applied Physics Laboratory.

Perspective: On Being a Student of Thermodynamics
Reid F. Cooper
The Mineralogical Society of America is a national society for all scientists involved in the knowledge of mineralogy, crystallography, geochemistry, petrology, and their applications to earth sciences. The Society promotes, through education and research, the understanding and application of mineralogy by industry, universities, government, and the public. Membership benefits include a 25% discount on subscriptions to Reviews in Mineralogy and Chemistry, lists of Monographs, Elements, reduced registration fees for MSA meetings and short courses, and participation in a society that supports the many facets of mineralogy.

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

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The Geological Society (GS) is an international organization founded in 1958 for the benefit of students and scientists involved in the practice, study and teaching of geochemistry. Our programs include co-hosting the annual Goldschmidt Conference, editorial oversight of Geochemica et Cosmochimica Acta (GCA), supporting geochemical symposia through our Meeting Assistance Program, and supporting student development through our Student Travel Grant Program. GS annually recognizes excellence in geochemistry through its medals, lectures and awards. Members receive a subscription to Elements, special member rates for GCA and G-cab, and publication and conference discounts.

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The German Society for Mineralogy (GS) is an international society for mineralogy. Membership benefits include reduced registration fees for the annual meeting. Membership is open to those who have earned a Ph.D. or its equivalent in mineralogy and related fields. Membership benefits include reduced registration fees for the annual meeting.

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The Deutsche Gesellschaft für Mineralogie (German Mineral Society) was founded in 1910 to further the knowledge of mineralogy and its applications. Membership benefits include the annual GeoJournal, Geochemistry: Exploration, Environment, Analysis, the AAG newsletter, EXPLOR, and Elements.

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The Clay Minerals Society is an international organization founded in 1953 for scientists, collectors, and educators to advance the study of meteorites and other extraterrestrial materials and their parent asteroids, comets, and planets. Membership benefits include reduced registration fees for SFMC meetings.

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The Association of Applied Geochemists is an international organization founded in 1970 that specializes in the field of applied geochemistry. The AAG aims to advance the science of geochemistry as it relates to exploration and the environment, further the common interests of exploration geochemists, facilitate the exchange of scientific knowledge, promote the exchange of information, and encourage research and development in the field of applied geochemistry. Membership includes the AAG journal, Geochemistry: Exploration, Environment, Analysis; the AAG newsletter, EXPLOR; and Elements.

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The Polskie Towarzystwo Mineralogiczno-Petrologiczne (Polish Mineralogical Society) was founded in 1969, draws together mineralogists and petrologists interested in mineralogy, crystallography, geochemistry, and economic geology. The Society promotes links between mineralogical science and education through its annual conferences, field trips, invited lectures, and publishing. Membership benefits include subscriptions to Mineralogia and Elements.

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The Mineralogical Society of Poland is a national society for all scientists involved in the knowledge of mineralogy, crystallography, petrology, and geochemistry. Membership benefits include reduced registration fees at annual conferences, field trips, invited lectures, and publishing. Membership benefits include subscriptions to Mineralogia and Elements.

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The Mudrock Association of Petroleum Geologists was founded in 1975 to promote the science of geochemistry in the public and private sectors.

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The Clay Minerals Society is a national society for all scientists involved in the knowledge of mineralogy, crystallography, geochemistry, petrology, and their applications to earth sciences. The Society promotes, through education and research, the understanding and application of mineralogy by industry, universities, government, and the public. Membership benefits include a 25% discount on subscriptions to Reviews in Mineralogy and Chemistry, lists of Monographs, Elements, reduced registration fees for MSA meetings and short courses, and participation in a society that supports the many facets of mineralogy.

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The Ceramic Society of America is a national society for all scientists involved in the knowledge of mineralogy, crystallography, geochemistry, petrology, and their applications to earth sciences. The Society promotes, through education and research, the understanding and application of mineralogy by industry, universities, government, and the public. Membership benefits include a 25% discount on subscriptions to Reviews in Mineralogy and Chemistry, lists of Monographs, Elements, reduced registration fees for MSA meetings and short courses, and participation in a society that supports the many facets of mineralogy.

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The Mineralogical Society of Great Britain and Ireland is an international society for all scientists involved in the knowledge of mineralogy, crystallography, geochemistry, petrology, and their applications to earth sciences. The Society aims to advance the science as well as other journals, a 25% discount on subscriptions to Reviews in Mineralogy and Chemistry, lists of Monographs, Elements, reduced registration fees for MSA meetings and short courses, and participation in a society that supports the many facets of mineralogy.

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When I was first exposed to thermodynamics as an undergraduate, I felt like the kid who opened the balloon to see how it works: I wasn’t left with much. It seemed like smoke and mirrors. Why would anyone envision such an intangible and non-intuitive way to understand chemical reactions? And, who came up with this approach in the first place?

I’ve since learned to appreciate, even delight in, the elegance of thermodynamics. We all have J. Willard Gibbs to thank. Nowadays, his name is almost universally recognized by scientists and engineers. Even the first letter of his surname is forever memorialized as the symbol for Gibbs free energy (the U.S. National Bureau of Standards uses $G$ rather than $G_t$, but the latter is recommended by the International Union of Pure and Applied Chemistry). His visage even graces a U.S. postage stamp, a rare honor for a scientist. During his lifetime, though, Gibbs’s genius mostly went unacknowledged, especially in his native America. Gibbs was educated at Yale University, and in 1863 received the first PhD in engineering awarded in the United States. After spending a year each in Paris, Berlin, and Heidelberg, he returned to Yale as Professor of Mathematical Physics, a position he held until two decades after his death, with the 1923 publication of Lewis and Randall’s classic chemistry text, Thermodynamics and the Free Energy of Chemical Substances.

Gibbs’s thermodynamics first found application in physics, then chemistry, and later engineering. Its utility in geology had to wait until enough data on the thermodynamic properties of compositionally complex minerals, melts, and fluids became available. The phase equilibria experiments of Norman Bowen, carried out between 1912 and 1956, constituted an important part of that data set. Bowen was educated in both geology and chemistry, and he surely was familiar with Gibbs’s work. Surprisingly, though, in leafing through Bowen’s The Evolution of the Igneous Rocks (1928), I could find no mention of Gibbs or even of any thermodynamic functions. Victor Goldschmidt’s Geochemistry, published posthumously in 1956, explains the chemical affinities of elements for oxide, silicate, sulfide, and metal phases in terms of their free energies of formation, but again Gibbs’s name is nowhere to be found. The first textbooks that really showed mineralogists, petrologists, and geochemists how to apply thermodynamic principles were authored by Robert Garrels in 1960 (Mineral Equilibria at Low Temperatures and Pressures) and by Raymond Kern and Alain Weibrod in 1964 (Thermodynamique de Base pour Minéralogistes, Pétrographes et Géologues). After a slow start, Gibbs’s concepts have become indispensable parts of our science.

I’ve heard it said that the sincerest form of flattery for scientists is to have their contributions become so ingrained that they need no reference. Gibbs should truly be flattered. I looked through my extensive collection of modern mineralogy, petrology, and geochemistry texts, and not a single one references his published work. Any reference to him (if there is one at all) only acknowledges his derivation of the phase rule, although our community did christen a mineral (gibbsite) in his honor. Thermodynamics is manifestly one of those areas where we stand on the shoulders of a giant. Thanks Dr. Gibbs, on behalf of geoscientists everywhere.

Hap McSween, University of Tennessee (mcsween@utk.edu)
**THIS ISSUE**

Guest editors Richet, Henderson, and Neuville take us from the atmosphere to the deep Earth with the seven papers they have assembled for this issue. In each of the illustrated Earth systems, thermodynamic principles can be applied to get a better understanding of the processes shaping them. Thermodynamics is more needed than ever: as is eloquently demonstrated, it can give insight into real global problems. As for me, I gained a new respect for clouds and raindrops after reading Andreas Bött’s paper. I wish you all some interesting discoveries.

Two new features make their debut in this issue. The Elements Toolkit (page 277) will present new technological developments of interest to our readers. The plan is to publish it every other issue. You can send your ideas and suggestions for coverage to Michael Wiedenbeck (michaelw@gfz-postdam.de), the feature editor.

David Mogk will coordinate our new Teaching MGP feature. In it, he or an invited contributor will present resources that are available for teaching the topic of the issue. In his first contribution, David illustrates the wealth of information available to teachers of thermodynamics (page 326).

Readers can contribute to many other features:

**Letters to the Editors:** Has an editorial spurred some thoughts? Have you a short news item of interest to the membership of Elements? Consider submitting a letter to the editor (treml@iet.inrs.ca).

**Triple Point** raises issues of broad interest. Since volume 1, this feature has explored different aspects of our science (teaching, publishing, historical aspects, etc.), our societies, funding, policy, and political issues. Contact Bruce Yardley (B.W.D. Yardley@leeds.ac.uk) or Marty Goldberg (mgold@usgs.gov) if you have an idea for a future topic.

**Elements’ Impact Factor Climbs to 3.569**

We are pleased to report that Elements’ impact factor is continuing the climb it started in 2006. Elements, launched in 2005, received its first impact factor from the Institute of Scientific Information for 2006 (1.562). The following year, its impact factor rose to 2.23. And from 3.069 in 2008, it climbed to 3.569 in 2009.

The 10 most cited articles from the time of publication to July 2010 were:

- The issues that have garnered the most citations are: Zircon (2007, v3n1, 174 citations); Arsenic (2006, v2n2, 163); Large Igneous Provinces (2005, v1n1, 105); Diamonds (2005, v1n2, 90); The Nuclear Fuel Cycle (2006, v2n6, 54); and Supervolcanoes (2008, v4n1, 65).

**THE OTHER SIDE OF THE COIN: BASIC RESEARCH IN U.S. UNIVERSITIES**

Passionate identification with basic research is often expressed in the U.S. scientific community. Peer-reviewed publications in basic-research disciplines dominate criteria for academic appointment, promotion, and tenure in American academic science departments. The U.S. National Science Foundation, whose policies since its founding in 1950 have largely excluded applied research, received an additional $3 billion through the Obama Administration’s Recovery Act budget in 2009.

Thus, I did a double take when I read in Susan Stipp’s parting editorial (Elements, June 2010) that “in the last 20 years basic research has become unpopular.” The contradiction was clarified when background research revealed that Stipp is head of the University of Copenhagen’s NanoGeoScience Centre, whose purpose is to foster applied research and train students whose employment would largely be in private industry. Denmark’s strong emphasis on applied research is mirrored in all other leading EU nations except the UK.

My recent comparisons between American and German institutions for chemistry and engineering offered wake-up calls. Distinguished American chemistry departments’ websites call attention to cutting-edge research and lists of peer-reviewed publications by faculty. Their German counterparts call no publications (although they certainly have them). Instead, they emphasize research and curricula that relate to the needs of society and prepare students to take up meaningful and challenging work.

The Technical University of Munich’s main divisions resemble those of the Georgia Institute of Technology (highly rated by NSF). But there the similarity stops. Georgia Tech’s schools have a strong independent research focus, and half the buildings on campus are devoted to languages, arts, humanities, sports facilities, and other functions. In contrast, TUM is focused on research and teaching that directly serves German social needs and industry. Specialized master’s programs, including administration and management, as well as doctoral programs, are closely coordinated with internship programs sponsored by German engineering and industrial firms. This system allows graduates to move smoothly into industrial jobs upon graduation.

These and other purposeful features let me understand why the U.S. has only 13% of its university students majoring in science and engineering, while Germany has 30–40%. And those graduates have rewarding and more stable futures ahead of them. In 2007 Germany had a trade surplus of $250 billion, whereas the U.S. had a deficit of nearly $900 billion. Germany’s rebound is now bringing it closer to precrash conditions. The U.S. anticipates no foreseeable break in the ongoing retrenchment of its research universities.

Germany’s industries are now world leaders in both renewable energy development and conventional manufacturing. Relegating applied research in U.S. universities to second-class status has helped create a stigma on American industry (including the minerals industry). Now there is no longer the “Golden Age of Research” that blossomed in the 1960s and 1970s.

There is much more to this story, the history of which I trace in a chapter of a book published in my new specialty of public policy research* (in my former career I concentrated on marine geochemistry and hydrochemistry). I suggest that if the U.S. scientific community takes voluntary initiatives and broadens its goals, it will be in a better position to aid economic recovery and retain the independence it now enjoys. If, on the other hand, the economy continues to sour, at some point Congress may discover that other nations are making better use of their scientific talent than the U.S., and then changes may be drastic.

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* The Conflict over Environmental Regulation in the United States: Origins, Outcomes and Comparison with the EU; Springer 2009, 321 pp

FROM THE EDITORS

Pierrette Tremblay
Managing Editor

LETTER TO THE EDITORS

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* The Conflict over Environmental Regulation in the United States: Origins, Outcomes and Comparison with the EU; Springer 2009, 321 pp
WELCOME TO THE TOOLKIT

From my laboratory perspective, I see scientific progress as a dynamic and ever-evolving human endeavor. This is certainly true for the Earth sciences, where lengthy periods of filling in the puzzle pieces are punctuated with breakthroughs in our understanding of how our planet works. But how are such leaps in knowledge achieved? Three aspects appear to interact to bring a sudden surge in our comprehension of nature:

- A steady flow of seemingly unrelated observations suddenly crosses a threshold where some new “truth” becomes apparent: the “long, hard toil route.”
- Discovery resulting from a new research strategy leads to a fully unanticipated conclusion: the “serendipitous route.”
- Finally, progress frequently can be attributed to “breakthrough technologies,” which flow into the hands of the broad research community.

An example of this last route to discovery is the explosion in data resulting from the introduction of laser ablation sampling technology in conjunction with ever-improving mass spectrometric methods. Over the past decade or two, this cost-effective and rapid analytical method has become an essential tool for many colleagues. Certainly, some of the resulting data are of questionable significance or dubious quality—as always, the value of the data rests in the hands of the individual practitioner. Nonetheless, it would be difficult for me to imagine modern-day geochemistry without the existence of laser ablation technology.

“The Elements Toolkit” is a feature that the editors of this magazine have asked me to provide at regular intervals, roughly every second issue. My goal is to present new technologies that seem to offer great potential to the research community. I will also highlight instrumentation or software that I see as powerful but underutilized tools of our trade. Perhaps my musings will give the broader community a picture of key strategies being applied in other disciplines. Of course, I would only be too happy if the dissemination of such ideas into the hands of the adventurous were to lead to serendipity...

I hope that you will find this and the upcoming Toolkit articles of interest. Perhaps some of the resources that I present will actually prove useful in your own research. And now, as a first contribution, I would like to briefly present a web resource that provides a glimpse of what might become in a few years “standard methodology” for Earth science researchers.

The Global Registration of Geologic Sampling

Have you ever felt that it would be really useful to have a list of all samples that have been collected in or near your field area? Of course, such a database would ideally provide both a basic description of the material and information about where one should look to obtain part of said sample. Better still, wouldn’t it be great if the sample numbers were linked to all literature citations in which the material is mentioned? And wouldn’t it also be a big advantage if all sample designators were unique and unambiguous? Well, such a web resource has been under construction for the past couple of years. The International Geo Sample Number (IGSN) registry, managed by the System for Earth Sample Registration (SESAR), addresses these issues. An IGSN is a unique and persistent identifier for geomatials, and such an identifier can easily be assigned by registering sample properties with SESAR via the Internet. If data in a publication are referenced to an IGSN, then key information about the sample can rapidly be retrieved from the SESAR database. Have a look at http://www.geosamples.org/.

As an example of what one might learn from this database, my search of all records from South Africa reports a total, as of mid-September 2010, of 603 registered samples. This certainly not a comprehensive record of geoologists’ activities in the country, but nonetheless it is a useful starting point. In addition to using this database with a geographic filter, it is also possible to conduct a search based on rock type. As a test, I randomly selected a filter based on intermediate plutonic rocks, the net result being only three entries, a rather meagre yield for fans of monzonite. This low result is despite the fact that some 4 million records are registered in the system. Looking at individual records, one finds many characteristics reported as “not provided,” meaning extra time at the computer will be necessary to determine if a given sample is relevant for the topic of study. Nonetheless, despite these shortcomings, this tool might already prove valuable to many, and one can hope that such a system will win ubiquitous support from the field geologists and lab analysts of the future. Interested in finding out a bit more? Have a look at “Facilitating Research in Mantle Petrology with Geoinformatics,” by K. Lehnert and J. Klump (2008) (www.cosis.net/abstracts/91KC/00250/91KC-A-00250-1.pdf).

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ABOUT THE AUTHOR

M ichael Wiedenbeck is in charge of the Potsdam Secondary Ion Mass Spectrometry facility, a position he has held since December 1998. He began his career as an isotope geochemist at the ETH-Zürich, being trained in the art of K–Ar and Rb–Sr age determinations. Having discovered that wet chemical isotope work can involve a Herculean struggle against the laboratory blank, he decided to move to Australia to become one of the early practitioners in the then emerging field of ion probe geochronology. His work on the Archean of Western Australia brought with it the epiphany that data quality in analytical geochemistry is critically dependent on access to high-quality calibration materials. Leaving Canberra, his next move was back to Europe, to the CRPG in Nancy, France, where he devoted a year’s effort to finding and characterizing homogeneous zircon crystals for calibrating U–Th–Pb age determinations. Subsequent career stops included Ahmedabad, India (more Archean SIMS geochronology); Oak Ridge, Tennessee (building a new type of SIMS instrument); and Albuquerque, New Mexico (running a multi-user SIMS facility).

Michael’s position as a senior scientist at the Helmholtz Center Potsdam has allowed him to invest a significant effort toward his passion for improving metrology in analytical geochemistry. Through his involvement with the International Association of Geoanalysts, of which he has been president since 2006, Michael has been involved with the ISO-based certification of five whole-rock Reference Materials; these remain some of the best-characterized Earth materials ever produced. With this experience in the production of highest-quality reference materials for bulk analytical methods, he is now turning his attention towards the needs of the microanalytical community.
GEOCHEMICAL JOURNAL AWARD FOR 2010 TO BAU AND KOSCHINSKY

The Geochemical Society of Japan, publisher of the Geochemical Journal, is proud to announce that the paper entitled “Oxidative scavenging of cerium on hydrous Fe oxide: Evidence from the distribution of rare earth elements and yttrium between Fe oxides and Mn oxides in hydrogenetic ferromanganese crusts” (Geochemical Journal 43: 37-47, 2009), co-authored by Prof. Michel Bau and Prof. Andrea Koschinsky of Bremen University, has been selected for the 2010 Geochemical Journal Award.

This award was created in 2003 to commemorate the 50th anniversary of the Geochemical Journal and was first awarded at the Goldschmidt Conference in Kurashiki. Every year, the Geochemical Journal Award honors the authors of outstanding research articles published during the previous year in the Geochemical Journal.

In their paper, Drs. Bau and Koschinsky present and discuss experimental data on the partitioning of redox-sensitive rare elements, such as cerium, between Fe and Mn oxides. The strongest point in this paper is that both the Mn oxides and the Fe oxides display pronounced positive Ce anomalies of almost identical size. This suggests that in the natural marine system oxidative scavenging of Ce from seawater is not restricted to Mn oxides but also occurs on hydrous Fe oxides, a phenomenon that was not previously well documented. Furthermore, preferential Ce removal from seawater does not result from the oxidation of dissolved Ce(III) within the marine water column; rather, Ce(III) is oxidized after its sorption at the metal (hydr)oxide surface.

This paper contributes to the understanding of the behavior of rare elements in ocean water, a field in which Dr. Bau is one of the leading geochemists. Understanding the behavior of peculiar rare elements, such as cerium, is fundamental for using them as paleoredox proxies.

“ELEMENTS 5” SPEAKERS AT IMA 2010

As part of Elements’ 5th anniversary celebrations, IMA 2010 presented a series of plenary lectures by guest editors and authors of previous issues of the magazine. We extend our thanks to these contributors for having enthusiastically responded to Ian Parsons’ and David Vaughan’s invitation to join in this celebration. We also thank the organizers of IMA 2010 for having given prominence to these lectures.

Éva Valsami-Jones (Natural History Museum, UK), co-guest editor of volume 4, number 2 (Phosphates and Global Sustainability), in the opening “Elements 5” lecture, summarized the different aspects of the global phosphorus cycle and presented results of the study ofapatite at the nanoscale.

Rod Ewing (University of Michigan, USA), founder of Elements and guest editor of volume 2, number 6 (The Nuclear Fuel Cycle), highlighted the role of mineralogy and geochemistry in the treatment of nuclear waste.

Nigel Kelly (Colorado School of Mines, USA) was a co-guest editor of volume 3, number 1 (Zircon). The zircon issue has the distinction of being the most heavily cited of all issues we have published so far. In his presentation, Nigel showed how research is helping to improve the interpretation of zircon ages and gave an overview of the processes that can be traced with individual grains.

Mihály Pósfai (University of Pannonia, Hungary), an author in the Mineral Magnetism issue (volume 5, number 4), presented a talk on magnets in organisms and how they can help us understand the mechanisms of magnetic sensing by organisms.

Nita Sahai (University of Wisconsin–Madison, USA), guest editor of the Medical Mineralogy and Geochemistry issue (volume 3, number 6), gave a talk on mineral interactions with the human body—some medically beneficial and some harmful.

Glenn Waychunas (Berkeley Nanogeoscience Center, USA) spoke about mineral–water interfaces and nanoparticles. He was an author in the Nanogeoscience issue (volume 4, number 6).
The memory of the Earth –
New tools to retrieve the information.

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On Being a Student of Thermodynamics: Trust Your Eyes; Use Your Imagination

Reid F. Cooper*

I am a student of thermodynamics. Yes, I have been teaching the subject to baccalaureate and graduate students in petrology and materials science for about 25 years. But in every course, almost every lecture, I perceive something new: some new (to me) subtlety in the ideas that facilitates deeper appreciation and understanding of some of the experimental data generated in my research group and that fosters a profound admiration for the many scholars who brought forth these ideas in the nineteenth century and refined them in the twentieth. In this process, I have identified and shared with my fellow learners two pieces of advice that are particularly valuable in applying thermodynamics to the analysis of textures in rocks, which is so very often the center of our interest in thermodynamics: trust your eyes; use your imagination. Let me explain, or at least try...

The textures of rocks—that is, the spatial distribution of minerals, the morphologies of the interfaces between grains (grain and heterophase boundaries), and the spatial differences of oxide composition (including compositional gradients)—are a result of a convolution of thermodynamics and kinetics. Beginning petrology students frequently struggle to understand that there is no textural information in an equilibrium phase diagram (indeed, there is no time in equilibrium thermodynamics). The amount of creative synthesis involved in the thought experiment of logically stepping through a time (t)—temperature (T)—pressure (P) protocol with an equilibrium phase diagram so as to predict a texture is profound. I might add that learning to teach this synthesis is simultaneously humbling and rewarding. For many students of petrology, this is the first example and practice of “trusting your eyes” in doing predictive science: we (the community) construe that the texture observed is a result of a chemical system subjected to a time-varying set of thermodynamic potentials, and so we apply equilibrium thermodynamic arguments—like phase diagrams—step-wise in time to develop an interpretation that is extrapolative.

One can learn to trust one’s eyes at a finer scale, too, which is particularly important in studying mineral reactions. As a simple, practical, and provocative illustration, consider the oxidation of solid-solution, ferromagnesian olivine beyond its stability limit. For the fayalite end-member, the chemical reaction is straightforward:

\[
3\text{Fe}_2\text{SiO}_4 + O_2 = 2\text{Fe}_3\text{O}_4 + 3\text{SiO}_2 ; \Delta G^0_{\text{FMQ}} ,
\]

fayalite + oxygen gas = magnetite + \(\alpha\)-quartz

where \(\Delta G^0_{\text{FMQ}}\) is the standard Gibbs free energy of this reaction. If we were considering the oxidation breakdown of pure fayalite, this reaction would describe the FMQ (fayalite–magnetite–quartz) oxygen buffer. In the actual case of ferromagnesian olivine, though, the fayalite component is dissolved into forsterite; as a consequence, the reaction (at a given \(P\) and \(T\)) would occur only at an oxygen activity (fugacity) that is greater than FMQ. The reaction texture is illustrated schematically in Figure 1. When exposed to an oxygen activity exceeding the stability of the fayalite component (e.g. annealing at ~900 °C and 1 atm in air), one discovers that the texture of the incomplete reaction includes (1) a specular, polycrystalline thin film of periclase (MgO) and magnesioferrite (MgFe\(_2\)O\(_4\)) covering the original surface (between \(\xi = 0\), the original surface, and \(\xi = \xi'\)); (2) fine (nanometer-scale) precipitates of pure magnetite (Fe\(_3\)O\(_4\)) and amorphous silica precipitated on lattice dislocations in the olivine and existing in a “matrix” of pure forsterite between \(\xi = 0\) and an internal reaction interface \(\xi = \xi''\); and (3) yet-to-be-reacted olivine solid solution at \(\xi'' > \xi''\) (Wu and Kohlstedt 1988). This process is “dislocation decoration”; deformation-effected dislocations in olivine can be studied with standard petrographic techniques following such oxidation (Kohlstedt et al. 1976); see Figure 2.

A strange texture! The reaction has not produced an equilibrium assemblage within the olivine: forsterite and silica should react to form enstatite (MgSiO\(_3\)); the chemical potential of MgO in the forsterite is sufficiently high that magnesioferrite should form instead of magnetite. The assemblage is metastable: if the specimen is annealed at high temperature for a time very, very long compared to that required for the reaction front at \(\xi = \xi'\) to march through, say, a millimeter-scale experimental specimen, enstatite and magnesioferrite will form. Not evident in the schematic, but important in the texture nevertheless, is the fact that microprobe analyses of the forsterite matrix between 0 and \(\xi''\) and ion-backscattering spectrometry analyses of the (new) surface thin film reveal no concentration gradients whatsoever of the component ions.

What, then, can be said? Trust your eyes! The magnetite (Mt) and silica (Sil) precipitated on the dislocations are pure; the activity of each is unity, to first order (the Gibbs free energy of \(\alpha\)-quartz and vitreous silica being quite similar). Thermodynamically, then, the reaction is easily analyzed. Using the mass-action equation,

\[
K_{eq} = \frac{a_{\text{Mt}}^2 a_{\text{Sil}}}{a_{\text{O}_2}^3} \equiv \exp \left( -\frac{\Delta G^0_{\text{FMQ}}}{RT} \right),
\]

where \(K_{eq}\) is the equilibrium constant and \(a_i\) is the activity of species \(i\), one can substitute unity for \(a_{\text{Mt}}\) and \(a_{\text{Sil}}\) and so discern the trade-off between the activity of fayalite (\(a_{\text{Fay}}\)) in the olivine solid solution and the oxygen activity (\(a_{\text{O}_2}\)) at which the fayalite component is no longer stable.

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**FIGURE 1** Schematic diagram of the (incomplete) oxidation of ferromagnesian olivine beyond its limit of stability. The original surface is at location 0. The reaction sees both external and internal reaction fronts, \(\xi\) and \(\xi''\), respectively. Reaction products include phase-pure magnetite and vitreous silica in a matrix of pure forsterite (Wu and Kohlstedt 1988).
The text and context reveal more. In this example, the oxygen activity at the free surface, $\xi$, is that of air (i.e. $a_{O_2} = 0.21$). The oxygen activity at $\xi'' = 0$ is that at which the olivine solid solution is no longer stable (as discerned from $K_{eq}$). So, clearly, there is a gradient in the chemical potential of oxygen ($\mu_{O_2}$) within the reacting specimen, i.e. $d\mu_{O_2}/d\xi = RT(d\ln a_{O_2}/d\xi^-)$. And yet, as already noted, one cannot identify concentration gradients of ion species between $\xi$ and $0$ and between 0 and $\xi''$. The thin film at the surface is a mixture of magnesium and ferric-iron oxides: there is no $SiO_2$ component in this two-phase film. The silica-free, surface thin film is critical in interpreting the dynamics of the reaction.

And so the second exhortation: use your imagination. Interpreting the texture to comprehend the dynamics in this case involves identifying the physical manifestation of the oxygen activity in olivine. Now, the thermodynamics we teach in petrology classes is typically that of Clausius, Joule, and Gibbs, which is based on state variables, that is, entropy, entropy, Gibbs free energy, and activity. These are ensemble or average values representative of the bonding and the vibrational/translational “chaos” of ions and molecules making up a system: “black-box” variables masking an atomic reality. The activity of a component in a mineral has as its physical manifestation a collection of point defects on the lattice. Point defects in minerals are atomic vacancies, substitutionals, and interstitials; they are equilibrium defects: there is sufficient entropy associated with their deployment on the lattice to “overcome” the enthalpy of their formation. The concentration of these defects rarely reaches 0.1 atomic percent, making their quantitative characterization beyond the capabilities of, for example, X-ray spectrometry on a microprobe. One employs imagination in the sense of contemplating the variations of concentrations of defects at different locations within a reaction microstructure: if there are activity gradients, there must be, physically, gradients in the concentrations of point defects.

The physical manifestation of the oxygen activity in olivine is a charge-compensating pair of point defects—vacancies on the divalent-cation ($Me^{2+} = Mg^{2+}$ and $Fe^{2+}$) sublattice (octahedral sites in the $O^2-$ array) and ferric-iron ions ($Fe^{3+}$) on the octahedral sites. It ends up that point defects in minerals have actual charges, that is, their presence in the lattice locally distorts the electronic structure of the mineral. Vacancies on the divalent cation sites in olivine have a 2− charge. $Fe^{3+}$ occupying a site where an $Fe^{2+}$ is “normally” present has an additional +1 charge. Creating this latter defect requires only the removal of an electron from the $Fe^{2+}$ present originally; the “lost” electron—called an electron “hole”—is highly mobile and easily “hops” from one iron ion to another nearby in the crystal.

Equilibrium thermodynamics is enforced for point defects: one can articulate defect-formation reactions, but these have requirements not only of conservation of matter but also of conservation of charge and, in minerals, conservation of lattice sites (that is, conservation of the mineral structure proper). So, relating oxygen activity to defect concentration in olivine can be written as:

$$3Fe^{2+}_{Me} + \frac{1}{2}O_2 = 2Fe^{3+}_{Me} + V^{Me}_S + FeO = 2h^+ + V^{Me}_S + FeO ; \Delta G^o$$

In this (Kröger-Vink) notation, the subscripts refer to lattice sites and the superscripts refer to charge on that site relative to whatever species occupies the site in the perfect crystal (e.g. Schmalzried 1981, p. 39). Thus, $Fe^{2+}_{Me}$ is an Fe$^{2+}$ occupying an appropriate $Me^{2+}$ octahedral site; it is electrically neutral (“X”) as a divalent cation normally occupies the site. A “dot” superscript denotes relative positive charge; a “prime” superscript denotes relative negative charge. Thus, $Fe^{3+}_{Me}$ is an $Fe^{3+}$ occupying a $Me^{2+}$ site (because of the high mobility of charge transfer, it is identified alternatively as an electron hole, $h^+$), and $V^{Me}_S$ is an octahedral-site vacancy with a 2− charge. Note the balances: beyond mass conservation, charge neutrality is maintained on both sides of the equation, as is site conservation (three octahedral sites accounted for on each side). Mass-action applies:

$$K_{eq} = \frac{a^{2+}_{Fe^{3+}}a^{Me}_{V^{Me}_S}a^{FeO}_{Fe^{2+}}}{a^{Fe^{3+}}_{Me}a^{1/2}_{O_2}} = \exp\left(-\frac{\Delta G^o}{RT}\right).$$

In the equation, the activities of $Fe^{3+}_{Me}$ and FeO are essentially fixed (constant), set by the situation, that is, by the fayalite composition of the olivine and by the fact that olivine (in its natural context) is also in equilibrium with orthopyroxene. Thus, one sees in the equation that an increase in oxygen activity results in an increase in the activities—and so the concentrations—of the defect species $h^+$ and $V^{Me}_S$.

One realizes, then (trust your eyes!), that in the olivine the equilibrium concentrations of vacancies and holes are much higher at $\xi = 0$ than at $\xi''$: flux of the defects “inward” ($j_{V^{Me}_S}$ and $j_{h^+}$ and attendant arrows in FIGURE 1) and the physically required counterflux of $Me^{2+}$ “outward” ($j_{Fe^{3+}_{Me}}$) is how the external oxygen activity is transferred into the reacting crystal. The loss of the cations from the olivine to the free surface—where they react with environmental oxygen to produce the silica-free, oxide thin film (plus $h^+$)—means that the divalent cation/oxygen anion ratio within the olivine is decreasing. The olivine oxidizes internally not by adding oxygen but rather by losing cations; too, one sees that oxidation occurs not by diffusion of an oxygen species but rather by the diffusive motion of the divalent cations in response to a gradient in $\mu_{O_2}$ (and proceeds at the rate of the cation flux). The high mobility of the electron holes “decouples” the fluxes of anions and cations, which is critical in facilitating the dynamics and so the texture. All minerals containing even low concentrations of transition-metal cations can anticipate similar decoupling.

This is a rather simple example of a thermodynamic approach to apprehending the development of a complex texture. As a fellow student, what I recommend is identifying points in a reaction texture where one can identify unequivocally (eyes!) values of certain chemical potentials (activities) and ask how those points “communicate” via defects (imagination!). Dealing similarly with more complex textures, for example, the development of a metamorphic symplectite, involves additional thought and information regarding, for instance, interface stability. Nevertheless, the eyes/imagination approach still applies, and is quite powerful. 

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**FIGURE 2** Dislocations in experimentally deformed San Carlos (AZ) peridot (transmitted, plane-polarized light). The ubiquitous dark dots are dislocation lines viewed end-on. The dislocations are visible because the crystal has been oxidized subsequent to deformation. This is the structure imaged between 0 and $\xi''$ in FIGURE 1.
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Frank J. Millero, professor of marine and physical chemistry at the Rosenstiel School of Marine and Atmospheric Science, University of Miami, received his BS (1961) from Ohio State University and his MS (1964) and PhD (1965) from Carnegie Mellon University in physical chemistry. After a brief interval in industry, he moved to the University of Miami in 1966. From 1986 to 2006 he was Associate Dean of Academic Studies at the School. He serves as an associate editor for a number of journals, and since 1993 has been editor-in-chief of Marine Chemistry. Millero’s research includes studies of the global carbon dioxide cycle in the world’s oceans, ionic interactions in seawater, trace metals in natural waters, and ocean acidification.

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Roger Powell is an ARC Australian Professorial Fellow in the School of Earth Sciences at the University of Melbourne. Following his first degree at the University of Durham, he did a DPhil at Oxford from 1970 to 1973. Following short stints elsewhere, he taught at the University of Leeds from 1975 to 1984. He then moved to the antipodes where he remains. He works on the application of mathematics, statistics, and thermodynamics to metamorphic rocks, and also provides software implementations of solutions to problems. The core of his work continues to be carried out in collaboration with Tim Holland.

Pascal Richet is a senior geophysicist at the Institut de Physique du Globe de Paris. He works mainly on the physics of minerals and melts under wide temperature and pressure ranges. In addition, he is involved in transferring fundamental research to problems of industrial interest and writes articles and books to promote the popularization, history, and philosophy of science. Examples are the \textit{Guide to the Volcanoes of France} and the \textit{Guide to the Volcanoes of French Overseas Territories} (Editions Belin, Paris, 2003 and 2007, both in French).

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Thermodynamics:
The Oldest Branch of Earth Sciences?

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1811-5209/10/0006-0287$2.50 DOI: 10.2113/gselements.6.5.287

All geological changes result from the transfer of matter and energy, the study of which is the goal of thermodynamics. Investigating natural processes thus necessarily involves thermodynamic considerations. This has long been practiced implicitly, as shown by the smart reflections made by “natural philosophers” from antiquity to the 18th century about topics ranging from atmospheric phenomena to the early history of the Earth. Since the early 19th century, investigations explicitly take advantage of a rigorous framework that deals with chemical and thermal aspects of the Earth’s activity. Far from being abstruse, these principles can in fact be summarized in a simple and concise way.

**Keywords:** Earth’s history, phase changes, solution models, thermodynamic principles

**INTRODUCTION**

*Thermodynamics.* The word sounds intimidating. The heat engine, complicated cycles and the entropy conundrum come to mind. And when geological applications are mentioned, people often wonder how useful results can be obtained for an object as complex and as big as the Earth. As a matter of fact, the newly born science called *thermodynamics* rapidly tackled many problems that were far removed from the mutual conversion of heat and work. Its theoretical framework was so flexible that, as shown by J. W. Gibbs (1839–1903), it could also account for any kind of chemical transformation. This should not have come as a surprise. Ever since the very beginning of science in Greece, natural phenomena had been a rich source of reflection. Without knowing it, early “natural philosophers” practiced thermodynamics qualitatively. The fundamental problem of change, which was at the basis of their thought, would in fact fall fully within the precinct of this discipline. Indeed, change results from transfer of matter and energy among the various parts of any system. This issue of *Elements* thus gathers a series of short reviews illustrating how thermodynamic methods are used to derive valuable information about the present and past of our planet, from its atmosphere to its core.

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**THERMODYNAMICS WITHOUT A NAME:**

**A HISTORICAL PERSPECTIVE**

Key ingredients of thermodynamics were recognized at the very beginning of science through observation of terrestrial phenomena. For instance, what we call today *phase transitions* was at the root of the reflections of Anaximenes (circa 550–480 BC). One of the earliest natural philosophers, he asserted that clouds, rain and hail were the results of progressive condensation of air, snow forming instead when some air got entrapped in the process. Shortly after, hail was explained in a remarkably accurate way by Anaxagoras (circa 500–428 BC). He stated that water freezes “when a cloud is pushed into the upper region, which is colder because there the reflections of the rays of the sun from the Earth cease.” For this reason, he thought that “hailstorms occur more often in summer and in hot places, because the greater heat pushes the clouds higher up from the Earth.” Anaxagoras also understood that the salinity of seawater resulted, in modern parlance, from water–rock interactions. “Water that is percolated through the earth and washes it becomes brackish,” he asserted, “because the earth has these sorts of flavours in itself.” As a proof, he noted that “both salt and niter [sodium carbonate] are mined from the earth.” At the same time, fundamental chemical principles were laid down by Empedocles (circa 495–435 BC) in his famous theory of the four elements. As illustrated by a burning log of green wood, which releases smoke, water and ash along with fire, everything was made up of *air*, *water* and *earth*, which represented our gas, liquid and solid states of matter, respectively; *fire*, on the other hand, was posited to be the main agent of change, something akin to our concept of energy. Because elements were indestructible and assembled in specific proportions in everything, conservation of mass and the notion of chemical composition were in addition sketched out. This theory would reign practically undisputed for more than two millennia because of the explanations it provided for a very wide range of phenomena. The Earth was a case in point. By assuming in *On the Heavens* that each element was moving spontaneously to its “natural” place, upward for air and still more so for fire, and downward for water and earth, Aristotle (circa 384–322 BC) accounted in a single stroke for gravity (and what is called today *equipotential surfaces*), the spherical figure of the Earth and the existence of...
The Earth’s internal layered structure as first depicted by Descartes (1644) before (top) and after (bottom) mountain formation caused by the phase change of the subterranean water. I: primal, originally “subtle” starry matter; M: opaque body, similar to the “crust” of sunspots; D: water; B and F: air.

The stage was set for William Thomson (1824–1907), who was to become baron Kelvin of Largs, to enter the fray. A pioneer of “thermo-dynamics,” he kept throughout his life a keen interest in geology that began in his youth (Thomson 1894). Solving Fourier’s equation for an Earth assumed to be initially molten at a temperature of 3870 °C, he found that between 20 and 400 million years were required to yield the geothermal gradient measured by Cordier (Fig. 2). Following Hermann von Helmholtz (1821–1894), he then assumed that the energy radiated by the Sun resulted from gravitational contraction, a process that could not last for more than 100 million years. Using two completely independent methods, Kelvin thus derived similar ages for both the Earth and the Sun. This most impressive achievement split the geological community and gave rise to a celebrated
geological controversy (Burchfield 1990). Because Kelvin assumed that there was no heat production within the Earth, the discovery of radioactivity eventually ruined his conclusions and incidentally opened the way to solving the star energy problem (Richet 1999). Nonetheless, Kelvin’s legacy is still alive through the strong emphasis he put on quantitative measurements and modeling of Earth processes, which some might take erroneously as quite recent ideas.

**THERMODYNAMICS IN A NUTSHELL**

In the very first application of chemical thermodynamics to geology, Jacobus H. van’t Hoff (1852–1911) accounted for crystallization of salts from brines. After the Earth had for so long been a source of inspiration for thermodynamics, geology was beginning to benefit from concepts set forth by physicists and chemists. As signaled by Fourier, the turning point had been the change from qualitative to quantitative methods, which led to the two fundamental laws of thermodynamics, namely, the conservation of energy and the increase of entropy for spontaneous transformations in a closed system. At a conceptual level, the major advance had been the introduction of entropy to account for the fact that one kind of energy, heat, is “a little more equal” than the others.

Notwithstanding this peculiarity of heat, all forms of energy are expressed in the same way and their changes take place in the same manner (see Richet 2001 for a detailed account). For instance, electrical energy (Eel) is the product of potential (U) and charge (q). Uel is an intensive property, remaining constant if, others things being equal, the size of the system of interest is, for example, doubled; on the other hand, q is an extensive property and is proportional to the size of the system. Electrical charges are neither created nor destroyed: they are conservative. And we know that electrical energy changes only through transfer of charge between different potentials, not through transfer of potential between different charges, so that

\[ E_{el} = U_{el}q \quad \text{and} \quad dE_{el} = U_{el}dq. \]  
(1)

The transformation is spontaneous when charges are transferred from a high to a low potential. During transfer, the high potential from which the charges move decreases, the low potential toward which the charges go increases, and the transfer ceases when both potentials have become equal. A state of equilibrium is thus reached when a transfer of extensity (electrical charge) has ensured an equal tension (potential) in the two reservoirs of energy involved.

In geological thermodynamics, the relevant kinds of energy are mechanical, chemical and thermal. For all of them, the formalism just described for electrical energy applies. For mechanical energy (W), the tension is of course pressure. If a system is split into two subsystems with different pressures and the boundary between them is allowed to move spontaneously, the volume of the high-pressure part will increase at the expense of that of the low-pressure subsystem until a constant pressure obtains. Because volume is gained by the high-pressure instead of the low-pressure part, however, the extensity of mechanical energy is not volume (V), but its negative (−V); thus we have

\[ W = -PV \quad \text{and} \quad dW = -PdV. \]  
(2)

For chemical energy (G), the extensities are the number of moles of all components (ni) of the system. The tensions are less intuitive. They are called chemical potentials (µ) and are defined such that simple expressions analogous to Equations (1) and (2) are obtained, namely,

\[ G = \sum \mu_ni \quad \text{and} \quad dG = \sum \mu_idn_i. \]  
(3)

For thermal energy (Q), the tension is again evident: it is temperature (T). The extensity is less obvious; it is entropy (S):

\[ Q = TS \quad \text{and} \quad dQ = TdS. \]  
(4)

Contrary to other extensities, however, entropy is not conservative. This is the essence of the second law of thermodynamics, which is not only beyond the scope of this introduction but also largely irrelevant for our present purpose.

We now define the internal energy (U) as the sum of these three forms of energy:

\[ U = \sum \mu_ni - PV + TS. \]  
(5)

All parameters of Equation (5) are state variables, that is, they do not depend on the history of the system but are unambiguously defined by its current state if internal equilibrium prevails. In this case, which is implicitly assumed to hold true in any application of thermodynamics, an important postulate is that only two variables are needed to specify the state of a system once the chemical composition is fixed; for convenience, pressure and temperature are usually selected in geological applications. Equilibrium is reached when tensions become uniform throughout the system, that is, when, entropy has flowed in appropriate amounts from hotter to colder phases, volume has been gained by compressed phases at the expense of less compressed phases and the various components have been transferred from the phases in which their chemical potential was high to those in which their potential was low. For equilibrium between phases α, β, γ, etc., we thus have simply

\[ T^\alpha = T^\beta = T^\gamma = \ldots = T, \]  
(6a)

\[ p^\alpha = p^\beta = p^\gamma = \ldots = P, \]  
(6b)

\[ \mu^\alpha = \mu^\beta = \mu^\gamma = \ldots. \]  
(6c)

Prediction of phase equilibrium at constant T and P then boils down to solving Equation (6c) for the system of interest. As an illustration, consider equilibrium between water and water vapour, or any two pure phases, in which case n1 = 1 and µ1 = G1. We first define enthalpy as \( H = U + PV \), and rewrite Equation (5) in another way:

\[ G = \sum \mu_ni = U + PV - TS = H - TS, \]  
(7)
before renaming $G$ as Gibbs free energy. It follows that the experimentally measurable isobaric heat capacity ($C_p$) at constant pressure,

$$C_p = \left(\frac{\partial H}{\partial T}\right)_p = T \left(\frac{\partial S}{\partial T}\right)_p,$$

allows the temperature dependence of $G$ to be determined for a given phase. Its pressure dependence is given by

$$(\partial G/\partial P)_T = V,$$  \hfill (9)

and it can also be determined readily if the equations of state, namely, the relations between $P$, $T$ and $V$, are known for the phases of interest. Solving Equation (6c) to find the $P$–$T$ curve at which the two phases coexist is thus tantamount to solving the equation

$$\Delta P = \Delta G = \left[\Delta H(T_0) + \int_{T_0}^{T} \Delta C_p \, dT\right] - T \left[\Delta S(T_0) + \int_{T_0}^{T} \Delta C_p / T \, dT\right] + \int_{P_0}^{P} \Delta V \, dP = 0$$

\hfill (10)

This can be done numerically if $\Delta C_p$, $\Delta H(T_0)$ and $\Delta S(T_0)$ are known from calorimetric experiments and if the equations of state of the two phases are also known.

The criterion (6c) is readily used when only one or two components have to be considered. For more complex systems, it can be expressed in more convenient ways. For instance, an equivalent criterion is that the Gibbs free energy be minimum for a system in equilibrium at constant $P$ and $T$. Strictly speaking, however, systems with pure phases do not exist because all components have to be present in all phases, possibly at vanishingly low concentrations, otherwise Equation (6c) would not be satisfied. A low concentration actually results from a basic structural incompatibility between a given component $i$ and its host phase $\alpha$, causing $\mu_i^{\alpha}$ to increase strongly with increasing amounts of $i$. High concentrations are, in contrast, found when there is an excellent structural match, so that $\mu_i^{\alpha}$ increases slowly. Hence, the fundamental problem in chemical thermodynamics is to know how chemical potentials vary with composition. In the ideal solution model, one assumes that components mix at random without thermal effects, in which case one finds that, at constant $T$ and $P$, chemical potentials are simple functions of mol fractions ($x$):

$$\mu_i = \mu_i^{\alpha} + RT \ln x_i,$$  \hfill (11)

where $R$ is the gas constant and $\mu_i^{\alpha}$ is the chemical potential of component $i$ in its standard state (that is, at the $T$ and $P$ and in the structural form for which thermochemical data are most conveniently determined).

The ideal model is a good approximation for gases at low pressure, for which molecular interactions are weak, but generally not for aqueous solutions, silicate melts or solid solutions. For real solutions, however, the analytical form of Equation (11) is so convenient to treat chemical equilibria that the activities ($a$) of the components are defined such that chemical potentials are, by definition, given by

$$\mu_i = \mu_i^{\alpha} + RT \ln a_i.$$  \hfill (12)

And because mol fractions are the compositional parameters that can be measured, it is useful to relate them to activities via activity coefficients ($\gamma$),

$$a_i = \gamma_i x_i,$$  \hfill (13)

so that $\gamma_1 = 1$ and $a_1 = x_1$ in an ideal solution. In summary, Equations (10) and (12) represent the needed formalism to calculate chemical equilibrium once the relations in Equation (13) are known. It is beyond the scope of this review to show how these relations are determined. Suffice it to say that the most reliable results are obtained when calorimetric and phase equilibria data are appropriately combined. Examples will be found in the following articles of the use of the principles briefly summarized here for equilibrium thermodynamics calculations.

**IN THIS ISSUE**

As was envisioned by Descartes, the Earth is made up of several concentric shells, the atmosphere, hydrosphere, crust, mantle and core (Fig. 3). The very existence of these envelopes indicates that they are separated by rather sharp
boundaries through which exchange of matter and energy is more or less limited. In the atmosphere and hydrosphere, energy comes primarily from the Sun. In the solid Earth, in contrast, energy has a deep origin and represents a combination of gravitational energy transformed into heat during the original accretion of the planet, radioactive energy and the heat released by very slow crystallization of the outer core. In all shells, however, the input of energy is dissipated either physically through mass transfer or chemically through a great many kinds of reactions.

From the atmosphere to the deepest recesses of the Earth, the examples in this issue of *Elements* illustrate the diversity of approaches offered by thermodynamics to solve specific questions. First, Bott (2010) discusses how the phase changes of water in the atmosphere account for various meteorological observations. Then, Millero and DiTrillo (2010) describe the effects of CO$_2$ dissolution on chemical equilibrium in the ocean, an important topic with respect to the current climate debate. How rocks and aqueous solutions interact is described in Zuddas (2010). Powell and Holland (2010) relate how the investigation of metamorphic reactions, which involve complex solid solutions, serves to decipher the history of continents. Continuing the descent, Richet and Ottonello (2010) present phase equilibria involving magmas, the agents that have most efficiently transferred heat and matter throughout geological history. In the final article, Saxena (2010) considers important aspects of the structure and dynamics of the mantle and core.

To some it might seem surprising that kinetic factors and irreversible effects can be so consistently ignored. For acid-base reactions in water the kinetics are indeed extremely rapid, but they are very slow for mineral reactions. Nonetheless, thermodynamics can be applied successfully in both cases if we follow the key initial step of defining the system of interest, that is, that part of the universe whose transformations will be considered at an appropriate timescale. Any observed departure from the equilibrium state can then be used to determine some detail of the process investigated. Perhaps even more important is the fact that the system of interest is defined such that the entropy created through the irreversible nature of actual transformations does not concern it, but only its surroundings. This is the reason why this created entropy can be simply ignored and why the same theoretical framework can be put to use in widely different problems or contexts.

At a large scale, adiabatic processes are, for instance, as important in the atmosphere as in the mantle. At a small scale, nucleation and growth in water and silicate melts obey the same rules. These are good examples of the universal applicability of thermodynamics. Albert Einstein (1879–1955) stressed it, when he noted that “a theory is the more impressive the greater the simplicity of its premises is, the more different kinds of things it relates, and the more extended is its area of applicability.” Therefore, he remarked on “the deep impression which classical thermodynamics made upon me. It is the only theory of universal content concerning which I am convinced that, within the framework of the applicability of its basic concepts, it will never be overthrown.”

**ACKNOWLEDGMENTS**

We thank all the authors who have contributed to this issue, as well as Pierreette Tremblay and Hap McSween for all their efforts in getting this issue to production. We also thank Joel Dyon of IPGP for drafting the figures of several papers. GSH acknowledges funding from NSERC via a Discovery grant.

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Activity (g) – a state variable characterizing the “effective concentration” of a component in a solution

Activity coefficient (γ) – the ratio between the “effective” and actual concentrations of a component in a solution

Adiabatic transformation – transformation at constant entropy

Chemical potential of a component (µ) – an extensive state variable characterizing the “strength” of the given component in the solution of interest, which must be the same in all phases of a system to achieve chemical equilibrium

Component – any entity that can be used to describe the chemical composition of a system (e.g. Si, O, Si4+ and O2- for silica). The components are independent when their number is minimum (2 for SiO2; for instance Si and O, or Si4+ and O2-).

Enthalpy (H) – a state variable accounting for heat exchanged at constant pressure

Entropy (S) – a state variable accounting for the microscopic distribution of matter and energy throughout a system

Equation of state (EOS) – the relationship between the pressure, temperature and volume of a system. The simplest EOS is that of one mol of ideal gases, namely, \( PV = RT \), as it does not depend on any parameter specific to the substance considered. For solids, liquids or dense gases, more complex equations must be used. Along the geothermal gradient, the thermal expansion due to increasing temperature is small compared to the compression resulting from high pressure. Only the latter effect will thus be described here through the Birch-Murnaghan equation used extensively in geophysics. At constant temperature, this EOS relates pressure and volume to the bulk modulus, \( K_b \), and its first pressure derivative, \( K_b' \), by

\[
P = \frac{3}{2} K_b \left[ \left( \frac{V_0}{V} \right)^{2/3} - 1 \right] \left( 1 + \frac{3}{2} K_b' - \frac{4}{3} K_b' \left( \frac{V_0}{V} \right) \right)
\]

where the subscripts 0 indicate the value of \( V, K_b \) and \( K_b' \) at zero pressure. These equations are actually derived from a 3rd-order expansion of the Helmholtz free energy in terms of finite strain. Empirically, their validity is justified by the fact that they account for compression curves as different as those shown in Figure 4, with values of \( K_{ bond} \) ranging from 3.6 to 4360 kbars for H2 and diamond, respectively. Its validity is also justified by the fact that values of \( K_b' \) are found to be generally close to 4 (for instance, 4.7 for H2 and 3.3 for diamond), the value for which Equation (14) reduces to its first term, indicating that the convergence of the expansion is actually rapid.

Extensive property – other things being equal, a property proportional to the size of the system (e.g. volume, enthalpy, entropy, Gibbs free energy, etc.)

First law of thermodynamics – expresses the fact that energy is conserved in all transformations, i.e. that any variation in a given form of energy is exactly compensated by the variations of others

Gibbs free energy (G) – the thermodynamic potential for transformations at constant temperature and pressure, which must be minimum for equilibrium to be achieved under these conditions

Heat capacity – the temperature derivative of enthalpy at constant pressure (Cp) or of internal energy at constant volume (Cv)

Intensive property – a property independent of the size of the system (e.g. pressure, temperature, chemical potential, index of refraction, viscosity, etc.)

Internal energy (U) – the sum of the kinetic and potential energies over all the degrees of freedom of the particles that constitute a system

Phase – a structurally homogeneous portion of matter in a system characterized by the same intensive properties (e.g. all the ice flakes in an ice bath constitute a single phase)

Phase rule – a rule stating that the variance, \( v \), of a system (namely, the number of variables that can be varied without causing a change in the number and nature of the phases that coexist) is given by \( v = c + 2 - q \), where \( c \) is the number of independent components and \( q \) the number of phases of the system

Second law of thermodynamics – states that the entropy of an isolated system can only increase as a result of spontaneous transformations

Solution – a gaseous, liquid or solid phase made up of several components mixed at the atomic scale

- **Athermal solution** – a solution whose components mix without heat effects

- **Ideal solution** – a solution whose components mix randomly and without heat effects

- **Regular solution** – a solution whose components mix randomly but with heat effects. For a binary system, the enthalpy of mixing is given by \( \Delta H_m = W_{12} (1-x_1^2) + W_{12} x_2^2 \). As will be seen in the papers in this issue, more complex equations are written for multicomponent systems, but they rest on the same basic assumption of binary enthalpic interactions, i.e. \( \Delta H_m = \sum W_{ij} x_i x_j \).

**Standard state of a component** – the reference state chosen for the component of interest, from which changes in thermodynamic functions are evaluated. It is often taken as the pure component in its stable phase at the pressure and temperature considered.

**State** – characterized by the intensive and extensive properties of the constitutive phases of a system

**State variable** – any variable that depends only on the current state of the system and not on its history

**System** – that particular portion of the universe under consideration. A system is open when it exchanges energy and matter with the surroundings and closed if it exchanges only energy.

**Transformation** – any process changing at least one state variable of a system

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**Figure 4** Room-temperature volume (A) and bulk modulus (B) as a function of pressure. The contrast between the extremely large compression of H2 and the slight volume change of diamond, C(d), illustrates the very strong dependence of volume properties on the strength of interatomic bonds. Data from Richet (2001)
Thermodynamic Processes in the Moist Atmosphere

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1811-5209/10/0006-0293$2.50 DOI: 10.2113/gselements.6.5.293

Thermodynamic principles play a key role in almost all processes occurring in the Earth’s atmosphere. They are formidable expressed in the thermal stratification of the atmosphere, in the appearance of various regional and large-scale wind systems, as well as in the formation of clouds and precipitation. It is important to note that the application of simplified thermodynamics is usually sufficient to describe large-scale atmospheric processes. However, for an in-depth understanding of the microphysical structure of clouds, a detailed investigation of the complex thermodynamic cloud processes is needed.

Key words: adiabatic process, cloud microphysics, phase diagram of water, thermodynamic diagram, tropical cyclone

FUNDAMENTAL PRINCIPLES IN ATMOSPHERIC THERMODYNAMICS

In order to describe the thermodynamic state of the atmosphere and its future development, it is necessary to formulate prognostic equations for the atmospheric wind field, the air temperature, the air pressure, and the masses of dry air, water vapor, liquid water, and ice. These equations are derived on the basis of several fundamental physical principles and axioms. Newton’s axioms lead to the prognostic equation for the atmospheric wind field, known as the Navier-Stokes equation. For the different masses, prognostic equations are formulated based on the principle of mass conservation. Prognostic equations for the internal energy or the enthalpy, as obtained from the first law of thermodynamics, may be used for the calculation of time rate changes of the temperature. Details about the derivation of the atmospheric thermohydrodynamic equation system may be found in standard textbooks on dynamics and thermodynamics (e.g. Bohren and Albrecht 1998; Zdunkowski and Bott 2003, 2004; North and Erukhimova 2009).

For the air pressure, \( p \), a diagnostic relation may be obtained from the ideal gas law for moist air, yielding

\[ p = \rho (m_d R_d + m_v R_v) T = \rho R_d T_v, \]

where \( \rho \) is the air density, \( m_d \), \( m_v \), and \( R_d \), \( R_v \) are the mass concentrations and gas constants of dry air and water vapor, respectively, and \( T \) is the air temperature. Equation (1) is also the defining relation for the virtual temperature, \( T_v \), which is commonly used in atmospheric thermodynamics. This quantity is the temperature of dry air having the same pressure and specific volume as the moist air. It is noteworthy that in Equation (1) the specific volumes of water and ice particles have been ignored. Under typical atmospheric conditions this assumption is certainly justified. Moreover, dry air is assumed to be an ideal gas. This treatment is based on the assumption that dry air consists of a constant mixture of ideal gases, i.e. nitrogen, oxygen, argon, carbon dioxide, and other trace gases. For atmospheric considerations, the spatiotemporal variation of the composition of dry air may safely be neglected.

THE THERMODYNAMICALLY FILTERED SYSTEM

In classical atmospheric thermodynamics it is assumed that the atmosphere is either subsaturated, yielding relative humidities, \( r_h \), below 100%, or saturated, that is, \( r_h = 100\% \). Saturation occurs if the water vapor is in chemical equilibrium with a plane water or ice surface. According to Gibbs’ phase rule, two phases of water may coexist in chemical equilibrium at different sets of temperature and pressure. Moreover, the three phases of water can occur simultaneously only at one temperature and pressure, the so-called triple point. The well-known Clausius-Clapeyron equations describe the phase diagram of water, i.e. curves of saturation vapor pressure, \( e_{sat} \), along which two different water phases coexist in chemical equilibrium.

Figure 1 shows qualitatively the phase diagram of water, in which the gas, liquid, and solid phases are separated by saturation vapor pressure curves. The abscissa denotes the temperature, \( T \), and the ordinate shows the partial pressure of water vapor, \( e \), which is simply called vapor pressure. The magenta arrows indicate direct transitions between the gas and solid phases, the black arrows denote condensation/evaporation, and the yellow arrows describe the freezing and melting of water and ice. At the critical point, the physical properties of the liquid and gas phases of water become identical. At temperatures higher than the critical temperature, it is no longer possible to convert the gas phase to the liquid phase by increasing the pressure, and one speaks of a supercritical fluid.

During a thermodynamic process, a system proceeds from an initial to a final thermodynamic state, thereby changing the values of its thermodynamic state variables. The thermodynamic process is called adiabatic if the system is insulated. In this case there will be no heat transfer between the system and its surroundings. If in addition the entropy of the system remains constant, then the thermodynamic
process is reversible and we speak of an isentropic process. Although, strictly speaking, there is a difference between isentropic and adiabatic processes, it is common practice to describe either process as adiabatic.

Consider the adiabatic vertical displacement of an air parcel consisting of dry air and water vapor. The displacement occurs in such a way that the air parcel remains subsaturated. Integration of the first law of thermodynamics in enthalpy form from $p_0$ to $p = 1000$ hPa shows that during the vertical lifting process the potential temperature, $\theta_i$, of the air parcel remains constant. $\theta_i$ is defined by

$$\theta_i = T(p/p_0)^{\kappa}, \quad \text{with} \ p_0 = 1000 \text{ hPa},$$

where $T$ is the temperature of the air parcel. The term $\kappa$ is called the exponent of the adiabat. To a very good approximation, during the vertical displacement in subsaturated air the water vapor content of the air parcel may be ignored, so that $\kappa$ can be approximated by the corresponding exponent of the adiabat for dry air; thus, $\kappa = \kappa_d = R_d/C_{p,d}$, where $C_{p,d}$ is the specific heat capacity of dry air at constant pressure (given in J kg$^{-1}$ K$^{-1}$). By assuming that the atmosphere is in hydrostatic equilibrium, it turns out that during the adiabatic lifting process the temperature of the air parcel decreases at a rate of nearly 1 °C per 100 meters, which is called the dry adiabatic lapse rate.

When an air parcel with temperature $T_i$ and vapor pressure $e_i$ is dry adiabatically cooled, e.g. by vertical lifting, after some time the parcel reaches its dew point temperature, $T_d$. At this temperature its vapor pressure (which remains constant during the dry adiabatic cooling) equals the saturation vapor pressure, $e_{sat}$. In Figure 1 the dry adiabatic cooling process is schematically indicated by the solid red arrow between the points 1 and 1'. Further cooling of the air parcel results in the formation of liquid water (or ice). Assuming at all times chemical equilibrium of the water phases, during the moist adiabatic cooling process, the air parcel moves from point 1' along the saturation pressure curve to point 2; see the dashed red arrow in Figure 1.

The amount of condensed water at point 2 is given as a function of the difference of the saturation vapor pressures, $e_1 - e_2$.

The transition of water from the gas phase to the liquid or solid phase is accompanied by the release of latent heat. Hence, the resulting adiabatic lapse rate is smaller for moist than for dry conditions. From the first law of thermodynamics, it follows that during the moist adiabatic process the so-called equivalent potential temperature, $\theta_e$, of the air parcel remains constant. $\theta_e$ is obtained in the following way. First, the air parcel is vertically lifted until all its water vapor has condensed. Then it is brought down dry adiabatically to the pressure level $p_0$. Here the temperature of the air parcel is the same as its equivalent potential temperature. A very good approximation to $\theta_e$ is given by the liquid water potential temperature, $\theta_i$, introduced by Betts (1973):

$$\theta_e = \theta_i = \theta \exp \left( l_v r_{sat}/C_{p,d} T \right),$$

where $l_v$ is the latent heat of vaporization and $r_{sat}$ is the saturation mixing ratio of water vapor. From this equation it may be seen that with decreasing saturation mixing ratio, $\theta_e$ reaches asymptotically the value of the potential temperature, $\theta$.

### EXAMPLES OF ATMOSPHERIC ADIABATIC PROCESSES

To describe many atmospheric processes it is often helpful to assume that they proceed adiabatically. Some examples will now be given. Turbulent mixing in the lowest part of the atmosphere, the so-called atmospheric boundary layer (ABL), produces a constant vertical distribution of the potential temperature, so that in the well-mixed subsaturated ABL the vertical temperature decrease is given by the dry adiabatic lapse rate. In synoptic meteorology, which deals with the analysis and forecasting of large-scale atmospheric processes, this fact may be used to obtain a good estimate of the temperature at the Earth’s surface. For this, the temperature distribution at the pressure level of 850 hPa, as predicted by a numerical weather-prediction model, is extrapolated to the ground by assuming dry adiabatic conditions below this level. However, this rule of thumb is successful only if the mixed ABL exceeds the 850 hPa level and is subsaturated, e.g. during the summer months.

In many regions the local weather is often affected by the occurrence of katabatic winds, which are usually rather cold and dry. These orographic wind systems are caused by gravitationally driven downhill flow of high-density air that has been radiatively cooled at higher elevations. Prominent examples are the drainage winds blowing from the ice sheets in Antarctica and Greenland. The Mistral is a katabatic wind frequently observed in Provence, France, while the Bora is a well-known fall wind in the Adriatic region. In Southern California the Santa Ana winds are northeasterly, offshore winds that originate in the Great Basin. The combination of strong gravitational forces acting on the cold air and funnel effects caused by the orographic structure of the particular region can result in very high and violent wind speeds, which may even reach hurricane force. Numerical simulations have revealed that the downslope wind velocities depend on the buoyancy deficit of the current and on the length and angle of the slope (see, for example, Princevac et al. 2008). During its downhill flow the air is dry adiabatically warmed. Usually this warming does not completely offset the previous strong radiative cooling of the air at higher elevations, so that the drainage winds remain rather cold. In some situations, however, adiabatic warming may be so strong that
at lower elevations the katabatic wind appears as a vigorous flow of warm or even hot air. For instance, the Santa Ana winds may lead to extremely hot and dry weather situations.

In addition to the dry adiabatic warming of the descending air, the release of latent heat sometimes becomes an important factor characterizing local wind systems. Foehn winds are observed in mountain regions all over the world; examples are the Föhn in the northern Alps, the Chinook east of the Rocky Mountains, the Halny in eastern Europe, the Bergwind in South Africa, and many others. Foehn winds occur when air is adiabatically lifted on the windward side of a mountain range and descends dry adiabatically on the lee side. If condensation takes place during the lifting process, then latent heat will be released, causing moist adiabatic cooling of the ascending air. On the lee side of the mountain, however, the descending air is dry adiabatically warmed and thus becomes much warmer than it was at the same elevation on the windward side.

CLOUDS AND PRECIPITATION

Clouds and precipitation are not only of utmost importance for life on Earth, they also undoubtedly represent the most impressive and complex phenomena of atmospheric thermodynamics. Of particular importance for the formation of clouds and precipitation is the thermal stratification of the atmosphere. In order to obtain and use this information, it is helpful to plot the vertical profiles of temperature, $T$, and dew point, $T_d$, in so-called thermodynamic diagrams. Figure 2, an example of the various forms of thermodynamic diagrams, depicts a so-called skew-$T$-log $p$ diagram. The diagram consists of isotherms, isobars, dry and moist adiabats, and lines of constant saturation mixing ratios. The thick black curves denote the observed vertical temperature ($T$; solid line) and dew point ($T_d$; dashed line) profiles of the atmosphere.

Consider now an air parcel that is adiabatically lifted from the ground. In the diagram the change of the temperature, $T_p$, of the parcel, caused by the lifting process, is represented by the blue curve. As long as the air parcel remains subsaturated, its temperature will follow a dry adiabat on the diagram. At the so-called lifting condensation level (LCL), the parcel will be saturated. The LCL is given by the intersection of the temperature curve, $T_p$, with the saturation mixing ratio line that corresponds to the dew point, $T_d$, with the saturation mixing ratio line that corresponds to the dew point at the ground. Further lifting of the air parcel causes moist adiabatic cooling so that above the LCL the $T_p$ curve follows a moist adiabat. At the level of free convection (LFC), the air parcel becomes warmer than the environment. Hence, above this level the air parcel will be vertically accelerated due to its positive buoyancy. Above the equilibrium level (EL), the air parcel will again be colder than the environment, thus decelerating its vertical movement.

The formation and intensity of convective cloud cells depends on the height to which the air parcel can ascend. This height is mainly controlled by the blue and the pink areas in the figure, which are obtained from the intersection points of the $T_p$ and $T$ curves. The blue area describes the energy that has to be applied in order to lift the air parcel from the ground to its LFC. This energy, which is also called convective inhibition (CIN), may be supplied to the air parcel by dynamic processes such as turbulent mixing, the flow of the parcel over a mountain, etc. The smaller the CIN the easier it is for the air parcel to reach its LFC. The pink area describes the so-called convective available potential energy (CAPE). This energy mainly stems from the release of latent heat during the moist adiabatic ascent of the air parcel. CAPE will be converted into kinetic energy of vertical motion of the rising air. The larger the CAPE the higher and faster the air parcel will ascend in the atmosphere. Updraft velocities of more than 20 m s$^{-1}$ may be reached (Heymsfield et al. 2009).

If the CAPE is large enough, the vertically lifted air forms a deep cumulus cloud called cumulus congestus. At still higher altitudes the cloud water starts to freeze. The freezing process is accompanied by the release of latent heat of fusion. Thus, the rising air attains even more buoyancy so that the height of the cloud increases further. In Figure 2, this is schematically shown by the magenta curve and the corresponding magenta area denoting the additional CAPE as obtained by the freezing process. As long as the EL of the liquid-water cloud is at a lower altitude than the 400 hPa level, a relatively small amount of additional CAPE by freezing might be sufficient to yield a drastic increase of the cloud-top pressure from EL to the new equilibrium level, EL’, at about 300 hPa. At this point a cumulonimbus capillatus forms (the latin word capillatus means “hairy”). This thundercloud is characterized by a fibrous structure in its upper region, illustrating that here the cloud consists of ice particles. If the cumulonimbus reaches very high altitudes, strong winds cause a horizontal flattening of the cloud, producing an anvil structure. This cloud type is called cumulonimbus capillatus incus (incus is the latin word for “anvil”). Figure 3 depicts a mesoscale convective systems (MCS) observed on a summer day over Sardinia. The system consists of several cumulus clouds at different stages of their lifetime. At the front of the MCS a well-developed cumulus congestus is seen, while at high altitudes a large cumulonimbus with an anvil structure has formed. This convective system produced severe rainfall, hail, and flooding.

**FIGURE 2** Skew-$T$ versus log $p$ diagram with vertical soundings of temperature, $T$, and dew point, $T_d$. $1000$ hPa corresponds to ground level. See text for explanations.
The life cycle of a thunderstorm can be subdivided into three stages. The cumulus stage is characterized by the upward motion of warm and moist air, forming a cumulus congestus. At this stage precipitation is not yet observed on the ground. In the mature stage the air reaches the equilibrium level, where it spreads out horizontally and forms a cumulonimbus capillatus. In addition to the updraft region, a small downdraft region forms within the cloud. Downdrafts are initiated by falling precipitation. Sinking air in the downdraft region is mixed with subsaturated air of the environment, so that the precipitation starts to evaporate. The associated cooling of the downdraft air by latent heat effects is very strong, thus increasing the negative buoyancy of the sinking air (Didlake and Houze 2009). This might result in very strong downbursts, sometimes exceeding 30 m s\(^{-1}\). The strength of the vertical winds within the cloud depends mainly on the CAPE and on the vertical shear of the horizontal wind (Kirkpatrick et al. 2009). Finally, in the dissipation stage, the downdraft reaches the ground where it spreads out horizontally. The cool downdraft air cuts off the supply of warm moist air in the updraft region, so the thunderstorm starts to dissipate.

Single-cell thunderstorms form in unstable atmospheric situations, for example, during the summer or after the passage of a cold front associated with the intrusion of cold air in the upper troposphere. These so-called air-mass thunderstorms are usually not very intense. However, severe thunderstorms may evolve along strong cold fronts. In supercell thunderstorms the cloud top can reach the tropopause or even the lower stratosphere. In these storms violent tornadoes may develop. Several severe, single-cell thunderstorms are often organized into multicell clusters. These clusters can evolve into MCS, such as squall lines, mesoscale convective complexes (MCC), and tropical cyclones. While single-cell thunderstorms have a typical lifetime of less than one hour and a horizontal extent of several kilometers, an MCC is defined as a system having a cloud-top area of at least 100,000 km\(^2\) with temperatures below \(-32°C\) and a cloud-top area of at least 50,000 km\(^2\) with temperatures below \(-52°C\). These conditions must hold for at least 6 hours.

Tropical cyclones are among the largest and most violent thermodynamic systems on Earth. The major energy source of a tropical cyclone is the release of latent heat by condensation of moisture in the rising air. This energy stems from the excessive solar energy stored in the ocean in the equatorial region. Usually water temperatures of 27°C over a depth of 50 m are needed for the formation of a tropical cyclone. Thus, the tropical cyclone season is during the summer months (see, for example, Brennan et al. 2009; Brown et al. 2010). The most intense tropical cyclones, called typhoons or hurricanes, are characterized by a so-called eye in their center. Here, the pressure is extremely low, the winds are calm, and often no clouds exist. The eye is surrounded by the eyewall, where the most severe weather is observed. The radius of tropical cyclones may vary between less than 200 km and more than 900 km. The cover of this issue shows a satellite image of hurricane Katrina (2005), which was one of the most devastating hurricanes in the history of the United States.

In a single thunderstorm an enormous amount of water will be produced. Typical values are on the order of 10\(^9\) kg of water. Considering that the latent heat of vaporization of water is about 2.5 \(\times 10^6\) J kg\(^{-1}\), it is evident that extremely large amounts of thermal energy are released to the atmosphere during a thunderstorm. In a tropical cyclone this may result in a release of heat energy on the order of \(10^{20}\) J per day. It is also noteworthy that the production of large amounts of cirrus anvil clouds by thunderstorms has a strong influence on the global climate (Theisen et al. 2009).
On the local scale, the vertical transport of thermal energy from the ABL into the free troposphere, due to the release of latent heat, is an important process controlling the vertical energy distribution in the atmosphere. On the global scale, the meridional transport of thermal energy in terms of latent heat plays a vital role in the maintenance of the global energy budget of Earth. This transport occurs when, in equatorial regions, a large amount of the incoming solar energy is used to evaporate water from the oceans. The water vapor is transported towards the poles where it condenses, thereby releasing the thermal energy that was needed for evaporation. The meridional transport of latent heat amounts to about 30% of the total transport of the excess thermal energy in the equatorial regions (Blüthgen and Weischet 1980). More recently, Fasullo and Trenberth (2008a, b) presented a detailed observational study of the global energy budget and its annual cycle.

**CLOUD MICROPHYSICS**

Atmospheric observations indicate that clouds consisting only of liquid water droplets also occur at temperatures well below 0 °C. Thus, water clouds are often supercooled. The formation of ice particles within clouds starts at a temperature of about −5 °C. The so-called mixed clouds containing water droplets and ice crystals are found at temperatures between −5 °C and −40 °C, with the fraction of ice particles increasing with decreasing temperature. Below −40 °C only pure ice clouds are generally observed.

In order to understand the thermodynamic processes occurring within clouds, a detailed investigation of cloud microstructure is necessary. The initiation of a phase change of a substance from vapor to liquid, from liquid to solid, or from vapor to solid is called nucleation. Heterogeneous nucleation takes place if other substances are involved in the phase change, whereas homogeneous nucleation describes the situation where this is not the case. As the formation of water droplets by homogeneous nucleation requires extremely high supersaturations of several hundred percent, this process is not observed in the atmosphere. On the other hand, the homogeneous nucleation of ice from supercooled water droplets is an important process controlling the formation of cirrus clouds at temperatures below −40 °C (Pruppacher and Klett 1997).

Heterogeneous nucleation of water droplets occurs on atmospheric aerosol particles (AP). These tiny particles exist everywhere in the atmosphere, but they have strongly varying number concentrations, sizes, and chemical compositions (Gieré and Querol 2010). The physicochemical characteristics of AP largely depend on how they were produced, for example, by evaporation of sea spray, wind erosion, or volcanic activity, or as emissions from terrestrial ecosystems or various anthropogenic sources, etc. AP that serve as nuclei for the formation of cloud droplets are called cloud condensation nuclei (CCN). Ice-forming nuclei (IN) are aerosol particles that are involved in the heterogeneous formation of ice particles.

A water droplet can exist over a long period of time only if it is in thermodynamic equilibrium with its environment. In this situation the vapor pressure at the droplet’s surface is described by the Köhler equation which, in an approximate form, may be written as

\[ e_a = e_{sat} \left(1 + \frac{A}{a} - \frac{B}{a^3}\right). \]  

(4)

Here, \( e_a \) denotes the vapor pressure at the droplet’s surface, \( a \) is the radius of the droplet, and \( A \) and \( B \) are functions of the physicochemical properties of the CCN. Detailed expressions for \( A \) and \( B \) may be found in standard textbooks on cloud physics (Mason 1957; Pruppacher and Klett 1997; Hobbs 2010). The term \( A/a \) yields an increase of the vapor pressure, \( e_a \), in comparison to the saturation vapor pressure over a flat surface, \( e_{sat} \). This term is caused by the curvature of the droplet surface and is therefore called the curvature effect. The term \( B/a^3 \), which produces a decrease of \( e_a \) compared to \( e_{sat} \), is called the solution effect because it results from the dissolution of salts in the droplet, such as NaCl, NH4SO4, NH3, and others. From Equation (4) it may be seen that for very small droplets the solution effect dominates, yielding \( e_a < e_{sat} \). With increasing radius the curvature effect becomes more and more important, so that \( e_a > e_{sat} \). Finally, if the droplet is large enough, \( e_a = e_{sat} \).

**FIGURE 4** depicts several Köhler curves describing the relationship given by Equation (4). The curves are plotted for an AP spectrum that is typical of the rural environment. With increasing relative humidity, an AP grows due to the diffusion of water vapor upon its surface. Under such conditions, the particle moves along the blue branch of its Köhler curve. As long as the supersaturation remains lower than the so-called critical supersaturation given by the red dot on the Köhler curve, the AP is in thermodynamic equilibrium. An increase of the supersaturation above the critical value brings the AP onto the green branch of its Köhler curve. Under these conditions, since \( e_a \) is lower than the supersaturation of the environment, the AP is in unstable thermodynamic equilibrium. As long as the environment remains supersaturated, an AP moving on its green curve will continue to grow by vapor diffusion. The situation where an AP enters the unstable part of its Köhler curve is called activation. All AP that have been activated form the cloud droplet spectrum.

The physicochemical properties of the AP have a strong impact on the microstructure of clouds. In regions with relatively high number concentrations of AP, at a given supersaturation a large number of AP will already be activated, resulting in a cloud with many but small droplets. In remote regions with low AP concentrations, for example,
somewhere over the ocean, at the same supersaturation only a relatively small number of AP will be activated, yielding a cloud with the same liquid water content. However, the water is partitioned onto relatively few but large droplets.

With increasing droplet size, the diffusional growth becomes more and more insufficient, finally yielding droplet radii of about 10–20 µm. The sedimentation velocity of these droplets is so small that they can barely reach the ground. For instance, a droplet of 10 µm radius needs about 14 hours to fall through a 500 m thick calm atmospheric layer, provided it does not evaporate during its descent. Considering that precipitation particles have radii exceeding 100 µm, it is obvious that additional processes are necessary to produce precipitation-sized particles. In a water cloud this occurs via the collision and coalescence of many cloud droplets. If a drop falls within the cloud it may collide and coalesce with smaller droplets having smaller fall velocities. The gravitational collisions might be enhanced by turbulent motion or by electric fields and charges of the droplets. However, the production of a single raindrop of 1 mm radius requires 10^6 cloud droplets of 10 µm radius. This is the reason why the precipitation rate is usually rather small in warm clouds. In order to obtain high precipitation rates, as for instance in thunderstorms, the ice phase must be involved.

In mixed clouds, freezing by homogeneous nucleation is the dominant process. However, in contrast to the CCN, the IN number concentrations are usually rather small. Observations have shown that in a mixed cloud at a temperature of about –5 °C, the number concentration of ice particles might be 10^4 times larger than the IN number concentration; see, for example, Pruppacher and Klett (1997) and references therein. Several processes yield high number concentrations of ice particles in mixed clouds; such particles are referred to as secondary ice particles. The most important processes are the mechanical fracturing of fragile ice crystals, such as needles and stellar ice crystals; the shattering of large freezing drops; and the production of ice splinters during the accretion and riming of supercooled cloud droplets on ice particles, which is called the Hallet-Mossop mechanism.

Since the saturation vapor pressure with respect to ice is less than that with respect to liquid water at the same temperature, the ice particles will grow at the expense of the liquid droplets in a mixed cloud. This is called the Bergeron-Findeisen process, after T. Bergeron and W. Findeisen who developed this theory in the 1930s. Once the ice particles have gained sufficient weight, they fall out as snow. Depending on the temperature field below the cloud, melting might occur, which results in large raindrops arriving at the ground.

Consider a large cloud with high liquid water content and a higher-altitude cirrus cloud that is formed aloft by large-scale lifting processes, e.g. in orographic terrain. The ice crystals produced in the cirrus cloud may gravitationally settle down into the liquid water cloud below. Now the Bergeron-Findeisen process starts to produce a drastic increase in the precipitation rate. This phenomenon is called a seeder-feeder mechanism.

**CONCLUDING REMARKS**

Thermodynamic principles play a vital role in almost all atmospheric processes. They operate on spatiotemporal scales ranging from the microphysical scale of cloud droplet formation to the global scale of atmospheric motion. To a large extent, the complexity of atmospheric thermodynamics is caused by the phase transitions of water. On the microscale, the formation of liquid water droplets and ice particles is strongly affected by the physical-chemical properties of the CCN and IN. Furthermore, complex interactions between the different hydrometeors occur during the generation of rain drops or snow. For large-scale investigations of atmospheric processes, it is usually sufficient to apply a simplified thermodynamic treatment by utilizing thermodynamically filtered systems. Moreover, it often seems justified to assume adiabatic motions. On the global scale, the meridional transport of energy by latent heat yields an important contribution to the Earth's energy budget. On all atmospheric scales, many important thermohydrodynamic processes are not yet fully understood. Hence, atmospheric thermodynamics will remain an interesting and challenging research field in the future.

**REFERENCES**


Use of Thermodynamics in Examining the Effects of Ocean Acidification

Frank J. Millero* and Benjamin R. DiTrolio*

INTRODUCTION

Over the last 200 years the concentration of CO₂ in the atmosphere has been increasing due to the burning of fossil fuels. This increase is larger than has occurred over the past 800,000 years. Equilibration of increasing amounts of CO₂ with surface waters will decrease the pH of the oceans (called ocean acidification) from a current value of 8.1 to values as low as 7.4 over the next 200 years. Decreasing the pH affects the production of solid CaCO₃ by microorganisms in surface waters and its subsequent dissolution. CO₂ dissolution in the ocean can also affect acid–base equilibria, metal complex formation, solid–liquid equilibria, and the adsorption of ions to charged surfaces. Thermodynamic principles can be used to understand these processes in natural waters.

KEYWORDS: pH, ocean acidification, carbonate system, metal complex formation

The burning of fossil fuels has increased the concentration of carbon dioxide (CO₂) in the atmosphere from 280 ppmv (volume parts per million) to 385 ppmv over the last 200 years. This increase is larger than has occurred over the past 800,000 years. Equilibration of increasing amounts of CO₂ with surface waters will decrease the pH of the oceans (called ocean acidification) from a current value of 8.1 to values as low as 7.4 over the next 200 years. Decreasing the pH affects the production of solid CaCO₃ by microorganisms in surface waters and its subsequent dissolution. CO₂ dissolution in the ocean can also affect acid–base equilibria, metal complex formation, solid–liquid equilibria, and the adsorption of ions to charged surfaces. Thermodynamic principles can be used to understand these processes in natural waters.

Figure 1 shows pH profiles with depth for the Atlantic and Pacific oceans. Currently ocean surface waters are in near equilibrium with the atmosphere and have the pH that is expected for surface waters for nearly constant normalized total alkalinity (NTA = TA•35/S, where TA is the total alkalinity and S is the salinity). Deep waters have a lower pH and a higher total alkalinity as a result of the dissolution of solid CaCO₃ [CaCO₃(s)] and oxidation of organic carbon by bacteria produced by phytoplankton near the ocean surface. Values for pH are as low as 7.4 at a depth of about 1000 m in the Pacific Ocean.

Decreasing pH lowers the concentrations of the OH⁻ and CO₃²⁻ ions in the oceans. The decrease in these anions is due to the equilibrium of OH⁻ with water (10⁻¹⁴/[H⁺] = [OH⁻]) and the reaction of H⁺ with CO₃²⁻ to form HCO₃⁻. For surface waters, the projected effect of ocean acidification on these two species is shown in Figure 5. This calculation is made by assuming that the NTA in surface waters does not change significantly with time. Direct measurements over time in Atlantic surface waters have not changed more than 10–20 µmol kg⁻¹ over the last 70 years (Bustos-Serrano et al. 2009). Decreased concentrations of these ions will affect the carbonate system and the speciation of metals. The lower concentrations of the CO₃²⁻ ion will result in a decrease in the saturation state of aragonite (Fig. 6).
Most of the recent interest in ocean acidification has concentrated on how the decrease in the saturation state affects the production and dissolution of CaCO3(s) formed by marine organisms (Guinotte and Fabry 2008; Fabry et al. 2008). As pH decreases, the growth of calcifying organisms will slow down and eventually the shells of these calcifiers and coral reefs may dissolve (Kleypas et al. 1999; Langdon and Atkinson 2005; Hoegh-Guldberg et al. 2007).

CO3²⁻ and OH⁻ ions are known to form strong complexes with divalent, trivalent, and tetravalent counter ions in natural waters. Thus, decreased concentrations of these ions, as well as of some organic ligands, will affect the speciation or form of metals in seawater. We show below how thermodynamic equilibrium can be used to understand the effects of ocean acidification on the carbonate system and on the speciation of metals in ocean waters.

**THERMODYNAMICS OF THE CARBONATE SYSTEM IN NATURAL WATERS**

The thermodynamics of the carbonate system in natural waters are governed by the following equilibria [(g), (aq), and (s) refer to gaseous, aqueous, and solid forms, respectively]:

\[
\begin{align*}
\text{CO}_2(g) &\leftrightarrow \text{CO}_2(aq) \quad (1) \\
\text{CO}_2(aq) + \text{H}_2\text{O} &\leftrightarrow \text{H}^+ + \text{HCO}_3^- \quad (2) \\
\text{HCO}_3^- &\leftrightarrow \text{H}^+ + \text{CO}_3^{2-} \quad (3) \\
\text{Ca}^{2+} + \text{CO}_3^{2-} &\leftrightarrow \text{CaCO}_3(s) \quad (4)
\end{align*}
\]

To examine the carbonate system in seawater, ocean chemists use stoichiometric equilibrium constants, which are given by (values are for S = 35.165 g/kg seawater at 25 °C):

\[
\begin{align*}
K_0^* &= K_0 a[H_2O] p\text{CO}_2/\gamma(\text{CO}_2) = [\text{CO}_2] p\text{CO}_2 \approx 10^{-1.55} \quad (5) \\
K_1^* &= K_1 \gamma(H^+) \gamma(\text{HCO}_3^-)/[\gamma(\text{CO}_2) a(H_2O)] = [\text{H}^+][\text{HCO}_3^-]/[\text{CO}_2] \approx 10^{-5.82} \quad (6) \\
K_2^* &= K_2 \gamma(H^+) \gamma(\text{CO}_3^{2-})/\gamma(\text{HCO}_3^-) = [\text{H}^+][\text{CO}_3^{2-}]/[\text{HCO}_3^-] \approx 10^{-8.95} \quad (7) \\
K_{sp}^* &= K_{sp}[\gamma(\text{Ca}^{2+}) \gamma(\text{CO}_3^{2-})] = [\text{Ca}^{2+}][\text{CO}_3^{2-}] \approx 10^{-6.3} \quad (8)
\end{align*}
\]

The values of \(K_i\) are the thermodynamic constants in pure water, the values of \(\gamma(i)\) are the total concentrations (g/kg salt), the values of \(\gamma(l)\) are the activity coefficients of species \(i\), and \(a(H_2O)\) is the activity of water in the solution. These constants are a function of temperature and ionic strength or salinity of seawater (Millero 2007; Millero et al. 2006). The constants are also available for NaCl solutions at ionic strengths up to 5 molar (M) from 0 to 100 °C and ionic strengths of 6 M (Millero and Pierrot 1998). These models calculate stoichiometric constants that are in good agreement with the measured values.

To unravel the CO₂ system in the oceans, it is necessary to measure at least two of the following parameters: pH, TA (total alkalinity), TCO₂ (total inorganic CO₂), and \(p\text{CO}_2\) (partial pressure of CO₂). These parameters are mutually related by the following equations (species concentrations are in square brackets):

\[
\begin{align*}
p\text{H} &= –\log[H^+] \quad (9) \\
\text{TA} &= [\text{HCO}_3^-] + 2[\text{CO}_3^{2-}] + [\text{B(OH)}_4^-] + \text{other minor bases} \quad (10) \\
\text{TCO}_2 &= [\text{CO}_2] + [\text{HCO}_3^-] + [\text{CO}_3^{2-}] \quad (11) \\
\text{CO}_2 &= K_0^*[\text{CO}_2] \quad (12)
\end{align*}
\]

To evaluate the concentration of the borate ion in Equation (10), one needs to know the dissociation constant for the dissociation of boric acid (Millero 2007). The methods used to determine these parameters in oceanography are available from the Carbon Dioxide Information Analysis Center, CDIAC (Dickson et al. 2007). Pairs of parameters used in most ocean studies include \(p\text{CO}_2\) and TCO₂, pH and TA or TCO₂, and TA and TCO₂.

These input parameters, combined with the stoichiometric thermodynamic constants, are used to determine the two unknown parameters not measured (pH, \(p\text{CO}_2\), TA, TCO₂) and the concentrations of HCO₃⁻, CO₃²⁻ and CO₂ needed to examine the carbonate system in ocean waters. Computer programs are available to calculate all the components of the CO₂ system in the oceans (Dickson et al. 2007) and in brines (Millero and Roy 1997) using any possible input of the four parameters that can be measured.
CALCIUM CARBONATE THERMODYNAMICS

The dissolution and precipitation of CaCO$_3$(s) in the ocean is examined using the saturation state of the mineral, defined as

$$\Omega = [Ca^{2+}] [CO_3^{2-}] / K_{sp}^*.$$  (13)

The concentration of Ca$^{2+}$, a major constituent of seawater, changes only when the total salts are increased or decreased. $K_{sp}^*$ in Equation (13) is the measured solubility of CaCO$_3$(s) in seawater at a given temperature, salinity, and pressure. Calcite and aragonite are the two forms of CaCO$_3$(s) present in ocean waters. They differ in crystal structure, with calcite being the more thermodynamically stable. Due to its relative thermodynamic instability, aragonite has a lower saturation state, $\Omega_A$, than calcite. Calcareous organisms secrete aragonite; thus it is $\Omega_A$ that must be considered when assessing future conditions for them. When $\Omega_A > 1$, the waters are supersaturated; when $\Omega_A < 1$, they are undersaturated; and when $\Omega_A = 1$, they are in equilibrium. Most ocean surface waters are supersaturated in aragonite, and deep waters are undersaturated due to the decrease of $CO_3^{2-}$ and increase of $K_{sp}^*$ with depth. As the surface oceans become more acidic, the values of $\Omega_A$ in surface waters will decrease (Fig. 6). Experimental measurements show that a decrease in $\Omega_A$ or $[CO_3^{2-}]$ makes it more difficult for calcareous organisms like corals to make CaCO$_3$(s) (Langdon and Atkinson 2005; Fabry et al. 2008). It is important to note that $\Omega_A$ must not drop below 1, otherwise organisms will be negatively affected. Langdon and Atkinson (2005) showed that, in the past, the rates of growth of corals forming aragonite were slower when the saturation state decreased (see Fig. 7). The calcification rates for different coral species were different, but they all decreased as $\Omega_A$ decreased. In addition to the stress on the growth of calcifying organisms due to decreases in $\Omega_A$, if the values fall below 1.0, aragonite skeletal structures of these organisms may dissolve (Kleypas et al. 1999; Hoegh-Guldberg et al. 2007; Fabry et al. 2008; Guinotte and Fabry 2008). The warming of the surface oceans is also a threat to corals, as an increase in temperature beyond the summer maximum can decrease aragonite production by corals (Marshall and Clode 2004).

Coral is not the only calciferous organism threatened by the prospect of ocean acidification. Planktonic species, such as pteropods, also form shells from aragonite. These organisms have been found to make up a substantial fraction of the biomass in high-latitude regions (Urban-Rich et al. 2001), particularly in the Southern Ocean. Using the IPCC IS92a “business as usual” CO$_2$-emission scenario, Orr et al. (2005) modeled $\Omega_A$ in this region and calculated that these waters will be undersaturated in aragonite by the year 2050. These workers measured the effects of undersaturated conditions on native pteropods and observed prominent shell dissolution. Pteropods in this region are thought to have a significant role in the export of carbon to the deep ocean (Hunt et al. 2008). If these calcifiers are unable to exist in undersaturated conditions, the global carbon cycle may change significantly. Pteropods, for example, are a food source for other organisms in surface waters. The saturation state of calcite is not expected to be less than 1.0 in most surface waters, so organisms utilizing calcite, like foraminifera, should not have their production rates affected by the expected changes in pH. These organisms are the major contributors of CaCO$_3$(s) to the deep oceans and sediments.

THERMODYNAMICS OF METAL SPECIATION

Metals in natural water systems interact with organic and inorganic ligands, resulting in fractionation of the total metal concentration among a number of different species. The distribution of species for a given metal is governed...
by the strength of the stoichiometric stability constant, $K_{M_X}$. For a single complex, MX, between a metal, M, and an inorganic ligand, X, the stability constant can be determined from

$$K_{M_X} = K_{MX} \frac{\gamma(M) \gamma(X)}{\gamma(MX)} = \frac{[MX]}{[M][X]}.$$  \hspace{1cm} (14)

As described above, $K_i$, $\gamma(i)$, and $[i]$ are, respectively, thermodynamic constants in pure water, activity coefficients, and stoichiometric concentrations. In order to account for the competitive speciation between a metal and multiple ligands, $K_{M_X}$ must be known for all relevant metal–ligand interactions. It is then possible to determine the fraction of each metal–ligand species by determining the fraction of the free metal in solution, $\alpha(M^{x+})$, and the fraction of the free ligand, $\alpha(X^{-})$, through a series of iterations. A number of methods have been used to calculate the speciation of metals using these relations. These methods have traditionally involved the use of an ion-pairing model (Millero and Schreiber 1982), a Pitzer (1991) formulation, or a hybrid of the two (Millero and Pierrot 2002). A comprehensive review of these methods and their applications is provided by Millero (2001).

Inorganic ligands in seawater consist of both pH-dependent species, such as OH$^-$, CO$_3^{2-}$, and HCO$_3^-$, and pH-independent species, such as Cl$^-$ and the less abundant halides. Metals that form strong complexes with halides (Cd$^{2+}$, Hg$^{2+}$) are not affected by decreases in pH. FIGURE 8 shows the inorganic speciation in seawater for Cu$^{2+}$ at the current pH of 8.1 and at the projected future level of 7.4. Free Cu$^{2+}$ will increase by 30% if pH decreases from 8.1 to 7.4, resulting in 45% of the total copper concentration not complexed with organic material being in the free form. This may increase the toxicity of Cu$^{2+}$ in surface ocean waters.

Surface concentrations of total Cu$^{2+}$ in the open ocean range on average between 0.6 and 2.5 nanomolar (nM) (Coale and Bruland 1988; Donat and van den Berg 1992). Inorganically complexed and free forms generally represent <1% of the total Cu$^{2+}$ present in surface waters (Coale and Bruland 1988; Donat and van den Berg 1992). The remaining Cu$^{2+}$ is strongly complexed with organic matter. This fact is important to note as Cu$^{2+}$ bound by organic ligand(s) is not bioavailable (Schreiber et al. 1985; Gonzalez-
Davila et al. 1995). Little is known regarding how the organic speciation of metals will change with decreasing pH, but preliminary data for Cu\(^{2+}\) suggest that the organically complexed fraction will decrease, resulting in higher concentrations of labile Cu\(^{2+}\) (Louis et al. 2009). Toxic thresholds of free Cu\(^{2+}\) for certain marine organisms have been observed to be on the order of 1 picomolar (pM) (Brand et al. 1986). This is a small percentage of the total Cu\(^{2+}\) in open-ocean surface waters (0.2–0.04%); thus subtle increases in free and inorganic copper could translate into toxic conditions (Millero et al. 2009).

The speciation and solubility of other metals significant to microorganisms—Mn, Fe, Ni, Co, Zn, and Cd—will also be affected by decreases in pH. Assessing these changes is an area in which thermodynamic research will play a significant role.

**CONCLUSIONS**

The continued burning of fossil fuels will increase the concentration of CO\(_2\) in the atmosphere. The increased solubility of this CO\(_2\) in the oceans will lead to a decrease in the pH. This so-called “ocean acidification” will affect the thermodynamic equilibrium of the carbonate system and the speciation of metals. The lower concentrations of CO\(_2\)\(^2-\) will slow the production of CaCO\(_3\) minerals by organisms and may dissolve coral reefs in some areas. The decrease in the pH will also make some metals more toxic (Cu\(^{2+}\)) and others more available (Fe\(^{2+}\)) for phytoplankton. Further studies are needed to determine the long-term effect of ocean acidification on the ecology of ocean waters. Unless dramatic changes in our use of fossil fuels are made, it will take thousands of years to return the pH of the oceans to their preindustrial levels.

**ACKNOWLEDGMENTS**

The authors wish to acknowledge the Oceanographic Section of the National Science Foundation and the National Oceanic and Atmospheric Administration for supporting their marine physical chemistry research.
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The chemical composition of groundwater results from the reaction of mineral dissolution and precipitation. We can use the thermodynamic approach to predict water composition under conditions where water and newly formed minerals are in equilibrium. Although some minerals exist in a state of equilibrium with water, other minerals are always unstable. In the latter case, we can evaluate the extent of the overall irreversible mass transfer between minerals and water to quantify the mineral surface area participating in the water–rock interaction. This parameter is fundamental to basic and applied research in areas such as the geological sequestration of CO₂ and the safe geological storage of waste.

**INTRODUCTION**

Water and other subsurface fluids are fundamental to several geological processes because they are always present in rock systems. Although the term water–rock interaction includes many possible processes in nature, such as river waters smoothing down rocks over time and ocean waves crashing onto a rocky shoreline, for geologists the term refers to the dominant chemical and thermal exchanges (reactions) that occur between groundwater and rocks. Natural water interacting with rocks induces both alteration of thermodynamically unstable minerals and formation of new, stable minerals. Water composition reflects the balance between the two processes. The reactions that occur during these interactions not only cause transformations of minerals but also affect the chemical composition and the quality of water above and below the Earth’s surface.

Using the thermodynamic equilibrium approach, it is possible to predict the evolution of water composition when macroscopic variables, such as temperature, pressure and affinity (also called the driving force of the reaction), can be modelled by simple laws with the help of kinetic equations. In this article I will discuss how evaluating the rate of the geochemical interaction between water and minerals can be used to predict the environmental impact of waste deposits over time.

**BALANCING GEOCHEMICAL MASS TRANSFER IN WATER SYSTEMS**

Garrels and Mackenzie (1967) explained that water composition can be described by a mineralogical transformation ‘budget’, balancing dissolution and precipitation. In the particular case of granites in the Sierra Nevada, they showed that the concentration of each dissolved element results from the balance between mineral dissolution in the rock and precipitation of newly formed minerals under stable thermodynamic conditions. In their model, they estimated the contributions of dissolution and precipitation for each dissolved element by assuming that the sources of dissolved Na, Ca and Mg were albite, anorthite and mica, and that the sources of dissolved K were feldspar and mica. By identifying the newly formed clay minerals (kaolinite, smectite or, more rarely, gibbsite), they estimated the amount of dissolved Si and Al from the dissolution–precipitation net mass balance. Garrels and Mackenzie (1967) assumed that the observed precipitation of kaolinite or secondary minerals is the cause of the low amount of aluminium in natural water. However, as emphasized by Garrels and Mackenzie (1967), this simple and elegant mass balance representation cannot be applied to the majority of natural conditions because it is difficult to quantify the exact composition of minerals that are inherently chemically heterogeneous.

**THE THERMODYNAMIC EQUILIBRIUM MODEL**

The mass budget approach was interpreted by Helgeson (1968) as an energy budget. Helgeson assumed that the instability of the minerals in the parent rock (mainly igneous and metamorphic rocks) at the Earth’s surface leads to a ‘natural’ dissolution process. Since water can reach equilibrium with newly formed minerals, he estimated the saturation index of the fluids with respect to newly formed clay minerals by calculating the ratio between the solute ionic activity product and the mineral solubility or stability constant. This approach assumes that there is an initial mineral dissolution resulting from the interaction with rainwater, where each dissolved element is assumed to be ‘soluble’ (or not controlled by newly formed minerals). At this stage of the process, the water is undersaturated with respect to clays or oxide minerals and the activity (effective concentration) of the dissolved ions results from the dissolution of the unstable minerals in the parent rock. Oxyhydroxides of aluminium and iron are very sparingly soluble, however, so they readily precipitate. In a second stage of the process, the activity of these dissolved elements is ‘controlled’ by the formation of new minerals. The silicon present in the water and originating from dissolution of aluminosilicate minerals in the parent rock may precipitate, forming oxides (SiO₂) or aluminosilicates (clay minerals) if the water is oversaturated with respect to these
minerals. The chemical evolution of the water composition in equilibrium with different minerals can be represented by activity diagrams (Fig. 1).

Although the thermodynamic approach has a rigorous theoretical basis, caution must be used when applying it to real conditions for the simple reason that the model uses fixed hypothetical Gibbs free energy values for clay minerals, whereas naturally occurring clays have heterogeneous compositions, and therefore, can have significantly different thermodynamic properties. Nevertheless, we can use theoretical activity diagrams to represent the evolution of the mass transfer process, although these diagrams must be considered approximate.

**THE ‘CLOSED’ SYSTEM**

Water–rock systems with a very low water-to-rock ratio can be considered to be closed systems. In such systems, the amount of dissolved chemical elements is very low compared to the amount of those elements present in the parent rock, and equilibrium is achieved through a limited number of internal processes. Here, the water acts as a ‘conveyor’ of matter from unstable weathered minerals to the newly formed stable minerals. For this reason, water has been defined as the vector of mineralogical transformation in closed systems (Giggenbach 1984; Zuddas et al. 1995).

Whatever the equilibrium state between water and newly formed minerals is, ion activities in water are controlled by various mineralogical buffers (mineral associations that stabilize the water composition). The water composition in equilibrium with the stable mineral assemblage must satisfy the Duhem postulate, according to which the state of equilibrium in a closed system of fixed size is determined once only two properties are fixed (be they intensive or extensive – see glossary for definitions of these and many other terms in Richet et al. 2010 this issue). In a complex system with a large number of constituents, it is difficult to identify and characterize independent reactions. In geochemical systems, if the number of major elements can be limited to 12 (Si, Al, Na, K, Ca, Mg, Fe, S, Cl, C, H, O), the number of potential minerals containing these elements is extremely large. The number of independent chemical components can be estimated from a matrix defined by the number of atoms of every chemical element contained in a mol of mineral constituents according to the Brinkley rule (Michard 1987).

As previously mentioned, chemical elements can be qualified as controlled (water incompatible) or mobile (water compatible). Controlled elements have an effective concentration in water high enough to be constituents of all newly formed minerals, while mobile elements are characterized by a strong affinity for water. In the case of mobile ions, the activity is not controlled by the solubility of newly formed minerals. Typically, in crystalline rocks, silica and aluminium are controlled elements, whereas chlorine and occasionally sulfates (present in rather low concentrations in both rock and incoming water) are generally mobile. The controlled versus mobile nature of a given element is not an intrinsic feature but rather is a function of the system characteristics. At the beginning of the interaction, when dissolution of the parent mineral is predominant, all dissolved ions behave as if they were mobile. As soon as the water becomes saturated with respect to mineral phases like Al-Fe oxyhydroxides, silica polymorphs or clay minerals, some of the elements become controlled by the solubility of these newly formed minerals.

Even in the case of water solutions with a high ionic strength, the thermodynamic description of the system is based on energy conservation, solution electrical neutrality and mass conservation. Contrary to controlled elements, which participate also in the mass action law, mobile ions participate only in the electroneutrality equation. As a result, their concentration cannot be deduced from water–mineral equilibrium constants, but it can be estimated if the amount of reacting water and the concentrations of the mobile ions in the rock are known. The ratio between these parameters is the water–rock ratio. Its determination is a real challenge to geologists in the field. If the mobile ion concentrations are known parameters (like temperature and pressure), the equilibrium water composition can be calculated with the assumptions that (1) the algebraic sum of the ionic charges representing the mobile and controlled ions is zero (electroneutrality equation) and (2) the phase rule is observed, so that the number of equilibrium minerals is equal to the number of controlled elements. A theoretical calculation (Fig. 2) shows that the water composition in equilibrium with some minerals (low-temperature albite, adularia, calcite, muscovite, quartz and prehnite at 60 °C) changes significantly as a function of the chloride concentration. In particular, the concentrations of several major controlled elements increase when the chloride concentration increases.

**Geological Storage of Waste**

Today, it is very important to predict the long-term stability of waste stored in the geological environment. From this perspective, characterizing the deep fluid environment of a potential storage site and understanding the fluid’s genesis and evolution are fundamental to preventing the migration of toxic elements into the rock and groundwater. The ideal geological site for waste storage is one that behaves as a closed system. For this purpose, the composition of the deep waters in granite, in clay mines and at geothermal sites can effectively address the chemistry of confined systems.

In a study of the very old waters of the abandoned Strippa mine in Sweden, Grimaud et al. (1990) showed that different mineralogical buffers can be found at different chloride concentrations when waters have the same temperature. Water at the Strippa mine has reacted with granitic rocks at low temperatures over a long period of time, probably for more than 20,000 years. After careful sampling and analysis of major and trace elements and isotope ratios by an international working group (Nordstrom et al. 1989; Moser et al. 1989; Fontes et al. 1989), Grimaud et al. (1990) divided the Strippa water into 4 mineral buffer groups: water with low pH (~7), with only Al and Si controlled; water with Ca, Mg and K controlled, but not Na; water with pH ~9 controlled by chalcedony, kaolinite, 

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**FIGURE 1** Activity diagram, log (Ca²⁺)/(H⁺)² versus log (Na⁺)/
(H⁺), illustrating how water composition depends on the minerals with which the water is in equilibrium. The coloured symbols correspond to measured compositions of water groups (Grimaud et al. 1990). Mineral stability fields are calculated by the thermodynamic equilibrium approach.
albite, laumontite, adularia and calcite; and a more mature water with pH ~10, controlled by the same mineral association, except that kaolinite is replaced by prehnite.

Waters from several other cratonic areas, like the Canadian and Scandinavian shields, and from areas in western Europe underlain by Palaeozoic rocks behave according to the equilibrium model described by Grimaud et al. (1990). These waters are in equilibrium, yet buffered, with newly formed stable minerals under closed-system conditions. These naturally occurring closed systems are of particular interest as potential sites for the storage of chemical and nuclear waste since they are both closed and in equilibrium even after the deposition of waste. The thermodynamic approach reliably predicts water composition in systems governed by acid–base reactions, which are very rapid. Unfortunately, this approach does not work when redox reactions, such as Fe$^{2+}$/Fe$^{3+}$ transformations, occur because the slowness of these reactions prevents equilibrium from being reached in natural contexts (Michard et al. 1996; Appelo and Postma 2007). Although redox equilibria are absent in natural systems, redox equilibrium modeling can be a useful tool. Although the models are not significant quantitatively, they are qualitatively instructive.

THE ‘OPEN’ SYSTEM

In open systems, the pH of water generally reflects the equilibrium CO$_2$ partial pressure that results from the ionic dissociation of carbonic acid. This acid is quite often the most abundant acid–base species. Because of the rock interaction, water composition changes from rain to groundwater and pH increases by 2–3 units. Thus pH variations may trace the advancement of the water–rock interaction, which can be considered as an acid–base titration: the weak acid is CO$_2$ (or carbonic acid) and the strong base is the rock.

From a thermodynamic point of view, open systems can be considered to be divided into discrete, neighbouring subsystems. The evolution of the water composition can thus be represented by a function called the degree of advancement of the process, $\zeta$, using equilibrium conditions. Mathematically, this function is a truncated Taylor expansion representing the discrete set of open subsystems labelled by a coordinate vector (Lichtner 1985; Marini et al. 2000). The variable $\zeta$ is generally related to the length of time the water–rock interaction process has been going on. This age parameter can usually be estimated from radioactive dating based on tritium decay. Tritium ($^3$H) has a half-life of 4500 days; its abundance decays exponentially with time and is, in the simplest case, approximately related to $\zeta$. If a linear relationship between analysed pH values and computed $\zeta$ is observed, the overall water–rock interaction process can be considered as the result of continuous rock titration (dissolution of Al-silicates and carbonates) driven mainly by the conversion of CO$_2$ to HCO$_3^-$ and by the connection of natural waters with different CO$_2$ reservoirs. Since the majority of surface and subsurface waters are very close to saturation with respect to kaolinite and quartz (or other silica polymorphs), dissolved silica and aluminium are controlled by these two equilibrium constraints throughout the entire process. Consequently, the evolution of the fluid chemistry can be reconstructed from dissolution reaction paths calculated based on the degree of advancement of the irreversible mass-transfer process (Marini et al. 2000).

During water–rock interaction it is important to evaluate what part of the rock is interacting with water. Water–mineral reactions take place at the surface of the mineral in contact with water. However, only the part of the mineral surface that is in contact with the circulating waters participates in the reaction. This mineral surface is often called the ‘reactive surface’ and its area is difficult to estimate in natural conditions. Marini et al. (2000) propose a method for estimating the reactive surface area of the various minerals reacting with water by a mathematical model based on the calculation of the $\zeta$ functions. An experimental calibration of the Marini methodology was recently verified by Scisielewski and Zuddas (2010). Figure 3 represents an estimation of the reactive surface area of albite during laboratory interaction of a granite-like rock with carbon dioxide–saturated fluids. The reactive surface area is not constant during water–rock interaction but, on the contrary, changes dramatically by 3 to 4 orders of magnitude during the investigated reaction time. These studies suggest that the reactive surface area of the mineral does not remain constant during the water–rock interaction processes. The decreasing reactive surface area observed in Figure 3 can be explained by the formation of new minerals.
coating the dissolving surfaces of the albite, thereby decreasing the surface exposed to the interacting water. The evaluation of the mineral reactive surface area during the water–rock interaction process is still a controversial topic in basic and applied research.

Geological Sequestration of CO₂

The geological sequestration of carbon dioxide is accomplished by artificially injecting CO₂ into natural aquifers. When CO₂ is introduced into groundwater, the initial pH decrease of the groundwater intensifies mineral-dissolution reactions. As soon as minerals begin to dissolve, water acidity is neutralized by the formation of bicarbonate ions. For example, in the case where anorthite (calcic end-member of the common mineral plagioclase) is dissolved and water reaches equilibrium with kaolinite (a typical mineral that buffers aluminum and silica in natural waters), we have:

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{CO}_2 + 3\text{H}_2\text{O} \rightarrow \text{Ca}^{2+} + 2\text{HCO}_3^- + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4
\] (1)

Plagioclase Kaolinite

This reaction shows that as mineral dissolution proceeds, CO₂ sequestration takes place by forming bicarbonate (\(\text{HCO}_3^-\)) ions. The amount of anorthite surface area able to react is the main limiting parameter of CO₂ sequestration. The success of greenhouse gas reduction technology therefore depends on the available surface area of the minerals participating in the dissolution reaction (Friedmann 2007).

When water reaches equilibrium with calcite and a carbonate mineral is formed, the reaction becomes:

\[
\text{CaAl}_2\text{Si}_2\text{O}_8 + 2\text{CO}_2 + 2\text{H}_2\text{O} \rightarrow \text{CaCO}_3 + \text{CO}_2 \uparrow + \text{Al}_2\text{Si}_2\text{O}_5(\text{OH})_4
\] (2)

Equation (2) shows that when the concentrations of divalent ions such as calcium (or magnesium, or sodium, or iron) are controlled by the precipitation of carbonate minerals (here calcite), less gaseous CO₂ is sequestered: in this reaction, 2 moles of CO₂ are consumed (left part of the equation) and one mole is produced. This indicates that when mineral carbonation takes place, the overall fixation of gaseous CO₂ is reduced, as observed in nature and in the laboratory (Giammar et al. 2005; McGrail et al. 2006). Mineral carbonation is thermodynamically favoured but proceeds slowly. Both in nature and in several artificial carbonation scenarios, the metal-silicate mineral dissolves and a metal carbonate may precipitate. In most cases, the dissolution rate of the silicate phase is slower than the corresponding carbonate precipitation rate. The key to optimizing sequestration is to accelerate mineral dissolution. Preliminary results (Scislewski and Zuddas 2010) suggested that changes in the amount of carbon dioxide in the mineralogical form are related to the amount of newly formed minerals that coat the dissolving mineral surface and in turn control the overall water–rock interaction process.

CONCLUSIONS

When rock minerals are exposed to acidified water, they may dissolve to produce clay minerals and zeolites or other small-sized minerals, such as insoluble oxides, hydroxides and colloidal suspensions. The chemical reactions that take place during these transformations can be used to define the conditions required for equilibrium when both reactants and products are stable. The application of the equilibrium thermodynamic laws allows us to determine environmental conditions under which each mineral is stable in a given compositional system and thus to potentially predict what happens to minerals when they are exposed to conditions outside their own stability field. The chemical composition and quality of water can be predicted using the solubility limits of certain mineral components, which may play a significant role in the composition of natural aqueous solutions.

One of the main questions concerns the effect of natural or artificial disruptions on the stability of the mineralogical buffers controlling the activity of the ions at equilibrium. This question may be solved when we have reliable analytical tools allowing us to evaluate how disruptions change the system entropy in natural water–rock interaction systems over time.

ACKNOWLEDGMENTS

This article benefited from discussions with Prof. G. Michard, Prof. D. Grimaud and Dr. P. Toolbo and from a decade of participation in sponsored and informal water–rock interaction activities. I thank my research group for their support and thought-provoking discussions.

REFERENCES


Metamorphic rocks, formed at elevated temperature and pressure from pre-existing rocks inside mountain belts, provide a seemingly unpromising target for the application of equilibrium thermodynamics. This is because metamorphic rocks develop their mineral assemblages along a pressure–temperature (P–T) path, with pressure and temperature continuously changing along the path. However, in a successful model for the formation of such rocks, involving the essential role of fluid or melt, the mineral assemblages observed at the Earth’s surface can be considered to reflect a state of frozen-in equilibrium as the rocks are exhumed towards the Earth’s surface. Equilibrium thermodynamics applied to such mineral assemblages allow P–T information to be extracted. Currently the best way to do this is via calculated phase diagrams, the most powerful being P–T pseudosections. These diagrams portray the variation of mineral assemblages with P–T for a specified rock composition. Pseudosections allow the P–T conditions of the frozen-in equilibrium to be estimated, and can also give information on the P–T path followed. Such paths are an essential input in constraining the processes involved in mountain-building and the evolution of continental crust.

Keywords: equilibrium in metamorphism, pseudosections, THERMOCALC, spinel stability

INTRODUCTION

Metamorphism involves the growth of new mineral assemblages in pre-existing sedimentary, igneous and metamorphic rocks, primarily under the influence of elevated pressure and temperature, and commonly associated deformation. In continental crust, the main environment in which metamorphism occurs is in mountain belts (orogenic belts), where thermally weakened crust is thickened as a consequence of compressive far-field stresses. In the modern Earth this occurs almost exclusively at convergent plate boundaries, where sedimentary and igneous rocks, as well as pre-existing metamorphic rocks (basement), are fed into developing orogens, as in the Andes, Alps and Himalayas. Because of the buoyancy of a plate composed of thickened crust, orogens are mountainous regions exposed to erosional processes. In time the crust is thinned by erosion to a more normal thickness, revealing the deeper levels of the orogen and the metamorphic rocks which formed there.

The basement of continental crust, beneath any obscuring sedimentary basins, is made up of the remains of old orogenic belts stitched together by continental collision related to the supercontinent cycle. Understanding crustal evolution, and in particular orogenic processes, involves reading the encoded geological record represented by the metamorphic rocks that make up the basement. Metamorphic rocks collected from ancient and modern orogens have followed a more or less complicated pressure (P) and temperature (T) path, from the Earth’s surface, through the bowels of the orogen and back to the Earth’s surface again. Commonly the only evidence for the P–T path that a rock has followed comes from its mineral assemblage and the textural relationships between the minerals. Yet P–T paths are a critical parameterisation of orogeny, as P paths reflect the depth history of rocks and T paths the thermal state as depth changed. Establishing P–T paths is essential to understanding orogeny and consequently the history of the continental crust.

The main tool for establishing P–T paths is equilibrium thermodynamics. First we present the rationale for using equilibrium thermodynamics, then we discuss the methods employed, with a focus on calculated phase equilibria.

DEVELOPMENT OF METAMORPHIC MINERAL ASSEMBLAGES

It is not self-evident that metamorphic rocks can be studied using equilibrium thermodynamics because what is observed in them (minerals, mineral compositions, textural relationships) develop along a P–T path with P and T changing more or less continuously. For the approach to be applicable, it is necessary to show that a part or all of a mineral assemblage in a rock represents a state of equilibrium that is preserved from a point along the P–T path.

The key is whether a metamorphosing rock has fluid or silicate melt along its grain boundaries, because their presence strongly promotes equilibration between the minerals, either directly or by allowing recrystallization in response to, for example, stress. Consider first a rock that has not been previously metamorphosed: most likely
Hydrous minerals and fluid are present. Even in nominally dry protoliths, such as basalt, hydration is commonly largely complete by the time the rock reaches low greenschist facies conditions. In the up-P–T (prograde) part of a rock’s history, progressive maintenance of equilibrium on some scale is consistent with observation. Hydrous minerals break down continuously (dehydration), and critically – much of the fluid thus generated is lost (under the influence of gravity, possibly aided by deformation). In the down-P–T (retrograde) part of a rock’s history, fluid is not there to reverse the prograde dehydration, and the mineral assemblage tends to be preserved; thus, little happens during the retrograde history (unless fluid is reintroduced into the rock). Dehydration relates to steep, but not vertical, P–T lines of water content in mineral assemblages. Preservation of mineral assemblages tends to occur close to, but not at, the maximum of the P–T path. These P–T conditions are commonly referred to as the metamorphic peak.

In this view, the mineral assemblage observed in such a first-cycle metamorphic rock at the Earth’s surface is that preserved from the metamorphic peak. Assuming this is an equilibrium mineral assemblage, equilibrium thermodynamics can, in principle, be used to determine the P–T conditions of the metamorphic peak. In practice, metamorphic rocks commonly show features that reflect the prograde history (for example, zoning of minerals and inclusions that have survived by being armoured from further reaction by their host) and retrograde history (for example, retrogressive replacement of peak minerals). On the one hand, these features may give information about the P–T path; on the other, with appropriately nuanced petrographic interpretation, a “main” mineral assemblage may be identified and be the subject of phase equilibria modelling.

The identification of a “main” metamorphic mineral assemblage, and its use in phase equilibria modelling, can be extended to metamorphism that involved partial melting and to metamorphic reworking (metamorphism of previously metamorphosed rocks), with the presence or absence of fluid (or melt) being central. In the case of reworking, rocks tend to lack a fluid and may not respond at all to changing P–T conditions, unless fluid addition and/or recrystallization are involved. Reworking may be restricted to shear zones.

The appropriateness of treating metamorphic mineral assemblages as if they reflect a preserved equilibrium has underpinned much of metamorphic geology in the last half-century. Initially, the recognition of the recurrence of mineral assemblage associations (the metamorphic facies concept) suggested an equilibrium explanation and militated against the control of mineral assemblages by dominantly kinetic processes. More recently the equilibrium assumption has been largely implicit, but recent discussions in a calculated phase equilibria context include Guiraud et al. (2001), White and Powell (2002), Powell et al. (2005) and Powell and Holland (2008). The success of using calculated phase equilibria to study metamorphic rocks provides, at least in part, an a posteriori justification of the assumption.

**APPLYING EQUILIBRIUM THERMODYNAMICS TO METAMORPHIC ROCKS**

Given a justification for using equilibrium thermodynamics to consider mineral assemblages in metamorphic rocks, there is still a considerable step before being able to do useful calculations on them. Assuming that the rocks themselves are well understood – in terms of field relationships, relative timings via the deformation history, petrography, mineral-chemistry maps, absolute timing via radiometric methods, and so on – various inputs are needed for calculations.

The essential input is thermodynamic descriptions of the phases (minerals, fluids, silicate melt) involved in the development of the mineral assemblage in a rock. Such descriptions can be considered in terms of the thermodynamic properties of the end-members of phases, and then the energetics of the way these end-members are combined to form the phases (the activity–composition, or a–x, relationships). It was recognised in the 1970s that calorimetric data alone were not precise enough to constrain the thermodynamic properties of end-members for rock calculations because their uncertainties were too large. Out of this grew the idea of internally consistent thermodynamic datasets which aimed to combine, and make consistent, calorimetric data with constraints from experimentally determined phase equilibria, primarily from “reversed” reactions in simple systems (e.g. Helgeson et al. 1978).

Until the early 1990s, the main use of thermodynamic calculations was in so-called conventional thermobarometry (determining the P–T of formation), in which an observed mineral assemblage and its mineral compositions would be combined with reactions written between the mineral end-members to constrain P–T. In some studies the focus was on individual, specially calibrated, reactions (e.g. Ferry and Spear 1978), whereas in others it involved combining information from as many reactions as possible (e.g. the average P–T approach of Powell and Holland 1988, 1994). Various problems are involved in such inverse modelling, not least the dependence on mineral composition, an aspect of observations that is harder to defend in terms of a preserved equilibrium. As thermodynamic datasets improved in scope, it became possible to envisage forward modelling of phase equilibria, for example, for specified rock compositions (so-called pseudosections) that would provide thermobarometric information without suffering from this limitation, and also supply various other benefits (as summarised in Powell and Holland 2008).

It was obvious that internally consistent thermodynamic datasets would have to be augmented with less-well-constrained data – for example, from natural assemblage information – if forward calculations even in relatively simple systems were to be undertaken. For example, for calculations in the system KFMASH (K₂O–FeO–MgO–Al₂O₃–SiO₂–H₂O), given that essential minerals involve not only the FeMg₁ substitution but also the Tschermaks (MgSiAl₁Al₂) substitution, data are needed for more than the experimentally well-constrained magnesian end-members. In 1990 came the first dataset that allowed calculations relating to rocks (Holland and Powell 1990), admittedly in fairly simple systems like KFMASH (e.g. Powell and Holland 1990). A significant update of this dataset is given in Holland and Powell (1998), and it is currently the de facto standard for metamorphic phase equilibria calculations.

In the 1990s, modelling metamorphic rocks using equilibrium thermodynamics was restricted to relatively simple systems by the thermodynamic descriptions of phases available then. At that stage, P–T projections (or petrogenetic grids), compatibility diagrams and pseudosections were used more or less equally. As summarised in Powell et al. (1998), P–T projections show all reactions and intersections of reactions for a chemical system, compatibility diagrams are constant P–T sections.
showing mineral assemblage and mineral composition information (like AFM: Thompson 1957), and P–T pseudosections show the mineral assemblages for a given rock composition.

Pseudosections are currently the most powerful way of modelling (Powell and Holland 2008). A P–T pseudosection is effectively a P–T “map” of mineral assemblages for the specified chemical bulk composition. A T–x pseudosection is a T “map” of mineral assemblages, at a constant P, for a chemical composition vector, x. A P–x pseudosection is at a constant T. The composition vector can be used to investigate mineral assemblages as a function of poorly constrained variables such as H2O or O2, or to span a range of actual rock compositions. Choosing a chemical composition to use in a pseudosection requires care and an understanding of the likely scale of equilibration in the rock being considered. Accepting this, the particular advantage of pseudosections in modelling mineral assemblages and thermobarometry is that the results do not depend on the observed mineral compositions; as well, pseudosections provide a context for the observed mineral assemblages in terms of alternatives as the P–T conditions vary (Powell and Holland 2008). Box A illustrates the various modelling approaches.

**Box A  TYPES OF MODELLING**

Use a model system, e.g. KFMASH, to:

- undertake calculations
- represent rocks, approximately

In a model system, minerals are represented by the proportions of their end-members or of their composition variables; for example, for garnet (g), (Ca,Mg,Fe3+)Al2SiO6.

- grossular (Ca), pyrope (Mg), almandine (Fe) end-members
- x(g) = Fe/(Fe + Mg), x(g) = Ca/(Ca + Fe + Mg) composition variables

An equilibrium mineral assemblage can be characterised in terms of

- (a) minerals involved
- (b) mineral compositions
- (c) rock composition

Types of modelling:

- inverse modelling – use (a) and (b), but not (c), to calculate P and T
- forward modelling – use (c), but not (a) or (b) directly, to calculate a P–T pseudosection, and then relate it to (a) and (b) information

The preeminence of pseudosections over other types of calculated phase diagrams is a consequence of the larger chemical systems that are now used in modelling. It is rarely possible to reduce the effective size of a larger system in order to draw compatibility diagrams. And P–T projections, in showing only reaction (invariant and univariant) information for a chemical system, are of little direct use because the great majority of rock compositions involve equilibria with less minerals than univariants, as observed on pseudosections. P–T projections in smaller systems may help in envisaging the topology of pseudosections in a larger system, particularly if they effectively constitute a “backbone” for that system (as KFMASH does for metapelite). But using smaller, petrologically unrepresentative systems for thermobarometry will generally give unreliable or biased results.

Since 1990, the pseudosection approach has gained momentum, driving and being driven by advances in a–x models for the phases involved in metamorphism. A key step in a–x model development and the implementation of such models in software was provided by Powell and Holland (1993) and Holland and Powell (1996a, b). As new models have been developed and old models improved, the power and the range of applicability of the pseudosection approach have grown. For example, with the haplogranitic model of Holland and Powell (2001), and various extensions since then, modelling of pelitic and greywacke-composition granulite facies rocks, in which partial melting plays a key role, has become possible (e.g. White and Powell 2002). Using the framework provided by Evans and Powell (2006), pseudosections involving mixed-solvent aqueous fluids can be calculated. The new general model for the amphiboles of Diener et al. (2007) now allows amphibole-bearing rocks to be modelled. And the progress continues.

For modelling most metamorphic rocks, the model system of choice is currently NCKFMASHITO (Na2O–CaO–Al2O3–FeO–MgO–Al2O3–SiO2–H2O–TiO2–O2), with CO2 added for considering carbonate-bearing rocks, and Cl (and now S) for considering aqueous solutions. The idea is to use a chemical system that is as close as feasible to that of rocks, with the obvious constraint that thermodynamic data must exist for the end-members of the phases in that system. Another obvious candidate for inclusion is MnO, on account of its role in stabilising garnet, but the data for many Mn end-members of minerals are currently not up to date (they are currently being revised, however).

Among the software used to calculate pseudosections, THERMOCALC (Powell and Holland 1988; Powell et al. 1998) is based on a non-linear equation solver and calculates the lines and points of pseudosections directly; the coordinates are then manually assembled for drawing (by DRAWPD). Other software, for example, Perplex (Connolly 1990), are Gibbs energy minimisers and can be good at locating fields in pseudosections, but lines and points have to be found by interpolation, with small fields being easily missed. Petrologically it is the lines and points (and those small fields) that are significant, so THERMOCALC is better suited for pseudosection calculation, particularly in bigger systems like NCKFMASHITO. Box B illustrates the method of calculation in inverse and forward modelling.

**PSEUDOSECTION CALCULATIONS: AN EXAMPLE**

A metamorphic geology example is used to illustrate some of the ideas relating to phase equilibria calculations on rocks. Whereas pseudosections can be used for thermobarometry, they are additionally a powerful way of understanding the dependence of mineral assemblage on P–T and on chemical aspects of rocks that are difficult or impossible to observe, for example, oxidation state. In the example below, the mineral assemblage of this typical rock composition is a rather subtle function of P–T and ferric iron content.

In the transition from the amphibolite facies to the granulite facies, hercynitic spinel (sp) may occur in quartz-saturated metapelitic rocks, with for example cordierite – biotite – sillimanite (cd + bi + sll), and alkali feldspar, plagioclase, quartz and, at metamorphic conditions, silicate melt (ksp + pl + q + lq), and one or more Fe–Ti oxides. In simple modelling, for example in AFM (i.e. KFMASH + ksp + q + lq), cd + bi + sll is a readily understood mineral assemblage, and, as a result of the reaction bi + sll = q + cd with increasing temperature, such an assemblage makes
CALCULATION METHOD IN INVERSE MODELING

FOR A MINERAL ASSEMBLAGE input to calculations from equilibrium relations:

- write balanced reactions between constituent end-members
- for each reaction, an equilibrium relation obtains:
  \[ 0 = \Delta G^o + RT \ln K \]
  where
  \[ \Delta G^o \] is a function of P and T and is derived from end-member properties
  \[ K \] is a function of mineral compositions

- There are \( m - n \) independent equilibrium relations in the model system, for \( m \) end-members and \( n \) oxides.

Input to calculations from oxide sum relations:

- Rock composition = sum (mineral composition \times\ mineral proportion)

In inverse modelling, to calculate P–T of formation:

- List end-members in the minerals of the mineral assemblage
- Write the \( m - n \) independent reactions, and for each, \[ 0 = \Delta G^o + RT \ln K \]
- Calculate \( K \), leaving \( m - n \) equations in P–T
- Combine, e.g. by weighted least squares in av P–T, to get “best” P–T

In forward modelling, to calculate mineral compositions and proportions:

- List end-members in the minerals of the mineral assemblage
- Write the \( m - n \) independent reactions, and for each, \[ 0 = \Delta G^o + RT \ln K \]
- Add the \( n - 1 \) oxide sum relations using the rock composition
- At specified P–T, unknowns are the mineral compositions and proportions
- Solve \((m - n) + (n - 1)\) equations for the unknowns way for g + cd assemblages. Until the role of ferric iron was included in the modelling, the presence of sp + bi was difficult to put in context.

A calculated P–T pseudosection in the NCKFMASHTO system for an aluminous metapelite is shown in Figure 1. For this composition, a small proportion of all-Fe-as-FeO
\[ \text{FeO}_{\text{total}} = 6.66 \] is considered to be \( \text{Fe}_2\text{O}_3 \), denoted by \( O = 0.07 \); thus the actual FeO = 6.66 - 2(0.07) = 6.52, and \( \text{Fe}_2\text{O}_3 = 0.07 \). All-Fe-as-ferric iron corresponds to \( O = 3.33 \), so \( O = 0.07 \) is \( x(O) = 0.07/3.33 = 0.021 \). Note the characteristic feature of pseudosections: boundary lines mark where a mineral appears or disappears (the blue line marks the limit of stability of spinel). Mineral modes (proportions) change continuously with P–T in such diagrams, and a boundary line occurs where a particular mode becomes zero. THERMOCALC calculates the lines, and the points where lines intersect, in terms of what modes are zero (to see how to do this, go to www.metamorph.geo.uni-mainz.de/ thermocalc and hit the “elements” button). The results for an example calculation are shown in Box C.

In Figure 1, with \( x(O) = 0.021 \), there is indeed a stability field for sp + bi (field outlined in red), the mineral assemblage observed in low-P transitional granulites. The phase relationships at lower \( x(O) \ (<0.025) \) are shown by black dashed lines: spinel is not stable in this P–T range, in line with modelling in simpler systems, like KFMASH and NCKFMASH.

Another sort of pseudosection can be used to study the dependence of phase relationships on \( x(O) \); a T–x pseudosection, where the \( x \) is \( x(O) \) (Fig. 2). The example shown is calculated for 4.5 kbar, for the lower range of \( x(O) \). The sp + bi field (bounded by the red line) extends over a wide range of \( x(O) \). In Figure 2, note how magnetite is replaced by spinel as a carrier of ferric iron as temperature increases at a particular \( x(O) \). Note also that magnetite replaces spinel as a carrier of ferric iron at high T with increasing \( x(O) \). Indeed at much higher \( x(O) \) magnetite itself is no longer stable, because ilmenite, as it becomes more hematite-rich, can accommodate the ferric iron in a more energetically favourable way than magnetite.

An interesting way to consider the phase relationships for the relatively narrow range of P–T conditions in which the assemblage bi + sp is stable is via a compatibility diagram. The starting point is to say that cd + bi + sill with ksp + pl + q + liq is an expected mineral assemblage, and then to say what additional minerals can be involved with them. With all these phases “in excess”, the phase relationships can be represented as in Figure 3, which is part of the Fe-Ti oxides triangle, FeO–Fe₂O₃–TiO₂ (personal communication K. Taylor-Jones). The focus is on the Fe-Ti oxides involved (ilmenite and magnetite), but it is also on spinel and garnet, which project onto this triangle. This shows that the “standard” cd + bi + sill assemblage can be joined by various combinations of ilmenite, magnetite, spinel and garnet, depending on the oxidation state and TiO₂ content. At slightly higher pressure, the crossing-tie-lines reaction sp + ilm = g + mt effectively precludes spinel from mineral assemblages in rocks, as is indeed reflected by observations in nature.

DISCUSSION AND CONCLUSIONS

Thermodynamic modelling of metamorphic rocks is currently in a vibrant state, but much still needs to be done. Obviously the quality of modelling can only be as good as the petrography, and this needs to be done with a phase equilibrium mindset so that the potential meaning of textural relationships can be properly ascribed. Advances
FIGURE 1 A calculated P–T pseudosection in the system NCKFMASHTO for the same bulk rock composition (aluminous pelite) as used by Powell and Holland (2008, Fig. 1): in mole %, SiO$_2$ = 65.47, TiO$_2$ = 0.65, Al$_2$O$_3$ = 14.49, CaO = 0.49, MgO = 2.55, FeO$_{total}$ = 6.66, K$_2$O = 2.8, Na$_2$O = 1.17, O = 0.07, and H$_2$O = 5.65. In this composition, the O corresponds to a small proportion of Fe$_2$O$_3$, meaning that actual FeO = 6.66 – 2(0.07) = 6.52, and FeO$_{2}$ = 0.07. The blue line marks the stability limit of spinel and the red line marks the stability field of spinel and biotite. Abbreviations: g = garnet, cd = cordierite, bi = biotite, sill = sillimanite, sp = hercynitic spinel, ilm = ilmenite, mt = magnetite, pl = plagioclase, ksp = alkali feldspar, q = quartz, liq = silicate melt. The red dashed line at P = 4.5 kbar corresponds to Figure 2. See text for discussion.

FIGURE 2 A calculated T–x pseudosection in the system NCKFMASHTO at P = 4.5 kbar for the same bulk composition as in Figure 1 but with O varying from 0 to 3.33, corresponding to x(O) = 0 to 1. The horizontal dashed line corresponds to the x(O) of Figure 1, and the vertical line relates to Figure 3. See caption of Figure 1 for abbreviations. See text for discussion.
A calculated FeO–Fe₂O₃–FeTiO₃ compatibility diagram at 4.5 kbar and 765 °C in the system NCKFMASHTO, in projection from the calculated compositions of bi + cd + sill + pl + ksp + q + liq. See caption of Figure 1 for abbreviations. See text for discussion.

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In mineral–chemical imaging have the capacity to help greatly in this. As more becomes known, progress will be made in understanding how mineral assemblages and, in particular, mineral compositions evolve during metamorphism, and are then preserved. In this way it is hoped that the subtle effects preserved from the prograde history and superimposed during the retrograde history can be used to extract more reliable P–T path information, in addition to the P–T of the metamorphic peak provided by the "main" mineral assemblage.

Such a view of metamorphic rocks is resolutely a P–T–X one. However, depending on the processes operating during metamorphism, volume (V) rather than P might be the more appropriate variable, for example. In the context of such conjugate pairs of variables, more useful phase diagrams may be calculated (Powell et al. 2005). A particular aspect currently being developed involves considering chemical potentials rather than compositions. This procedure is useful in studying textural relationships among minerals in which, for example, equilibration was in progress when the relationships were preserved, as in corona development during cooling (White et al. 2008; see also the photomicrograph on page 309). In combination with quantitative modelling of diffusion, such an approach has the capacity to inform understanding of equilibration and indeed, how mineral assemblages evolve and are preserved (Carlson 2002).

In the thermodynamic modelling itself, better thermodynamic descriptions (both end-member properties and activity–composition relationships) of phases are needed, extending also into chemical systems not currently available to study. At least some of these advances will come via natural mineral assemblage calibration, for example, where calibration by experiment is impossible or prohibitively slow.
Throughout geological history, partial melting of mantle rocks and magma ascent and crystallization have played key roles in shaping the Earth. The importance of magmas stems from their liquid nature, that is, from their high atomic mobility and lack of long-range order. Compared to crystals, magmas thus have peculiar thermodynamic properties. A few examples illustrate how solid–liquid and liquid–volatile equilibria can be predicted. Given the almost infinite diversity of conditions of chemical composition, temperature and pressure in nature, thermodynamic modelling has become a necessary tool for understanding magmatic processes.

**A TOOL FOR UNDERSTANDING IGNEOUS PROCESSES**

Volcanic eruptions are a most dramatic illustration of the boundless power of nature. Although magmas are the cause of these phenomena, their origin and evolution have long remained elusive. The confusion of ideas that still prevailed at the end of the 18th century is illustrated by the term pyroxene (from pyros, fire, and xenos, foreign), which was coined when this mineral was thought to result from incomplete melting of the source rock by subterranean fires. From clever field observations, however, Dolomieu (of dolomite fame) concluded in 1797 that lavas originated from the deep, dense, “pasty and viscous” matter upon which the solid crust rested all over the world. At the same time, experimental petrology was initiated by Hall (1798), who observed that the vitreous or stony character of the product formed when molten basalt was cooled depended on its rate of quenching. Hence, the presence of xenocrysts, such as pyroxene, in lavas was no longer seen as indicative of incomplete fusion but the result of partial crystallization of the melt.

Just as fossils were doing for sedimentary terranes, crystals came to represent a valuable source of information on igneous rocks. Accounting for the diversity of these rocks in the Earth’s crust became the main goal of the fledgling discipline of igneous petrology, but it was recognized early on that a variety of tools had to be used to understand the natural record in terms of magma formation and evolution. As implicitly illustrated by the pyroxene story, thermodynamics played a critical role in this respect. Of course, experimental petrology has been of paramount importance in determining which phases are stable under given conditions of temperature, pressure and chemical composition. Without the thermodynamic framework provided by the phase rule, however, interpretation of these results would be at least ambiguous, if not really thorny. Without thermodynamic modelling, interpolation or extrapolation to real processes of such experimental data, which pertain to necessarily restricted ranges of relevant conditions, would, in addition, be impossible. And this need for modelling has become even more pressing ever since the field of igneous petrology was enlarged to include Earth’s mantle, which mostly escapes direct observation. In short, thermodynamics as applied to magmatic processes has now grown to such an extent that we can only highlight a few points here.

**MAGMAS AS MOLTEN SUBSTANCES**

Magmas owe their importance to the efficient way they transport energy and matter, at all scales, in response to pressure and temperature gradients. This efficiency results from the high atomic mobility that is the hallmark of melts, as evidenced in daily life by the easy way in which a liquid flows. Contrary to solids, either crystalline or vitreous, where atoms occupy essentially fixed positions, liquids are characterized by dynamic disorder, that is, by unceasing structural rearrangements made possible by the excess thermal energy, with respect to solids, that they acquire on melting. The nature of these structural changes is constrained by Le Châtelier’s laws:

\[
(\partial G/\partial T)_P = -S \quad \text{and} \quad (\partial G/\partial P)_T = V.
\]

Under equilibrium conditions, increases in temperature \((T)\) and pressure \((P)\) thus cause increases in entropy \((S)\) and decreases in volume \((V)\), respectively, to ensure a minimum value for the Gibbs free energy \((G)\) of the melt. Because it scales as viscosity, the rate of these structural rearrangements decreases on cooling. If crystallization is bypassed, this rate eventually vanishes in a narrow temperature interval, the glass transition range, where the frozen-in atomic configuration of the liquid becomes the structure of a disordered solid, a glass.

From a geological standpoint, two important consequences follow. First, the disordered nature of glasses and melts allows a wide range of elements to coexist in a single phase, as illustrated by the fact that a single liquid forms through melting of a rock made up of a number of mineral phases. Second, part of the heat given to a melt does not result in a temperature increase, but in exploration of atomic positions of higher potential energy which are associated with...
higher entropy. The heat capacity ($C_p$), enthalpy ($H$) and entropy can thus be split into two different contributions: a vibrational part, akin to the properties of solids, and a configurational part, which determines thermochemical differences between melts and crystals (Fig. 1) (Richet and Neuville 1992). A similar distinction holds for volume properties. Since the positions of higher potential energy explored by atoms in liquids are generally associated with longer interatomic distances, the density ($\rho$) of a melt is lower than that of a crystalline assemblage of the same composition, whereas its thermal expansion coefficient, $\alpha$, given by $1/V (\partial V/\partial T)_p$, is higher.

For a mineral that melts without composition change, the higher entropy and lower density of the liquid compared to the crystal cause the melting temperature to increase with pressure, as stated by the Clausius-Clapeyron equation:

$$\frac{dT}{dP} = \frac{\Delta V_f}{\Delta S_f},$$  

where $\Delta V_f$ and $\Delta S_f$ are the volume and entropy of melting. Although Equation (2) has no counterpart for calculating the variations with pressure of the liquidus and solidus temperatures of a rock, the same effect obtains because mixing in the liquid state of the individual mineral components results in further increases of the entropy of the melt. Since melting begins to take place when the geothermal gradient intersects the solidus of mantle rocks, the former curve has a steeper slope than the latter.

Importantly, the lack of long-range order in a liquid makes possible a wide range of densification mechanisms, such as pressure-induced changes of Si and Al from 4 to higher coordination by oxygen (Fig. 2); such changes are not available to a given crystal where only changes in bond angles and distances are possible if long-range symmetry is to be maintained. Because of this configurational contribution, a melt has a higher compressibility $[\beta_f = -1/V (\partial V/\partial P)_T]$ and lower bulk modulus ($K_f = 1/\beta_f$) than its isochemical crystalline assemblage. For diopside (CaMgSi$_2$O$_6$), which can be used as a model system for basalt, the room-pressure bulk modulus, $K_{T0}$, is about 23 and 91 GPa at 1700 K for the melt and crystal, respectively (see Richet and Neuville 1992). The density contrast between these two kinds of phases (melt and crystal) thus decreases with increasing pressure, but less strongly than indicated by these figures. As illustrated by the analysis made for SiO$_2$ (Fig. 2), the reason is that the rate of structural rearrangements decreases with increasing pressure so that the increase of $K_f$ with pressure is also much higher for the melt than for the crystal, with values of $K_{Tf} = (\partial K/\partial P)_f$ at room pressure of about 10 and 4, respectively. These parameters control both the pressure dependence of the Gibbs free energy and the buoyancy of magma, which allows it to rise from its site of formation at depth to the surface. In view of this dual importance, efforts are being made to use atomistic simulations to complement the limited database resulting from the considerable difficulty of making volume measurements on melts at very high pressures (Ghiorso 2004).

**PHASE EQUILIBRIA AND THERMODYNAMIC MODELLING**

As extensively determined since the first half of the 20th century, liquidus and solidus data still constitute the main source of thermodynamic information for silicate melts (see Levin et al. 1964). These data refer to conditions of chemical equilibrium, which are actually relevant to natural processes in view of their high temperatures and long timescales. The state of equilibrium that is reached eventually gets frozen in at some stage, however, when the kinetics of the reaction of interest become too slow compared with the cooling rate of the system.

An example of fundamental petrological importance for basalt and andesite petrogenesis is the melting relations of plagioclase feldspars (Fig. 3). On cooling, a melt of composition Y forms a first crystal of composition X. Depending on whether the crystal is removed from the system (fractional crystallization) or keeps equilibrating with the melt (batch crystallization), its composition varies from X to Y or from X to pure albite along the solidus, and that of the melt along the liquidus from Y to Z or from Y to pure albite, respectively. Similar differences apply for fractional and batch melting, with the consequence that the melt becomes enriched in the least refractory component whenever the transformation is not total. Analogous evolutions are observed in phase diagrams with different topologies. As expounded long ago by Bowen (1928), they are the basis of magma differentiation, which leads from basaltic to felsic melts.
In the simplest thermodynamic model of plagioclase melting, the end-member compositions CaAl$_2$Si$_2$O$_8$ (An, anorthite) and NaAlSi$_3$O$_8$ (Ab, albite) are chosen as components and are assumed to mix ideally, that is, randomly and without any thermal effect. From reported heat capacities for the liquid and solid phases and enthalpies of fusion (see Richet and Bottin 1986), one readily calculates liquidus and solidus branches by finding the crystal (c) and liquid (l) compositions for which the chemical potential ($\mu$) equations

$$\mu_{\text{An}}^c = \mu_{\text{An}}^l \quad \text{and} \quad \mu_{\text{Ab}}^c = \mu_{\text{Ab}}^l$$

are satisfied at a given temperature (see Richet et al. 2010 this issue). Agreement with the experimental data is excellent for the liquidus and fair for the solidus (FIG. 3). As expected, ideal mixing is more clearly followed in the liquid than in the solid phase, for which better agreement is achieved through inclusion of an enthalpy term and adjustment of the entropy term to account for the lack of Al–O–Al linkages in plagioclases.

When metal oxides are added to pure SiO$_2$, however, the structure changes markedly from a three-dimensional open network of SiO$_4$ tetrahedra to the isolated SiO$_4$ tetrahedra of orthosilicates. This depolymerization is described by reactions such as

$$\text{Si–O–Si} + \text{Na}_2\text{O} \rightarrow 2 \text{Si–O–Na}$$

but an important difficulty of thermodynamic modelling is that there is no way to define a unique set of components relevant throughout the wide composition ranges of interest, that is, a set of components whose entropy of mixing remains close to ideal from pure-SiO$_2$ to SiO$_2$-poor melts. As a result, the numerous models found in the literature differ from one another not only by the functional forms they posit for the activity–composition relationships but also by their choices of components. In spite of their differences, most models share the common point that they can be considered as tools for performing mathematical fits whose extrapolation to composition ranges not dealt with in their calibration is problematic.

The model developed by Ghiorso and co-workers in the freeware code MELTS (http://melts.ofm-research.org) is the most extensively used in geology because it has been specifically tailored to basal petrogenesis (Ghiorso and Sack 1995). It relies on a set of 14 components, which are either oxides (SiO$_2$, TiO$_2$, Al$_2$O$_3$, Fe$_2$O$_3$, CaO, P$_2$O$_5$, SrO, H$_2$O) or more complex entities (Na$_2$SiO$_3$, K$_2$SiO$_3$, Mg$_2$SiO$_4$, Ca$_2$SiO$_4$, Mn$_2$SiO$_4$, Fe$_2$SiO$_4$, and all except H$_2$O) are referred to 8 oxygen atoms (Si$_8$O$_{22}$, etc.). These components were selected because their thermodynamic properties could be retrieved from a combination of thermochemical and phase equilibria data and, as illustrated by modelling of plagioclase melting, because part of the complicated interactions between individual atoms is automatically taken care of when complex components are used. The Gibbs free energy of the melt is assumed to be of the so-called regular form:

$$G(P,T) = \sum_i n_i \mu_i^T + RT \left( \sum_i n_i \right) \ln \chi_i + 1/2 \left( \sum_i n_i \right) \sum_{ij} W_{ij} \chi_i \chi_j,$$

where $n_i$ is the number of moles of the $i$th component and $\chi_i$ is its mol fraction. The first term is the weighted sum of the standard state chemical potentials ($\mu_i^0$) of the components at the $P$–$T$ of interest; the second is the ideal entropy of mixing; and the third is the enthalpy of mixing expressed in terms of binary interaction parameters, $W_{ij}$ between components $i$ and $j$ which are determined from fits made with Equation (5) to input phase equilibria data for complex systems only. Likewise, use is made of the non-ideal solution models available for the solid solutions of interest, such as spinels, olivines, pyroxenes and plagioclases. For given pressure, temperature and composition, equilibrium is reached when $G$ is minimum, whereas the nature and composition of the solid phases is such that chemical potential equalities analogous to Equation (3) are satisfied for all components. The predictions of energy and chemical evolution as a function of pressure, temperature, oxygen fugacity and water content made reliably with this model are now well established. As for the effects of pressure, Ghiorso and co-workers are working to extend equations of state to 100 GPa and 5000 K with the help of atomistic simulations.

Alternatively, only oxide components have been used by Pelton and co-workers to set up the “quasi-chemical” model at the core of the FACT commercial package (e.g. Pelton and Wu 1999). This model is probably the most popular in metallurgy and the glass industry because it depicts the topological complexity of phase diagrams with unmatched precision thanks to the long series expansion used for both enthalpy and entropy contributions to the activity. For instance, 6, 4 and 4 fit parameters are introduced for the binary systems CaO–SiO$_2$, CaO–Al$_2$O$_3$ and Al$_2$O$_3$–SiO$_2$, respectively, whereas 2 ternary interaction parameters are in addition needed for CaO–Al$_2$O$_3$–SiO$_2$ melts (Eriksson and Pelton 1993). The results obtained for this complex phase diagram of enormous industrial interest illustrate the usefulness of the method. The effects of pressure, however, are not accounted for.

**VOLATILE DISSOLUTION**

Undoubtedly, the most spectacular illustration of the role played by volatiles in melts is the kilometre-high column of a Plinian eruption, where millions of tons of ejecta are self-sustained by a jet of gases exsolved at the fragmentation level with a velocity of several hundred metres per second. Understanding the way in which volatile solubility depends on pressure, temperature and composition is thus an important issue. The assumption that volatiles dissolve in a melt in molecular form can be made for only a few
species, such as the noble gases, He, Ne, Ar, Kr and Xe (Lux 1987). In contrast, the major volatiles H2O, CO2 and SO2 have a complex reactive solubility. This is why water induces large melting point depressions, which reach for instance 800 K for quartz at a pressure of 1 GPa (FIG. 4).

Comprehensive models have been set up for dealing with H2O and CO2 dissolution (e.g. Papale et al. 2006). For illustration purposes, however, a simple regular-type solution model analogous to Equation (5) broadly accounts for the trend of FIGURE 4. Written in terms of the chemical potential, equilibrium between quartz and SiO2 in the melt implies that

\[
\mu_{\text{SiO}_2}\text{l} = \mu_{\text{SiO}_2}\text{l}^0 + \mu_{\text{Si-O}} + \frac{x_{\text{H}_2\text{O}}}{W_{\text{Si-H}}}\mu_{\text{Si-O}}\text{l} + RT \ln \left(1 - x_{\text{H}_2\text{O}}\right),
\]

where \(\mu_{\text{SiO}_2}\text{l}^0\) is the chemical potential of pure SiO2 melt at the \(T-P\) of interest, \(x_{\text{H}_2\text{O}}\) is the mol fraction of H2O in the melt and \(W_{\text{Si-H}}\) is an interaction parameter. Under dry conditions, the increase of the melting temperature of quartz with pressure is calculated without any fit parameter from available volume and thermochemical data for quartz and SiO2 melt (Fig. 4). Under wet conditions, a pressure-dependent interaction parameter, \(W_{\text{Si-H}}(k) = -22.4 + 1.94 P\) (kbar), is needed in Equation (6) to match the experimental liquidus and solubility data along the liquidus (FIGS. 4, 5). This negative term enhances slightly the large decrease of \(\mu_{\text{SiO}_2}\text{l}\) originating in the entropy of mixing term of Equation (6), which causes the strong decrease of the melting temperature under water pressure. As for the water solubilities calculated in this way, they do not vary linearly with the square root of water fugacity (see below) and become too low at the highest pressures (FIG. 5). Excellent agreement with the experimental data requires a more complicated model with either more fit parameters or at least two water species instead of the single one embodied in Equation (6). This illustrates the usual trade-off that can be made between the choice of components of structural significance and the use of activity–composition relationships with a high number of fit parameters.

The complex reactive solubility of H2O, CO2 and SO2 is in fact intimately related to the acid–base properties of these species. These features can be addressed with a third kind of thermodynamic model based on a polymeric description of silicate melts (Ottonello 2001; Ottonello et al. 2001; Moretti and Ottonello 2005). The starting point is the equilibrium between the various oxygen species in the liquid, i.e. \(O^0\) (bridging), \(O^-\) (non-bridging) and \(O^{2-}\) (free), which lies behind Equation (4):

\[
O^0 + O^{2-} \leftrightarrow 2 O^-.
\]

(7)

It appears that CO2 is an acidic oxide because it accepts an electron when reacting with a free oxygen ion, \(O^{2-}\), of the melt to form a carbonate ion:

\[
CO_2 + O^{2-} \leftrightarrow CO_3^{2-}.
\]

(8)

As observed (see Mysen and Richet 2005), the solubility of CO2 is favoured in basic melts, where Equation (8) is displaced to the right-hand side. In contrast, water is a basic oxide as it depolymerizes the silicate network in the same way as metal oxides [see Equation (4)], and creates hydroxyl (OH) terminations:

\[
\text{Si} - \text{Si} + H_2O \leftrightarrow 2 \text{Si} - O - H.
\]

(9)

This reaction predominates in the first stage of dissolution, before dissolved molecular water must also be taken into account, as indicated by spectroscopic studies (e.g. Stolper 1982). Denoting by \(K\) the equilibrium constant of Equation (9), we write that water solubility is then proportional to the square root of the water fugacity in the gaseous phase, \(f_{H_2O}\):

\[
x_{H_2O} = 1/2 (K f_{H_2O})^{1/2},
\]

(10)

where \([O^0]\) is the mol fraction of bridging oxygens. These differing solution mechanisms of H2O and CO2 manifest themselves in phase equilibria. As an example, the primary phase field of forsterite in the CaO–MgO–Al2O3–SiO2 system expands and contracts upon dissolution of H2O or CO2, respectively, whereas that of enstatite correlates with the opposite way (Kushiro and Yoder 1968).

**CONCLUSIONS**

Although modelling complexities have not been considered, this review illustrates how solid–liquid and fluid–liquid equilibria can be calculated throughout the extremely wide \(P-T\) range relevant to magmatic activity. Of course, such predictions are most reliable at lower

---

**FIGURE 4** Melting curve of quartz under dry (dotted line) and wet (green line) conditions. The diagram shows experimental data (Jackson 1976; Boettcher 1984) and \(P-T\) curves calculated with Equation (6) and the relevant thermochemical and elastic data. The numbers shown are water solubilities (mol\% H2O) calculated along the wet liquidus.

**FIGURE 5** Water solubility \((x_{H_2O})\) in an SiO2 melt against the square root of water fugacity \((f_{H_2O})\). The experimental data are from Kennedy et al. (1962) and the values have been calculated with the assumption of either an ideal solution model (dashed curve) or the non-ideal model of Equation (6) (solid curve).
pressures where models are calibrated with abundant experimental data. But high pressures are also of fundamental interest because magma forms at great depth. In subduction zone settings, melting results from reaction of solid peridotite with the water released when the oceanic lithosphere is subducted, producing magmas that eventually yield the andesite lava series (Grove et al. 2006). The basalt lava series originates via decompression of peridotite in convecting cells ascending at speeds of a few centimetres per year. Thermodynamically, the process has been described in different ways that cannot be summarized in a few lines (see Ganguly 2005; Stolper and Asimow 2007). Suffice it to say that as a first approximation, the heat exchanged by the plume with its surroundings can be neglected, so that magma ascent takes place under adiabatic conditions. Melting is then triggered by the pressure decrease, which causes the solidus curve of mantle peridotites to intersect the geothermal gradient at depths of the order of 100 km.

Two final points will be mentioned. First, the rates of magma ascent and volatile exsolution strongly depend on melt viscosity. Viscosity is closely related to atomic mobility and is quantitatively related to configurational entropy, the thermodynamic measure of disorder. Investigation of the thermodynamic properties of melts thus has clear implications for the temperature, pressure and composition dependencies of viscosity (e.g., Richet 2009). The second point deals with crystallization, which can be assumed to take place under equilibrium conditions only between the solidus and liquidus. At high degrees of supercooling, crystallization proceeds irreversibly instead, and kinetic factors need to be considered. Of particular significance is that crystals are often metastable and tend to be structurally disordered and non-stoichiometric, being enriched in the elements that diffuse fastest in the melt, that is, in network-modifier cations (Bouhifd et al. 2004; Roskosz et al. 2006); in such cases, the models presented in this review no longer apply.

That kinetic factors are important is also shown by the differences in texture between volcanic and plutonic rocks. Crystal formation is described as a two-step process: nucleation and crystal growth, whose rates vary in different ways with the extent of supercooling (Fig. 6). Depending on the time-temperature history, two limiting cases are distinguished. In plutonic rocks, crystal growth predominates over nucleation, yielding a few, large crystals. In volcanic rocks, in contrast, the small size of crystals and the presence of a glassy or microcrystalline matrix indicate instead abundant nucleation and short-lived crystal growth. Consideration of kinetic factors is, therefore, a necessary complement to equilibrium thermodynamics when attempting to reconstruct the history of a magmatic system.

**Figure 6** Rates of crystal nucleation and growth as functions of the extent of supercooling. By definition, the rate of growth tends to zero at the liquidus temperature, where the Gibbs free energy of the transformation is zero.

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**CHEMICAL ANALYST**

University of Wyoming

The Department of Geology and Geophysics, University of Wyoming, seeks applicants for a Chemical Analyst position in the Geochemistry Analytical Laboratory (GAL). The GAL contains analytical instrumentation ranging from standardized titrations to quadrupole ICP-MS for analysis of water, gasses and solids. The GAL's mission is to provide analytical support for Geology and Geophysics faculty as well as to serve some of the broader analytical needs of the university community. The Chemical Analyst will maintain and run instrumentation for users, teach a course in analytical geochemistry, train students to use instrumentation independently, and lead continuous efforts to upgrade and modernize GAL equipment as needed. In addition to performing these service duties, the Chemical Analyst will be classified as an Academic Professional Research Scientist and will be expected to perform independent research. Minimum qualifications include experience with wet-chemical analysis and a strong track record in both analytical service and research. Applications should consist of a cover letter, a CV, a statement of analytical and research areas of expertise, and a list of at least three independent referees compiled in electronic form and sent to ChemSearch@uwyo.edu, referencing the Chemical Analyst position. Applications are due by November 15, 2010.

**Harvard University**

Assistant Curator

Harvard Mineralogical and Geological Museum

The Department of Earth and Planetary Sciences and Mineralogical Museum seek a dynamic Earth scientist to manage and develop the Department's extensive rock and ore collections in support of research and teaching. The challenge is to integrate contemporary faculty research samples with archival collections assembled over the last century into an actively managed, digitally cataloged and web accessible earth history archive, and to promote the use of the collection internally and externally. Successful candidates will have an advanced degree in earth sciences (PhD preferred), knowledge of Earth history, experience and knowledge of relational database and management, and be able to work well in a team with faculty and supervise assistants. Field work as well as understanding of diverse geological samples are desirable. Salary and level of the position will depend on experience. The Harvard Mineralogical and Geological Museum has one of the largest collections of rocks and minerals in the world, some of which are displayed in the Harvard Museum of Natural History. As the scientific aims of the Department have changed towards rocks and Earth processes, the direction and resources of the Museum need to change to serve the research needs of current and future faculty, to provide curation of rock specimens that can be useful and accessible for a broader community, and to orient the public collections to correspond to current understanding of the Earth system. The person occupying the new position will take a leading role in that expansion of the Museum's purview. The initial period for this position is a two-year term.

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- To measure energetics of phase transitions in refractory materials
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- Applications include studies of energetics in the field of ceramic, nuclear and inorganic nano- materials
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**Inspir ing Imagination for Material Science**

**Elements**

October 2010
The validity and usefulness of thermodynamic models commonly used to model the physical and chemical properties of Earth’s interior at high to ultrahigh pressures and their associated geophysical databases are discussed. All calorimetric data used in these models must have the quality of fitting to experimental phase diagrams derived from work not only at high temperatures and pressures but also under ambient conditions. The density and temperature profiles calculated for Earth’s mantle and core and the phase diagram of iron calculated under core conditions illustrate how thermodynamic modeling helps us understand the physics of Earth’s deep interior.

**INTRODUCTION**

Thermodynamic modeling is a valuable source of information on the nature, composition, and pressure–temperature stability fields of the phases that make up inaccessible regions of the Earth’s interior. It complements phase equilibria experiments and also helps us interpret experimental results that deal with only part of the relevant conditions of temperature, pressure, and chemical composition. Thermodynamic models rely on calorimetric and equation-of-state data, but they always involve fitting model parameters because many solutions, be they fluid, liquid, or solid, are thermodynamically nonideal, that is, the solution components do not mix in a random way without heat effects. In a perfect world, all input data would be determined independently with high precision, so that one could evaluate in a rigorous manner the validity of the activity–composition relationships assumed in a specific model to predict experimental phase equilibria data. In the real world, however, things are quite different. First, the precision of the thermophysical data can be insufficient to calculate reliably the small Gibbs free energy differences in which one is interested. Second, some of these input data are missing, which requires that we consider them to some extent as additional fit parameters and, thus, make them model dependent. Because thermodynamic models and databases are intricately associated, this article will review briefly some databases currently used by geoscientists and then one model will be selected to illustrate how we can get important information about the Earth’s mantle and core.

**THEORETICAL FRAMEWORK**

The Gibbs free energy ($G$) of each phase is expressed as a function of temperature, pressure, and composition (Sundman et al. 1985). For a pure phase and end-members of solid solutions at a certain pressure and temperature, $G$ is expressed as

$$G(P, T) = H_0 + \int_{298}^{T} C_P \, dT - T \left( S_{298} + \int_{298}^{T} C_V \, dT \right) + \int_{298}^{P} V \, dP,$$

where $S_{298}$ is entropy, $H_0$ is enthalpy, both at 298 K, and $C_p$ is the heat capacity as given empirically by

$$C_p = a + bT + cT^{-2} + dT^{-2} + eT^{-3} + fT^{-0.5},$$

To integrate the $V \, dP$ term of Equation (1), the choice of a suitable equation of state is critical. To account for the marked decrease of compressibility ($\beta_T$) with increasing pressure, Saxena et al. (1993) used third-order Birch-Murnaghan equations for the MgO–FeO–Al$_2$O$_3$–SiO$_2$ system:

$$P_{\text{iso}} = \frac{3}{2} K_a \left[ \left( \frac{V}{V_0} \right)^{\frac{3}{2}} - \left( \frac{V}{V_0} \right) \right] - \frac{3}{4} \left( 1 - \frac{3}{4} K'_{0.5} \right) \left( \frac{V}{V_0} \right)^{1.5} + \cdots,$$

where $K_{T0} = \frac{1}{\beta_T} - V\partial P/\partial V|_T$ and $K'_{T0} = \partial K_T/\partial P|_T$ are the isothermal bulk modulus and its pressure derivative at room pressure, respectively, both of which depend on temperature. At this point the constraint stemming from the relation $C_p - C_v = TV\alpha^2 K_T$, where $C_v$ is the isochoric heat capacity and $\alpha$ is the thermal expansion coefficient, can be difficult to satisfy for some phases because of scant equation-of-state data or inadequate temperature dependences for $\alpha$ and the bulk moduli. Consistency among the various energy contributions is naturally achieved if one uses theoretical models such as the Mie-Grüneisen, whereby the heat capacity and Grüneisen parameter ($\gamma = \alpha VK_T/C_v$) are assumed to be close to their high-temperature limits (Anderson 1995; see also Stixrude and Lithgow-Bertelloni 2005). For semiempirical equations of state such as the Birch-Murnaghan, however, a large number of experimental data are needed to ensure reliable results.

For phases with variable compositions, one also needs to know how the Gibbs free energy varies from one end-member to another. Whereas solid solutions in ternary systems can be easily modeled, for example as done by...
The calculated CaSiO$_3$–MgSiO$_3$ pseudobinary join as

\[ \Delta G^{\text{mix}} = \sum_{ij} \left( Y_i \cdot Y_j \cdot G_{ij} + R \cdot T \cdot \sum_i a_i \cdot Y_i + \Delta G^\text{ex} \right), \]

where \( Y_i \) is the mole fraction of constituent \( i \) on sublattice \( s \), \( a_i \) is the number of sites on sublattice \( s \) per mole of formula unit of phase, and \( \Delta G^\text{ex} \) is excess Gibbs free energy of mixing expressed as

\[ \Delta G^\text{ex} = \sum_j \left( \sum_i \right) L_{ij} \]

where \( L_{ij} \) are binary interaction parameters. Higher-order interaction parameters can be included, giving more complicated excess free energy expressions. Whereas the sublattice model is thermodynamically rigorous, it becomes very unwieldy as the number of components increases, which is typical of mantle silicates, and several of the components are “fictive” end-members whose thermophysical properties escape experimental determination.

THERMOPHYSICAL DATABASES

With Equations (1) to (4), the Gibbs free energy of a possibly complex system is related to a variety of thermophysical parameters. Several methods can then be used to calculate the phase assemblage that corresponds to its minimum value. This optimization is carried out by computer programs that take into account all available experimental information on a system simultaneously, for example, THERMO-CALC (Sundman et al. 1985), Thermocalc (Holland and Powell 2001), and ChemSage/FACTSAGE (Bale et al. 2002). The output is, on the one hand, an optimized thermophysical database and, on the other hand, the calculated phase diagrams of interest.

As a matter of fact, a phase diagram is so sensitive to the thermodynamic data used that changing the Gibbs free energy of a phase within the uncertainty limits of calorimetric data may lead to drastic changes in the calculated phase boundaries. Conversely, using only experimental phase equilibrium to extract thermophysical data, one could obtain values outside the uncertainty limits of calorimetric data and poor extrapolation to more complex systems. This is why diverse kinds of experimental information have to be optimized simultaneously—namely, phase equilibrium data along with available calorimetric, electrochemical, and volumetric measurements—to derive an internally consistent database. Because of the compositional complexity of the phases of interest and the extreme conditions of temperature and pressure, setting up a thermophysical database is in fact a particularly arduous task for geologic systems.

Specifically, data assessment is generally based on simultaneous evaluation of all possible reactions to extract an internally consistent set of pressure–temperature–volume relationships (i.e. equations of state) and of values of \( \Delta H^\circ \) (enthalpy of formation from the elements), \( S^\circ \) (entropy), and \( C_P^\circ \) (heat capacity) compliant with calorimetry and phase equilibrium experiments. The evaluation is based on physical principles that make it possible to extrapolate the results to industrially interesting multicomponent systems, for which much work is also done. When multicomponent-system data are extrapolated from assessed binary and ternary systems, it is required that these systems be internally consistent, which takes time and effort to achieve. At present the properties of a number of industrially interesting, as well as scientifically challenging, materials have been collected into databases. Most of these are available for a fee.

To build an internally consistent database, we have to start from certain core values. The best way to do this is to start with calorimetric data and relate these to an experimental phase diagram. This is the so-called Calphad method. The goal is to fix the thermochemical data at ambient conditions in such a way that one can calculate phase boundaries that agree with the experimental points within specified errors. This is illustrated in FIGURE 1 for the CaSiO$_3$–MgSiO$_3$ system. Such a database includes all possible phases in the system, i.e. CaO, MgO, and SiO$_2$, in addition to the two silicates, and must also account for all solid and liquid solutions as well as phase transitions.

The phase diagram of FIGURE 1 would not be calculated correctly if data were picked up from different databases, for example, CaSiO$_3$ data from one source and MgSiO$_3$ data from another. In a different context, however, such as high-pressure calculations, we might succeed with a randomly chosen dataset if the high-pressure thermophysical properties were adjusted so as to fit the high-pressure phase diagram. But this would be a serious mistake jeopardizing the whole concept of thermodynamic validity. No database should be accepted if it does not meet the basic criterion of reproducing experimental phase diagrams under ambient conditions, provided, of course, that the latter data are trustworthy. Besides, geophysicists should make certain that their chosen data are compatible with the databases used in other disciplines worldwide, for example, the data under standard conditions that produce correct oxide phase diagrams (e.g. Jung et al. 2005).
EXPERIMENTAL BASIS

Thanks to the efforts of thermochemists, developments have led to the systematization and organization of data in internally consistent thermochemical databases at 298.15 K and 1 bar pressure. For instance, Holland and Powell (2001), Berman and Aranovich (1996), and Gottschalk (1997) dealt with solid–solid phase equilibrium in metamorphic rocks to pressures of about 5 GPa. Use of these models at higher pressures is in principle possible, but this would imply that they incorporate the appropriate high-pressure input information. For melts, Ghiorso (e.g., Ghiorso and Sack 1995) pursued modeling for compositions close to basalt in a series of publications. These petrologic models do an excellent job of computing equilibrium systems in the crust, but they are difficult to extend to the deep interior because of the scarcity of high-pressure data.

For deep geophysical applications, any database must begin with the CaO–MgO–FeO–Al2O3–SiO2 (CMFAS) system, which approximates mantle compositions. If time and resources permit, the database must be extended to include Na2O and K2O. Then the task consists of assessing all binary resources permit, the database must be extended to include which approximates mantle compositions. If time and review all the remaining available data to extend the assessment is the pseudobinary system CaSiO3–MgSiO3 and ternary, and some quaternary systems, at ambient pressure up to liquidus temperatures. An example of such an assessment is the pseudobinary system CaSiO3–MgSiO3 (Fig. 1). In a second step, the database is extended to high-pressure conditions, as done by Saxena et al. (1993) and Fabrichnaya et al. (2003), for the whole Fe-CMFAS system. The database of Fabrichnaya et al. (2003), which is based on optimized experimental phase diagrams such as shown in Figure 1, can be used up to pressures of about 25 GPa and liquidus temperatures. On the other hand, Stixrude and Lithgow-Bertelloni (2005) based their calculations on equations that work well from high to extremely high pressures. They picked thermochemical data from various sources and used regular solution models.

The experimental data available until 2003 on SiO2, Fe–O, MgO–SiO2, Fe–Mg–Si–O, Al2O3–SiO2, FeO–Al2O3–SiO2, MgO–Al2O3–SiO2, and MgO–FeO–Al2O3–SiO2 were reviewed by Fabrichnaya et al. (2003). Additional data have appeared since then and should be included in new assessments. Examples are Mg–Si–O (Katsura et al. 2003; Fei et al. 2004; Litasov et al. 2005). There is further need to review all the remaining available data to extend the system to include CaO, K2O, and Na2O.

For melts at one atmosphere, FACTSAGE uses a library of assessed data on many binary and ternary oxide systems (Pelton 2004). In addition data on slags and melts exist for many metals. All these data require the determination of high-pressure equations of state for melts. The slag model as available in the FACT database (Pelton 2004) may be used for this purpose. Alternatively, it is possible to use a wealth of available experimental information from geological systems to constrain the existing multicomponent slag model and estimate the effects of high pressures and temperatures on melt volumes. Examples of such data are the experiments of Ohtani (1979), Ohtani and Kumazawa (1981), Presnall and Gasparik (1990), and Zerr et al. (1997) for pure and binary melts, and Takahashi (1986), Zhang and Herzberg (1994), Agee (1997), Trommes and Frost (2002), and Ohtani (2008 personal communication) for multicomponent systems.

MANTLE AND CORE PHYSICS AND MINERALOGY

In his book, Anderson (1995) described very clearly how the various thermodynamic properties are connected to the geophysical properties of the solids. An important aspect of the geophysical-thermodynamic database is to ensure that well-assessed thermodynamic data can be used for geophysical calculations aimed at determining (1) the phase assemblages that match the seismologically determined relations between density and wave velocities as a function of depth and (2) the phase changes that give rise to the discontinuities observed in these relations. It is critical that the database be internally consistent with regard to the variation of heat capacities with bulk moduli and thermal expansion. The database should thus contain a listing of the most recent data on density and bulk and shear moduli. One can expect that a thermochemical-geophysical database of this type would permit calculations of reference models for many different pressure-temperature-composition regimes in the Earth. We can envisage several applications, such as the calculation of the adiabatic gradient (isentropic and isenthalpic) to the depth of the outer core and then within the core, and the thermal expansion and bulk modulus of the mantle and the core at various depths.

An interesting example of such applications is provided in the study by Ganguly et al. (2009) performed with the currently available CaO–FeO–MgO–Al2O3–SiO2 database. From the calculated mineralogy and adiabatic gradient, they discussed the thermal structure and the penetration of subducting oceanic slabs of various compositions through mantle discontinuities (Fig. 2). The mineralogical data were then converted, using the appropriate P–V–T relation, to bulk densities. The calculated adiabatic density versus depth profile of the mantle between 200 and 725 km depths was found to be in good agreement with geophysical and experimental data. The density data of the different compositional units were combined with the calculated thermal structures from calculations of slab mantle systems to construct equilibrium density profiles as a function of depth to 700 km. The mean equilibrium densities of the slabs within the transition zone (400–660 km) were found to be ~0.04–0.05 g/cm3 greater than those of the ambient mantle within the same depth interval. For the entire upper mantle, the density differences between the slabs and the ambient mantle are slightly less than the above values, but the slabs still remain heavier than the latter. At 670 km, the slabs are lighter than the ambient lower mantle because of the commencement of perovskite-forming reactions within the mantle and displacements of these reaction boundaries to higher pressures within the slabs as a consequence of their negative P–T slopes. In the absence of perovskite-forming reactions within the slabs, neutral buoyancy would be achieved when the slabs have penetrated ~100 km into the lower mantle. As a complement (Fig. 3), we also show the isentropic adiabatic temperature curve for the mantle as calculated with the thermodynamic databases of Saxena et al. (1993) and Fabrichnaya (2003).

We now turn to the more elusive nature of the Earth’s core. Recent data on iron from shock and static experiments are combined with theoretical studies to construct an iron phase diagram (Fig. 4) to the relevant pressures and temperatures. The experimental data for the iron phase diagram to a pressure of ~100 GPa and melting temperatures to ~3000 K were used recently to determine the phase equilibrium boundaries of the BCC (body-centered cubic), δ-BCC, FCC (face-centered cubic), HCP (hexagonal close-packed), and melt phases. These calculations provide us with an internally consistent database, based on an equation of state that is consistent with Birch-Murnaghan’s; this database permits calculation of thermodynamic quantities to extreme pressures and temperatures. The calculations are extended to include a “theta” phase, whose stability field is determined by the following topological constraints: (1) the triple point for HCP–theta–melt could
lie within the uncertainty of the Brown-McQueen data point of $T = 4400 \pm 300$ K at $P = 200$ GPa; (2) a melting point at $5100 \pm 300$ K at $P = 243$ GPa, and (3) the occurrence of a BCC phase at a temperature of $3400 \pm 100$ K at $P = 225$ GPa. Additionally, we should consider the iron melting data of several selected data points that follow the arguments of Aitta (2006). These data are shown in Figure 4.

The thermodynamically evaluated estimation of the iron phase diagram puts a definite limit on the isentropic adiabatic temperature of the core (Fig. 5). For pure iron under inner core conditions, the adiabatic gradient starts at a pressure of 364 GPa (6371 km) at a temperature of 6517 K and a density of 13.705, which is 7.5% higher than given by the seismologically based reference PREM model (Dziewonski and Anderson 1981). The temperature decreases to 6391 K at the top of the inner core at a pressure of 329 GPa (5159 km). A pure-iron outer core has an adiabatic temperature gradient starting from the inner–outer core boundary pressure and temperature to the pressure and temperature at the top of the outer core, 135 GPa (2891 km) and 4750 K, respectively.

If nickel has to be mixed with iron because of cosmochemical considerations based on the composition of iron meteorites, a large amount of a lower-density element, such
as S, Si, or O, will have to be in solid solution to lower the density of the inner core, which would cause the temperature of the inner core to drop by several hundred degrees. Thus 6517 K is the absolute upper temperature of the inner core. The density of liquid iron at the conditions of the outer core exceeds the density given by the PREM model. The temperature of 4750 K outer core exceeds the density given by the PREM model core. The density of liquid iron at the conditions of the adiabatic temperatures. The temperature of 4750 K is, therefore, the absolute upper limit at the top of the outer core. The average heat capacity of pure iron in the inner core is 27.24 J/mol, yielding a heat content of 155.17 × 10^21 joules for the iron core (the mass of the inner core is 102 × 10^21 kg).

CONCLUSIONS
Thermodynamic models can be used to understand the physical and thermal state of inaccessible regions within the Earth, if properly constrained to meet all the requirements of compatibility with experimental phase diagrams, thermochemistry, and pressure–volume–temperature equations of state. The calculated properties can be compared with those obtained by geophysical experiments, and unique information can be obtained on how the density and mineralogical composition vary in Earth’s interior.

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Presnall DC, Gasparik T (1990) Melting of enstatite (Mg2SiO4) from 10 to 16.5 GPa and the forsterite (Mg2SiO4) — majorite (Mg2SiO4) eutectic at 16.5 GPa: Implications for the origin of the mantle. Journal of Geophysical Research 95(B10): 15771-15777
Thermodynamics makes the world go round. It drives global geochemoal cycling from the solid Earth, through the hydrosphere, atmosphere, and biosphere. Through approaches like thermoderametry and pressure-temperature-time (P-T-t) paths, it provides insights into many of Earth’s processes, such as phase transitions and melt reactions; such insights allow us to interpret plate tectonics and the evolution of the Earth system. These facts are precisely why ALL geoscience students should gain a firm understanding of the principles and applications of thermodynamics in their pre-professional training. A single exposure to thermodynamics in an isolated course is not enough. Thermodynamics must be practiced early and often. Opportunities abound to engage thermodynamics across the geoscience curriculum and at all instructional levels.

Extensive collections of online teaching resources have been developed to support teaching and learning about thermodynamics. They include class-ready teaching activities, laboratory exercises, visualizations, links to related websites, recommended reading lists, and related resources on teaching methods and assessments. Most of these resources have been developed, organized, and reviewed by geoscience faculty through the On the Cutting Edge program for faculty professional development (http://serc.carleton.edu/1573) or through other community-based projects sponsored by the U.S. National Science Foundation. The instructional activities in these collections are focused on student learning, and all employ active, experiential learning approaches using a variety of teaching methods (see Elements, volume 3, number 2, April 2007, and a bibliography of teaching strategies at http://serc.carleton.edu/17525). Beyond gaining a mastery of the concepts of thermodynamics, complementary learning goals include the development of quantitative skills, the use of authentic data to solve geologic problems, and the use of modeling and visualization programs to represent and explain Earth phenomena. Here is a sampling of the online instructional resources that can serve as an instructor’s companion to this issue of Elements.

For the application of thermodynamics to the solid Earth (Powell and Holland 2010 this issue) with a focus on igneous and metamorphic petrology, there is a comprehensive curriculum entitled “Teaching Phase Equilibria” (http://serc.carleton.edu/19562). This module includes tutorials for students and teaching activities for faculty. It starts with Gibbs’ phase rule and progresses to topics such as phase diagrams, mineral compositions and chemographic projections, an introduction to thermodynamics, the Clapeyron equation, the method of Schreinemakers, types of igneous and metamorphic reactions, activity models, thermobarometry and P-T-t paths, and worked examples using advanced modeling programs such as TWQ, Perplex, Melts, and ThermoCalc (http://serc.carleton.edu/19573). A good example of the type of exercise is Sumit Chakraborty’s “Learning Thermodynamics and Using Spreadsheets” (http://serc.carleton.edu/25381). In addition to the use of internally consistent thermodynamic databases, instructional activities have been developed using the American Mineralogist Crystal Structure Database in activities such as Kent Ratajeski’s “Crystal Structures as Geobarometers” (http://serc.carleton.edu/7399). A collection of animated PDFs of binary and ternary igneous phase diagrams (Fig. 1; http://serc.carleton.edu/19564), developed by Dex Perkins and John Brady, demonstrate the use of the lever rule to determine the state of numerous common rock-forming systems as a function of temperature (always a challenge for students to master, but made significantly easier through the use of these visualizations). Other visualizations include topics like Dave Hirsch’s “AFM Projection 3D Movie” (http://serc.carleton.edu/6661) and Roger Powell’s QuickTime movies of metamorphic AFM diagrams and the NCfM system over a range of physical conditions (http://serc.carleton.edu/17552).

Water-rock interactions (Zuddas 2010) are represented in activities such as Andy Knudsen’s “Introduction to Equilibrium Thermodynamics: Salt Dissolution” (http://serc.carleton.edu/26805) and Barb Dutrow’s “Timing of Mineralization in the Palm of your Hand: Cross-Cutting Relations, Copper Minerals and Ore-Forming Hydrothermal Fluid Evolution” (http://serc.carleton.edu/24565), in which the evolution of the fluid that developed alteration in cross-cutting veins is explained using activity–activity diagrams. Thermodynamics applied to atmospheric science (Bott 2010) is demonstrated in Tony Hansen’s “Atmospheric Vertical Structure and the First Law of Thermodynamics” (http://serc.carleton.edu/36975), and thermodynamics applied to the ocean system (Millero and DiTrolllote 2010) is demonstrated in Paul Quay’s “What Is the Fate of CO2 Produced by Fossil Fuel Combustion?” (http://serc.carleton.edu/36976).

Other thematic collections of resources have been developed to promote instruction about mineral physics and Earth’s deep interior (Saxena 2010; see http://serc.carleton.edu/31415 and the Understanding Deep Earth website, http://serc.carleton.edu/36598), and to complement the 2008 MSA/GS short course and RIMG volume 69, Minerals, Inclusions and Volcanic Processes (Richet 2010; see http://serc.carleton.edu/28510). In addition, all of the original teaching activities published in the Teaching Mineralogy volume [1997, Brady, Mogk and Perkins (eds.), published by MSA] are now available online, with activities such as Dave Bailey’s “Heat Capacity of Minerals: A Hands-On Introduction to Chemical Thermodynamics” (http://serc.carleton.edu/23863). There is also a “primer” on geochemical instrumentetion and analysis, which introduces students to the methods used to acquire geochemical data (mineral, whole-rock, isotopic) that can then be used in thermodynamic modeling of the Earth system (http://serc.carleton.edu/18410).

Although we’ve made a good start, we need help in building these collections of instructional resources on the applications of thermodynamics to Earth systems. Please contribute additional teaching activities or recommend websites or articles you use in your own classes by submitting to: http://serc.carleton.edu/7074. If all the academic readers of Elements were to contribute just one teaching activity or resource, just imagine what a rich collection of teaching materials we would be able to share for the benefit of all!

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Figure 1

The binary alkali feldspar temperature–time composition (T–T; isotopic) phase diagram at low pressure, developed as an animated PDF by Dex Perkins. This phase diagram represents a closed system at equilibrium conditions (essential information required to appropriately interpret this diagram). The vertical line represents the starting bulk composition of the system (arbitrarily picked to be 38% albite and 62% orthoclase). The dashed line shows the isotherm at 450 °C. At equilibrium, the state of the system is constrained to contain two solid phases that have compositions of Ab45Or55 and Ab49Or51 in relative proportions of 71% and 29%, respectively, based on the “lever rule.”
FROM THE PRESIDENT

It is my great pleasure to introduce the Meteoritical Society to the readers of Elements and Elements to our members. Our society is an international organization founded in 1933 for scientists, collectors, and educators to advance the study of meteorites, cosmic dust, and other extraterrestrial materials and their parent asteroids, comets, and planets.

Some of our 970 members already receive Elements through membership in other societies, but for three-quarters of our members, the previous issue of Elements was their first. The council of the Meteoritical Society decided to join the societies sponsoring Elements because it offers a great way for our members to communicate with other scientists, educators, and collectors, and for our council and officers to inform our own members and others about Meteoritical Society activities.

The Meteoritical Society has its own journal, Meteoritics and Planetary Science, which is now published for the society by Wiley. In addition we cosponsor Geochimica et Cosmochimica Acta with the Geochemical Society. Elements has already published many articles written by our members, including papers on exploration of the Moon, water on Mars, early Earth, diamonds, fluids in planetary systems, nanogeoscience, platinum-group elements, mineral magnetism, mineral evolution, and sulfur. Two upcoming issues of Elements will focus on cosmochemistry (February 2011) and terrestrial impact craters (February 2012).

To our members: welcome to Elements; to nonmembers: consider joining our society if you are interested in the mineralogy, petrology, and geochemistry of extraterrestrial materials.

Hiroko Nagahara, President
The Meteoritical Society

2010 SOCIETY AWARD WINNERS

The society gives four major awards each year: the Leonard Medal, the Barringer Medal and Award, the Nier Prize, and the Service Award. In addition, a number of student awards are given each year, including the Gordon McKay Award and the Paul Pellas-Graham Ryder Award. For more information on these awards, see the society webpage.

Leonard Medal to Hiroshi Takeda

Hiroshi Takeda, Emeritus Professor at the University of Tokyo, was awarded this year’s Leonard Medal for his outstanding contributions in meteoritics, especially his petrologic studies of the achondrites—howardites, eucrites, and diogenites—and the lunar crust, which have elucidated the geological evolution of the asteroid Vesta and the Moon. The citation was given by Larry Nyquist of NASA’s Johnson Space Center. The Leonard Medal honors outstanding contributions to the science of meteoritics and closely allied fields. It was established in 1962 to honor the first president of the society, Frederick C. Leonard.

Barringer Medal to William K. Hartmann

This year’s Barringer Medal was awarded to William K. Hartmann, cofounder of the Planetary Science Institute. Bill was awarded this medal, which is sponsored by the Barringer Crater Company, as a result of his distinguished career studying cratering on the Moon, Mars, and throughout the solar system, and how it has shaped the surfaces of planetary bodies. The citation was given by Clark Chapman of the Southwest Research Institute.

ANNUAL MEETINGS

2010 Annual Meeting Report

The 73rd Annual Meeting of the Meteoritical Society was held in Manhattan, New York, 26–30 July 2010. Over 440 scientific abstracts were submitted, a new record for this meeting. A total of 434 registrants (115 students), were joined by 51 guests, making this the third-largest Meteoritical Society meeting ever. Over $65,000 of philanthropic and grant-funded travel support was awarded to 59 students and early-career research scientists from around the world. There were 216 oral presentations and over 220 poster presentations. Topics included impacts, planetary science, the ages of ancient rocks, organic material in the solar system, models for preplanetary disks, and ancient components incorporated into meteorites, including presolar grains formed around other stars. Sean Solomon (principal investigator, MESSENGER mission) gave the Barringer Invitational Lecture at the American Museum of Natural History. The meeting abstracts and program are available online at www.lpi.usra.edu/meetings/metsoc2010/pdf/program.pdf.

A preconference workshop, “Disks, Meteorites, Planetesimals,” brought together observers of disks around young stellar objects, modelers, and meteoritists. During a postconference symposium, “Chondrules: Their Role in Early Solar System History,” scientists reviewed new findings on these abundant components of primitive meteorites. The program and abstracts are available at www.lpi.usra.edu/publications/abstracts.shtml.

Altogether, this was a singular meeting of a vibrant scientific society. Science quality was very high and attendance was near record-breaking.

Denton Ebel, American Museum of Natural History

Annual Meeting Schedule

<table>
<thead>
<tr>
<th>Year</th>
<th>Location</th>
<th>Dates</th>
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<tr>
<td>2011</td>
<td>Greenwich, England</td>
<td>August 8–12</td>
</tr>
<tr>
<td>2012</td>
<td>Cairns, Australia</td>
<td>dates to be announced</td>
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<tr>
<td>2013</td>
<td>Edmonton, Alberta, Canada</td>
<td>July 29–August 2</td>
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<tr>
<td>2014</td>
<td>Casablanca, Morocco</td>
<td>September, dates to be announced</td>
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THE PRESIDENT’S CORNER

Why is it that we love ternary diagrams? I suspect we all have our favorites, like sand–silt–clay or bicarbonate–chloride–sulfate. I must confess that one of my favorites is muscovite–dioctahedral–octahedral, which highlights tetrahedral and octahedral charge within the dioctahedral layer types. Take a look and you’ll see some clay minerals that are near and dear to many of us. OK, now you are probably wondering where I am going with this and what this has to do with the CMS. The CMS is arguably one of the most “self-contained” interdisciplinary societies I know. Staying ahead of the relentless challenges of electronic publication, conferencing, and public outreach is difficult. The foundation upon which the CMS tries to accomplish these missions is based on the triad of industry–government–academia (I–G–A). I report herein to our membership and other readers that the CMS is meeting this challenge and that its success can clearly be attributed to the melding of this triple-space I–G–A composition. Industry members remind us that at the end of the day, society needs clay products and that clay science and economics are not disconnected. Government members interface with the political and regulatory aspects of clays in our products and our environment, and they perform outreach to the public about clay science’s role in policy-making. Academic members pursue basic research and train clay scientists for future generations. End members rarely exist in nature and that is the beauty of ternary diagrams. It gives a chance to see how we, as individuals and as a society, move around compositionally and that is the beauty of ternary diagrams. It gives a chance to see how we, as individuals and as a society, move around compositionally. This first message is to say thanks to CMS volunteers who spend their time working to keep us moving forward. Goals during my tenure include embracing more students into CMS governance, outreach, and publication. My e-mail address is schroe@uga.edu. Please send me your ideas, comments, and occasional snivels. I am truly honored and humbled to be at the helm and promise to try my best to keep the CMS productive. I only ask the same of you, in whatever part of I–G–A space you reside. Cheers.

Paul Schroeder, President
The Clay Minerals Society

What the Students Said!

The CMS has always regarded itself as a very student-oriented society. Here is what three of the students attending the SEA-CSSJ-CMS trilateral meeting in Spain had to say...

“Participating in the 2010 Trilateral Meeting on Clays was for me, as a geology student, a very exciting and rewarding experience. It was my first big, international, scientific conference and I have to admit that I was a bit confused at the beginning. Nevertheless I quickly realized that the 2010 TMC was a perfect occasion to learn about the main fields of interest of clay scientists from all over the world. It was also possible to meet in person the authors of the books and papers I read, which was amazing. I could also find out what my colleagues are doing as a part of their master’s or PhD theses. I found this part of the conference the most interesting because I could see how clay science evolves outside my country. The talks were interesting and inspiring. Participating in this event broadened my knowledge of clay mineralogy. I encourage other students to participate in meetings like this because the benefits are great.”

2010 Student Travel Award winners (LEFT TO RIGHT): Marek Szczerba, Tom Naumann, Ines Mulder, Sara Moron, Artur Kuligiewicz, Irshad Bibi, Ali Hooshiar (MIDDLE: Elena Kuznetsova)

“After the meeting I went home with 2 kg of clay samples, a list of recent papers from Spain, Japan, Australia, and the USA, and new contacts for potential field trips and sampling for my research group in Germany. My mind is full of the many good discussions and the feedback that I received at my poster during the busy poster session and of images of the local surroundings and food, whether the snail in the paella, the ham museum in Madrid, or the wild flamenco dance at the gala dinner in Sevilla. Overall I loved the international and friendly atmosphere of the workshop and field trip, and enjoyed meeting great people from all over the world. I had a great time meeting my old friends and colleagues from Texas, and it was wonderful to get to know so many new people.”

“The Clay Minerals Society travel grant allowed me to present my research to an international audience at the Trilateral Meeting on Clays in Spain. Experts from different areas within the clay minerals community provided me with great feedback for my research, which aims to show how clays can be used as a paleoclimatic indicator. The talks were also very instructive: I was exposed to new and exciting investigations on clay materials and nanotechnology. I am very grateful to have been given this opportunity to travel to Spain and discuss my results. I was also honored to have received the award for best geology poster. This award was a pleasant surprise for me and encourages me to continue my research.”

Mark Your Calendar

The 2011 CMS meeting will be held September 25–30, in South Lake Tahoe, Nevada, USA. Stay tuned for more details.

www.clays.org
EARLY CAREER AWARD

For the fifth consecutive year, the IAG has given out its Early Career Researcher Award, which highlights geoanalytical excellence as shown in an abstract submitted to the Goldschmidt Conference. Eligibility for this award is based on three criteria specified by the IAG’s governing council: (1) the first author of the abstract must either be pursuing a university degree related to geoanalysis or have completed his/her most recent degree within the past five years, (2) the abstract must be the result of work conducted largely by the first author and must address one of the core interests of the IAG, and (3) the first author must personally be presenting his/her work at the Goldschmidt meeting. This year 636 abstracts were submitted to the IAG for consideration; hence there were many high-quality submissions to be considered by the IAG’s panel of six judges. The IAG is very pleased to report that its Early Career Researcher Award for 2010 was presented to Dr. Regina Mertz-Kraus of the Max-Planck Institut für Chemie in Mainz, Germany, for her abstract titled “Combined Th-U Isotope and Multi-Element Analyses by LA–ICP–MS.” The IAG congratulates Dr. Mertz-Kraus for the excellence of her contribution and wishes her a bright future in the field of geoanalysis.

Dr. Regina Mertz-Kraus receiving the 2010 Early Career Researcher Award from IAG president Dr. Michael Wiedenbeck at the Goldschmidt Conference in Knoxville, USA

IAG BOOTH AT GOLDSCHMIDT

Enlarging further the IAG’s activities at the Goldschmidt Conference, the IAG joined up with GEOROC and GeoReM this year in sponsoring an information booth located in the main exhibit hall where the poster sessions were held. This new initiative was a certain success as around 100 delegates expressed an interest in the activities of these three organizations. IAG’s new partnership with these two database operators, both with years of experience in showcasing their services at international meetings, is a natural one. Both GEOROC and GeoReM provide the user community with easy access to large volumes of high-quality geochemical data, whereas one of the IAG’s core missions is to give analytical geochemists the means to assure that their data quality is fit for the required purpose.

QUALITY ASSURANCE WORKSHOPS

The year 2010 has brought further progress in the IAG’s efforts to provide the geochemical community access to the latest concepts in quality assurance and laboratory best practice. For the first time this year the IAG held its Quality Assurance in Analytical Geochemistry single-day workshop at three different venues located on three different continents. Reflecting the truly international structure of the IAG, these venues were Knoxville, USA (13 June 2010); Canberra, Australia (9 July 2010); and Münster, Germany (23 September 2010).

Held in conjunction with major national or international meetings over the past four years, these workshops have become a key source of up-to-date information for geoanalysts wishing to assure the reliability of their data or who seek a deeper understanding of metrology theory as applied to the analysis of Earth materials. Future workshops are planned for 2011, and the IAG encourages everyone interested in this topic to attend—chances are good that a workshop will be held in a place near where you live.

Participants at the Quality Assurance workshop held during Geoscience Australia in Canberra. Left to right: Simon Francis, Lachlan Hallett, Janet Muhling, Lesley Wyborn, Liz Webber (IAG member and workshop organizer), Kyle Horner, Terry Mernagh, Paulo Abballe, Lili Yu, and Bozana Krsteska
COMMUNICATING SCIENCE

Some 3400 pages of material for publication will pass through the Society this year, and part of the job that I do is to polish those pages so that they read a little better. As I write this, the June issue of Elements has just arrived and I have read the contributions by Bruce Yardley and Susan Stipp with interest. They talk about a subject which fascinates me. How do the things that we write or communicate to our colleagues and others add value to knowledge of the subject? This question applies in many areas of life.

I am interested in sport. Many analysts are employed on sports programmes to enhance our enjoyment of the game in question. Sometimes they manage to achieve this. How? For me, it’s not by being controversial or argumentative or dogmatic but by providing insight – telling me things I didn’t know already. Boris Becker is a wonderful person to listen to in tennis commentary. He tells me things that I, as someone with just a passing interest in tennis, didn’t know.

In 1984 Nadeau et al. wrote about the “fundamental particle” in clay science. Real insight, but without an open-minded editor (David Morgan) and reviewers, it might not have passed through the editorial gates of MinSoc journal Clay Minerals. It’s not just funders, but editors and reviewers also, who have an important say in what is published and so how science is advanced.

Kevin Murphy, Executive Director


POSTGRADUATE STUDENT BURSARY REPORT

I would like to thank the Mineralogical Society of Great Britain and Ireland for the bursary that allowed me to attend the Goldschmidt 2010 Conference in Knoxville, Tennessee, USA. It was a great experience and an excellent opportunity to present my research to a broad audience. Furthermore, it allowed me to network with fellow researchers from all over the world.

For me, the conference started on Sunday with a hike in the Smoky Mountains that was organized by the conference conveners. It was a perfect way to make new friends and contacts in different fields and disciplines while enjoying scenic views in the Smokies. The hike was followed by a reception at the conference center, where I met more attendees and saw many researchers again from my former university and from previous conferences and short courses I attended.

The sessions were organized such that on every day of the meeting I found interesting talks to attend. At the poster sessions, which were held late in the afternoon, I was able to discuss science with colleagues in front of their posters, and, later in the evening, everyone gathered there to meet up with old and new friends and go for supper together.

On Thursday, I gave my talk about the stability of phlogopite in the presence of carbonate. The talk went well and I got some good feedback from members of the audience.

Andreas Enggist

University of Alberta, Canada

MEETINGS

Nature’s Treasures 3 – December 12, 2010

Following on the success of Nature’s Treasures 1 and 2 (see report with pictures and copies of the presentations at www.minersoc.org/pages/meetings/nature/nature-archive.html and www.minersoc.org/pages/meetings/nature2/nature2-archive.html), this is another one-day meeting, co-organized by Gem-A (the Gemmological Association of Great Britain), the Russell Society, the Mineralogical Society, and this year for the first time, Rockwatch, in association with the Natural History Museum, London.

The aim is to provide a day of short talks which will appeal to anyone with an interest in minerals and gems, including members of all four organizations. Students from schools and universities are welcome, and members of Rockwatch, in particular, are encouraged to participate.

The day will commence at 10 am with coffee and registration, followed by the first talk at 10.30 am. Lunch will be followed by some displays, with more talks in the afternoon.

Provisional Programme

Morning session: Analysis and Identification

Fred Mosselmans
Illuminating the sciences:
The Diamond Light Source

Pete Treloar
Non-destructive techniques in the analysis of minerals and gems

Terry Williams
Micro-computed tomography (micro-CT) applied to mineralogical samples

Doug Garrod
And you thought it was natural!

Afternoon session: General

Ron Callender
Scottish gold

Maggie Campbell Pedersen
Gems from life

Caroline Smith
Meteorites

William Burgess
Nature’s treachery: Arsenic in the Bengal basin

For registration information go to: www.minersoc.org/pages/meetings/nature3/nature3.html

Frontiers in Environmental Geoscience 2011

The Frontiers in Environmental Geoscience 2011 meeting will be held in Aberystwyth, Wales, on 21–24 June 2011. The list of proposed sessions is as follows:

- Reactivity and toxicity of nano-et micro-particles in natural and contaminated environments
- Applied mineralogy of the critical zone: metal reactions at mineral surfaces
- Mine drainage – mineralogy, geochemistry, remediation
- Shining synchrotron light on the natural environment: metals, microbes and minerals
- Geochemical and biogeochemical behaviour of radionuclides and toxic elements in the environment
- Ash and aerosol emissions from active volcanoes: characterisations, processes and impacts
- Biologic mineralization: Paleoarchives, natural functional materials and bacterial mineralization processes

Professor Jill Banfield of the University of California, Berkeley, will deliver the 2011 Hallimond Lecture, and Prof. Georges Calas of the University of Paris will deliver a keynote talk at the meeting. Check www.minersoc.org/pages/meetings/frontiers-2011/frontiers-2011.html for information.

Aberystwyth, Wales
New Volumes and New Editorial Policy

I am delighted to announce that the series EMU Notes in Mineralogy has resumed publication with a new organisation and editorial policy. The EMU Executive Committee recently approved a list of EMU schools for the coming years, which will generate new volumes. They will be presented in due time in Elements and on the EMU website, www.univie.ac.at/Mineralogie/EMU/. Starting next year, however, the series will be open to host volumes originating from schools organised by other societies or groups of scientists in cooperation with the EMU. Proposals and editorial plans in any field of the mineralogical sciences should be sent to the new series editor, Giovanni Ferraris (giovanni.ferraris@unito.it). In line with its tradition and to avoid overlap with other series, such as the RIM&G series published by MSA and GS, EMU Notes will be tailored not only to provide reviews of important and rapidly evolving topics but also to fit the requirements of master’s and PhD courses. Also the process for recognition by the Institute for Scientific Information has been started.

A further important improvement is an agreement with the Mineralogical Society of Great Britain and Ireland, by which it will publish and distribute the new volumes of the series. Kevin Murphy is acting as technical editor of the new EMU Notes in Mineralogy and has started his job with an enthusiastic and collaborative attitude. EMU Notes will hereafter be sold online through the new MinSoc website in both paper and electronic versions; we are also considering distribution by single chapters.

The EMU Executive Committee is pleased with this effective joint venture, and is fostering collaboration with other member societies in the development of other initiatives. More details on the contents of older, recent and future EMU Notes volumes can be found on the EMU website.

Robert Oberti, EMU President

Volume 8  Nanoscopic Approaches in Earth and Planetary Sciences
FRANK E. BRENGER and GUNTRAM JORDAN, editors

• R. Wirth: Focused ion beam (FIB): site-specific sample preparation, nano-analysis, nano-characterization and nano-machining
• F. E. Brener: Nanopetrology of pyroxenes: reconstruction of geodynamic parameters using TEM techniques
• U. Golla-Schindler and P. A. van Aken: Electron energy-loss spectroscopy and energy-filtered transmission electron microscopy: Nanoscale determination of Fe3+/Fe2+ ratios and valence-state mapping
• J. Lyon and T. Henkel: Secondary ion mass spectrometry – less conventional applications: TOF-SIMS, molecules and surfaces
• B. W. Sinha and P. Hoppe: Ion microprobe analysis: Basic principles, state-of-the-art instruments and recent applications with emphasis on the geosciences
• L. Vincze, G. Silversmit, B. Vekemans, R. Terzano and F. Brener: Synchrotron radiation micro- and nano-spectroscopy
• C. M. Pina and G. Jordan: Reactivity of mineral surfaces at nano-scale: kinetics and mechanisms of growth and dissolution
• U. Becker, M. Reich and S. Biswas: Nanoparticle-host interactions in natural systems

Now available for purchase at www.minersoc.org/pages/EMU-notes/EMU-notes.html

List price: £40/€50; price for individuals: £20/€25 plus packaging and postage

Volume 9  Advances in the Characterization of Industrial Minerals
GEORGE CHRISTIDIS, editor

• P. W. Scott: The geological setting for industrial mineral resources
• D. L. Bish and M. Plotze: X-ray powder diffraction with emphasis on qualitative and quantitative analysis in industrial mineralogy
• J. R. Hart, Y. Zhu and E. Pirard: Particle size and shape characterization: current technology and practice
• K. Emmerich: Thermal analysis for characterization and processing of industrial minerals
• J. Madejo, E. Balan and S. Petit: Application of vibrational spectroscopy to the characterization of phyllosilicates and other industrial minerals
• M. J. Powecheby and C. M. MacRae: Electron microbeam analysis techniques used for the characterization of industrial minerals
• E. Pirard and P. Sardini: Image analysis for advanced characterization of industrial minerals and geometrals
• G. E. Christidis: Industrial clays
• R. A. Schoonheydt and F. Bergaya: Industrial clay minerals as nanomaterials
• J. Elsen, G. Mertens and R. Snellings: Portland cement and other calcareous hydraulic binders: history, production and mineralogy

Available at end-December 2010 for purchase at www.minersoc.org/pages/EMU-notes/EMU-notes.html

List price: £40/€50; price for individuals: £20/€25 plus packaging and postage

Volume 10  Ion Partitioning in Ambient-Temperature Aqueous Systems
MANUEL PRIETO and HEATHER STOLL, editors

• M. Prieto: Thermodynamics of ion partitioning in solid solution–aqueous solution systems
• A. Putnis: Effects of kinetics and mechanisms of crystal growth on ion-partitioning in solid solution–aqueous solution (SS–AS) systems
• D. A. Kulik: Geochemical thermodynamic modelling of ion partitioning
• M. E. Böttcher and M. Dietzel: Metal-ion partitioning during low-temperature precipitation and dissolution of anhydrous carbonates and sulphates
• C. V. Putnis and L. Fernandez Diaz: Ion partitioning and element mobilization during mineral replacement reactions in natural and experimental systems
• C. Monnin and G. Hoareau: Chemical equilibrium between aqueous fluids and minerals in the marine environment
• I. J. Fairchild and A. Hartland: Trace element variations in stalagnites: controls by climate and by karst system processes
• A. Godelitsas and J. M. Astilleros: Dissolution, sorption/precipitation, formation of solid solutions and crystal growth phenomena on mineral surfaces: implications for the removal of toxic metals from the environment
• E. H. Oelkers and S. R. Gislason: Water-CO2-rock interaction during carbon sequestration
• D. Bosbach: Solid-solution formation and the long-term safety of nuclear-waste disposal
• A. L. Cohen and G. A. Gaetani: Ion partitioning and the geochemistry of coral skeletons: solving the mystery of the vital effect
• H. M. Stoll: Ion partitioning and trace-element proxies in foraminifera and coccoliths

Now available for purchase at www.minersoc.org/pages/EMU-notes/EMU-notes.html

List price: £40/€50; price for individuals: £20/€25 plus packaging and postage
GEOCHEMISTRY AT THE CROSSROADS: WHICH PATH TO CHOOSE?

I returned last June from the Goldschmidt Conference in Knoxville, USA, invigorated. Few things have been more exciting to our community than the growth of the Goldschmidt Conference. Just 16 years ago I attended the fourth annual Goldschmidt meeting in Edinburgh, Scotland, with 450 participants. The most recent European Goldschmidt meeting in Davos last year was attended by just over 3000 scientists and the Knoxville meeting by 2200.

As much as by the booming attendance, I have been impressed by the high profile of some of our plenary speakers. In Davos, Sir David King, former chief science advisor of Great Britain, urged us to consider the challenges of global sustainable development. This year in Knoxville, Senator Lamar Alexander chose our conference as a forum to promote his efforts for the widespread use of nuclear energy, as our community has provided much of the scientific basis for the safe storage of nuclear waste.

The attendance of these and other high-profile speakers at our recent Goldschmidt Conferences demonstrates that the world is looking to us for solutions to key global problems, including how to best manage our resources, how to arrest global warming, how to address future energy needs, and how to manage waste products. But I wonder if our community is up to the challenge. Is our goal to work towards addressing these critical societal problems or is it to maximize the number of citations to our publications? Evidence suggests we as a community are unsure. For example, through recent efforts, our community understands better the weathering rate on Mars than the chemistry of many major elements on the Earth’s surface. We are at a crossroads. How will we as a community proceed?

If the geochemical community does not provide solutions to these critical societal sustainability issues, who will? And if some of our community embraces these challenges, how can we adequately publicize the advances? How will we enable the public to make enlightened, scientifically sound choices rather than accepting the cheaper and superficial solutions often championed by government and industry? I urge our scientific societies and future Goldschmidt organizers to build on the momentum of the last two Goldschmidt meetings to further encourage our community to focus on solving critical global problems and to find new and creative ways to inform the public about how geochemistry can provide new, safer and sustainable solutions.

Eric Oelkers, EAG President

GOLDSCHMIDT 2010 FOR AN EAG MEDALLIST: A PERSONAL PERSPECTIVE

The 2010 Goldschmidt Conference was as usual very exciting. For a geobiologist, it is clearly the place to be, considering all the people from the community you can meet there. Even though I was initially not sure to attend, the trip to Knoxville became a must when I was informed that I would receive the Houtermans Award. I was first notified by the president of the European Association of Geochemistry, Eric Oelkers, on my birthday (elegant thought, Eric!). I read the announcement letter after a birthday party, and I admit that I was not able at that time to fully realize its significance. I was unaware that close friends had put my name forward, so I was genuinely surprised. Of course, I felt honored at once to receive this award from my peers. But after a few days of receiving e-mails from friends and colleagues, the honor grew stronger. I can now tell what this award represents to me: it is first a pleasure—a pleasure to share it with my former advisers, including Jean-Alix, Thierry, Philippe, and my PhD and postdoc supervisors, François and Gordon. I guess that you always try to make these people proud of you. I also share this recognition with all my past and present collaborators, with whom I already share the unique thrill of understanding something new. When you get a paper rejected or proposals turned down, such an award provides some relief, a little self-confidence, and it tells you that you are not completely wrong. A piece of this award thus goes to Andreas, Céline, Fériel, Martin, Nicolas, Olivier, Purificacio, Tolek and Virginie. Finally, I share this award with my former and present students. I have been lucky to have supervised very talented students since I returned to Paris in 2005. Jennyfer, Sylvain, Kevin, and now Estelle, Matthieu, and Julie have been working or are working on very diverse topics, such as the preservation of fossils and the fate of organic carbon in metamorphic rocks, biominerallization of Fe by bacteria, and modern and Archean stromatolites. Finally, it is rewarding to contribute to the recognition of geomicrobiology. Some of our elders (not that old actually) did a lot at the end of the 20th century to bring the field into the forefront of science. It is thanks to them that a new breed of geomicrobiologists, ready to handle both biology and geochemistry tools, can now grow and participate in the bright future of geomicrobiology.

Karim Benzerara, Institut de Physique du Globe de Paris, France

THE EAG WEBSITE GETS A NEW LOOK!

We invite you to visit the EAG’s redesigned website at www.eag.eu.com. The new architecture of this website, built on a Content Management System, makes it easier to navigate and find information about the EAG. The site includes job offers, short course sponsorship programs, upcoming conferences, and much more, while presenting beautiful images from the field and laboratory work of our scientists. To join the EAG or discover the benefits to our members, please visit our new membership page at www.eag.eu.com/membership.

Contributions from the geochemical community are welcome, and should you wish to post information, please contact Marie-Aude Hulshoff at office@eag.eu.com.
President’s Message

At the beginning of my two-year term as IAGC president, I want to thank our outgoing president, Russell Harmon, for his commitment to IAGC during his many years of service as Council member, vice-president, and president. During his term as president, which began in 2006, the statutes and by-laws of the IAGC were amended, an operations handbook was prepared, and several new awards were established. Among the latter are the IAGC student research grants, the aim of which is to attract more students to the association. He also organized IAGC’s 40th anniversary celebrations during the Goldschmidt Conference in Cologne in 2007.

IAGC has been a healthy and growing society over the past years. Our journal, Applied Geochemistry, is going strong thanks to the excellent management of our experienced executive editor, Ron Fuge. The IAGC working groups (Geochemistry of the Earth’s Surface, Water–Rock Interaction, Global Geochemical Baselines, Urban Geochemistry, and Applied Isotope Geochemistry) are the foundation of the society and continue to grow. Important and very successful meetings held by the working groups often result in special issues of Applied Geochemistry.

The continued success of the IAGC relies on the efforts of a relatively small group of members who serve as officers, Council members, and working group leaders. Without their dedication, it would be impossible to run a relatively small association like ours. You will find their names on the back cover of every IAGC newsletter (see our website, http://www.iagc.ca), and I am sure you will recognize many of the names from their scientific contributions to applied geochemistry. Although we depend heavily on the voluntary work of our members, the workload scientists face in their daily lives increases steadily, and most organizations are no longer willing to back this type of commitment by their staff. It is thus an important task to motivate more, and especially young, members to become active in the IAGC.

At present, IAGC relies almost exclusively on income generated by our journal, Applied Geochemistry. That may change in the not too distant future, and in the next few years, we will need to attract new members and look at new opportunities for generating income. I would like to see an increase in communication throughout the whole organization —let’s use the modern and inexpensive communication channels available to us to stay in closer contact. One of our weaknesses is that, although we have many sponsored working group conferences, there is no IAGC-run conference series. Maybe such an initiative would be a means to increase direct communication among our members and create income for the association. We will need new business ideas, and I urge all members with suggestions to bring them forward in personal discussions with me or with any other officer or Council member of the association.

We are now seeing a growing realization at the political level of the importance of applied geochemistry in many fields of human activity. Knowledge of both geoscience and chemistry is urgently needed to understand, address, and solve many of the environmental problems of modern society. In particular, the interplay between the geosphere and the biosphere will need our full attention during the coming years. Who is better prepared than an applied geochemist to address this issue?

Clemens Reimann
IAGC President

9th International Symposium on the Geochemistry of the Earth’s Surface (GES-9)

3–7 June 2011, University of Colorado at Boulder, USA

The Ninth International Symposium on the Geochemistry of the Earth’s Surface continues a triennial series begun 25 years ago by the Geochemistry of the Earth’s Surface (GES) Working Group of the International Association of Geochemistry. These symposia cover the geochemistry of rock, water, air, and life on the surface of the Earth, in both natural and perturbed systems. The 2011 meeting theme—Geochemical Landscapes in the Anthropocene—highlights human participation, both passive and active, in geochemical systems. The meeting will also serve as a gathering point for researchers interested in Critical Zone science. The University of Colorado campus is a leader in environmental research, and is renowned for its beautiful setting at the foot of the Colorado Front Range.

The meeting format is intended to foster scientific growth and dialogue. Invited speakers will give in-depth talks on conference themes in daily plenary sessions. Conference delegates will bring posters to stimulate discussion during focused poster sessions. A half-day mid-conference break can be used to explore the local environment on your own, or to take an optional field trip to the Boulder Creek Critical Zone Observatory (http://czo.colorado.edu/) or to Rocky Mountain National Park. These trips will take participants into the Colorado Front Range and will emphasize research on weathering and biogeochemistry.

GES-9 conference themes

Microbial Geochemistry • Environmental Geochemistry • Organic Contaminants • Critical Zone Processes • Rivers as Landscape Integrators • Global Geochemical Cycles

Invited speakers (preliminary)

Kyungsoo Yoo (U. Minnesota, USA), Sue Brantley (Penn State U., USA), François Chabaux (U. Strasbourg, France), Kristin Schirmer (EAWAG, Switzerland), Fred Mackenzie (U. Hawai’i, USA), Jérôme Gaillardet (IPGP, France), Baerbel Honisch (Lamont Doherty, USA), Niels Hovius (U. Cambridge, UK), Derek Vance (Bristol, UK), Eric Oelkers (U. Toulouse, France), Eric Sundquist (USGS, USA), Mark Hodson (U. Reading, UK), Nikolaos Nikolaidis (Tech. Univ. of Crete), Jane Plant (Imperial College, UK), Thomas Hofstetter (EAWAG, Switzerland), Herbert Buxton (USGS, USA), Jean-Dominique Meunier (CNRS, Aix-en-Provence, France)

Suzanne Anderson
INSTAAR and Dept. of Geography, University of Colorado, Boulder, CO 80309, USA; e-mail: Suzanne.anderson@colorado.edu
Numerical simulation of the Ries event is becoming increasingly important. The theory about the creation of suevite, named after Swabia (Latin: Suevia), the part of Bavaria containing the Ries Crater, must be reevaluated. Up to now the role of water during an impact has been neglected. Because the presence of water (ice) on Mars has been proven, the mechanical and dynamic effects of crater creation on Mars are more closely related to those on Earth than on the Moon. When choosing possible landing sites on Mars or the Moon, it will be important to select the ideal distance from the crater rim to find the most interesting materials, especially those from the lowest part of the surface before the impact. Landing in the crater center is not a good idea: you will find only minerals that fell last, probably from the original top soil. As gravity on Mars and the Moon is 1/3 and 1/6, respectively, there is less air to slow down the descent of the impacting body, and this results in much deeper (several kilometers) craters on Mars and the Moon than on Earth.

On Saturday night conference attendees and VIPs celebrated three anniversaries in the Kloesterle convention center:

- 50 years (July 27, 1960): scientific proof that the Ries Crater is an impact crater
- 40 years (Aug 10, 1970): training of NASA Apollo 14 and 17 astronauts in the Ries area
- 20 years (May 06, 1990): opening of the Ries Crater museum, a worldwide leader in the transfer of scientific and public knowledge

Prof. Ernst Messerschmid (ESA, STS-061A), the second German astronaut (1985, Spacelab D1), delivered a keynote address about the highlights of several decades of manned space travel and about future plans. Prof. Dieter Stoeffler, one of the most active impact-research scientists, presented a keynote talk entitled “What is the Importance of the Ries for Moon Research and for Plans to Send Astronauts to Nearby Celestial Bodies?”

The city of Noerdlingen is almost perfectly circular, with a completely preserved, roofed, medieval city wall. Its diameter, about 1 km, is similar to the diameter of the meteorite that formed the Ries Crater. Both scientists and interested laymen can pick up research material (mineral samples) from the ground and take it home or to a laboratory for further analysis. The Ries is the only “National Geopark” in Bavaria (www.geopark-ries.de).

The Ries Crater is not the largest impact crater in the world, but it is the largest permanently inhabited one and is the most accessible large one. The crater structure is clearly visible: it features an inner crater...
On 26 June 2010, the traditional Petrology and Petrophysics Section meeting of the German Mineralogical Society was held once more. At the invitation of Prof. Alan Woodland and Dr. Kevin Klimm, 44 scientists and young researchers from all over Germany convened at the Institute of Geosciences of Goethe University in Frankfurt/Main to present their latest scientific results and discuss them with colleagues. Many participants had met the evening before to exchange news and get early information about the meeting program.

After a short introduction by Allan Woodland, the program started with a presentation by Prof. Katsura (Bavarian GeoInstitute, Bayreuth, Germany), who explained in detail multi-anvil experiments, including X-ray diffractometry measurements under high pressure and temperature conditions. Other contributors presented experimental studies on the formation of reaction rims on mineral surfaces, water–rock interaction, and the composition of the Archean and Proterozoic atmosphere and seawater. Field-related studies, such as fluid processes in subduction channels, metasomatic processes in eclogites, research on the eastern Antarctic Annandagstoppane granite, and Ta–Nb mineralization processes in Colombia, were also detailed. Other workers described new methods in X-ray microcomputer tomography and electron backscatter diffractometry, as well as the atomistic simulation of silicate melts. One talk dealt with a new Internet platform on which petrologists can discuss problems or ask questions. Find further information about this at www.expet-network.com. With a total of 16 presentations, the diverse program allowed participants to look outside their own scientific interests and get insights into different subjects.

During lunch break and after the scientific program was completed, participants had the opportunity to visit the new Institute and laboratories. The evening ended with sporting events and a delicious BBQ with cold drinks (with the kind support of Springer). The 2011 meeting will be organized by colleagues of the Ruhr University in Bochum.

Katja Beier, Kiel

Participants at this year’s Petrology and Petrophysics Section meeting in front of the Institute of Geosciences, Goethe University, Frankfurt/Main. PHOTO: ALAN WOODLAND

Seminarios de la Sociedad Española de Mineralogía

XXX Reunión de la Sociedad Española de Mineralogía
Workshop on Biominerals and Biomineralization Processes
Madrid, 13-16 de septiembre 2010

This book, like the others in the series (with the exception of volumes 1 and 2, which are in the process of being digitalized) can be downloaded at no cost from the SEM website (www.ehu.es/sem/revista/seminarios.htm).

This seventh volume of the SEM Seminar Series inaugurates a new format, typography, and image. These changes, while improving many visual aspects, seek the harmonization of the editorial products of the SEM (the Seminar series and the journal MACLA) with the new corporate image of the society.

Hermann Strass, Noerdlingen, Germany techcon.hstrass@t-online.de

DMG PETROLOGY AND PETROPHYSICS SECTION MEETING

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Katja Beier, Kiel

Participants at this year’s Petrology and Petrophysics Section meeting in front of the Institute of Geosciences, Goethe University, Frankfurt/Main. PHOTO: ALAN WOODLAND

Sociiedad Española de Mineralogía

www.ehu.es/sem

BIOMINERALS AND BIOMINERALIZATION PROCESSES: NEW VOLUME OF THE SEM SEMINAR SERIES

Understanding the complex interplay between the organic and inorganic factors controlling the formation of biominerals represents one of the most challenging goals of modern mineralogy. Biominerals and Biomineralization Processes, the seventh volume in the Seminar Series of the Mineralogical Society of Spain, is aimed at providing young and senior researchers with an updated and comprehensive view of recent advances in the field of biominalization. The volume collects the invited lectures delivered at a workshop held in Madrid on 13 September 2010. The first chapter introduces the hierarchical architecture of most biomaterials, from which their mechanical properties derive. The second chapter provides a detailed review of the state of knowledge about bacteria-mediated magnetite crystallization. The third contribution focuses on the microstructural and crystallographic features characteristic of shells. The fourth and fifth chapters discuss the so-called “vital effects”—how they influence the geochemical signature of biominerals and the applicability of such signatures as proxies for palaeoclimate reconstructions. The final chapter reviews the impact of contaminants on biominalization and the suitability of biominerals as contamination pathfinders.

Lurdes Fernández-Díaz and José Manuel Astilleros, researchers in the Department of Mineralogy of the Complutense University of Madrid, are the special editors of this volume.
Mineralogy and other MSA fields are dynamic sciences that evolve over time with new discoveries, technology, scientific priorities, funding opportunities, personnel, and politics. As with all teaching, mineralogy instruction lags behind advances in the discipline due to pedagogical inertia, the lack of availability of new instruments for classroom use, and the time needed to develop new instructional materials. I believe that teachers of mineralogy must be especially vigilant in staying current and in making our courses relevant to all geoscientists, because we have lost ground in the past in spite of the fundamental role of mineralogy in understanding geologic problems. In these economically tight times, we must be proactive and imaginative in promoting our discipline among our students and scientific colleagues.

Increased attention has been given to pedagogy in the Earth sciences in recent years, through topical sessions at meetings, workshops on teaching, and programs in Earth science teaching at some universities. MSA has supported these efforts through sales of Teaching Mineralogy (now available online, along with other resources, thanks to Dave Mogk at http://serc.carleton.edu/NAGTWorkshops/mineralogy/table_contents). More information and registration:

Mineralogical Society of America and Geochemical Society
Short Course Announcement

DIFFUSION IN MINERALS AND MELTS

December 11–12, 2010
Napa Valley Marriott Hotel & Spa
Napa, CA, USA
(before Fall AGU Meeting)

Convenors

Youxue Zhang
University of Michigan

Daniele Cherniak
Rensselaer Polytechnic Institute

The short course will focus on diffusion of all elements in minerals and melts at high to moderate temperatures. Topics include: theoretical background on diffusion, experimental methods and analytical techniques in diffusion studies, and summary and assessment of diffusion data in minerals and melts.

More information and registration: www.minsocam.org

http://serc.carleton.edu/NAGTWorkshops/mineralogy/table_contents

Results of the 2010 election: The 2011 president of the Society is David L. Bish and the vice-president is Michael F. Hochella. Darrell J. Henry was reelected to another term as treasurer, and Mickey Gunter, secretary, remains in office. The new councilors are Pamela C. Burnley and Guy L. Hovis. They join continuing councilors Wendy A. Bohrson, Sumit Chakraborty, Peter C. Burns, and Carol D. Frost.

MSA Council approved posting preprints of papers in press in the American Mineralogist on the MSA website at the time of their acceptance. At the moment the preprints are accessible to MSA members with journal subscriptions or to institutions that directly subscribe through MSA, unless the manuscript is an open access document. These preprints are the unedited manuscripts accepted for publication. They will undergo copyediting, layout, and review of the proof before being published, so always consult the final, published document as well.

Looking ahead, the 2011 short course Applied Mineralogy of Cement and Concrete (Maarten Broekmans, organizer) will be held at the 10th International Congress for Applied Mineralogy (ICAM), Trondheim, Norway, 1–5 August 2011. The meeting abstract deadline is 15 November 2010 (www.icam2011.org).
• Members and Fellows who are in the senior, honorary, and life categories are sent renewal notices. They need not pay dues, but are sent notices as the best way to prompt an update of membership information, particularly postal and e-mail addresses.

Members qualify for Senior Member or Senior Fellow status if they have reached the age of 65, have retired from full-time professional employment, and have been a member of the Society for at least 30 years. Senior Members and Fellows retain all benefits of MSA membership (receiving *Element*, voting, getting reduced rates on MSA products, etc.), but need not pay dues. They can subscribe to the paper or electronic versions of *American Mineralogist* or other journals, purchase Society publications, and attend short courses at member rates. If you are interested in senior status, select Senior Member or Fellow dues on your next renewal and tell us in the text box that you would like to become a Senior Member.

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

• You can now order through MSA print copies of numbers in the GRS GemResearch Swisslab publication *Contributions to Gemology*. These contain a wealth of information on the localities, mines, geology, and physical and chemical properties of a variety of gem materials. Many of these publications are available at no cost online as well. Descriptions are on the MSA website.

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

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**AMERICAN MINERALOLOGIST UNDERGRADUATE AWARDS**

The Society welcomes the exceptional students listed below to the program’s honor roll and wishes to thank the sponsors for enabling the Mineralogical Society of America to join in recognizing them. MSA’s American Mineralogist Undergraduate (AMU) Award is for students who have shown an outstanding interest and ability in mineralogy, petrology, crystallography, and geochemistry. Each student is presented a certificate at an awards ceremony at his or her university or college and receives an MSA student membership and a Reviews in Mineralogy or Monograph volume chosen by the sponsor, student, or both. Past AMU awardees are listed on the MSA website, as well as instructions on how MSA members can nominate their students for the award.

**Helewutei Amakali**
Appalachian State University
Sponsored by Dr. Sarah Carmichael

**Seth M. Hewitt**
Appalachian State University
Sponsored by Dr. Richard Abbott

**Daniel S. Ambuehl**
University of Oklahoma
Sponsored by Dr. David London

**Masashi Kogawa**
Kyushu University
Sponsored by Dr. Satoshi Utsunomiya

**Tengku Faisal Tengku Amir**
Texas A&M University
Sponsored by Dr. Robert Popp

**Kimberly A. Landreth**
The University of Akron – Wayne College
Sponsored by Dr. Adil Wadia

**Kirsten C. Bauer**
Universität Frankfurt
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**Kristin E. Lazzeri**
Towson University
Sponsored by Dr. David Vanko

**James L. Bridgeman**
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Sponsored by Dr. William Ranson

**Alicia Lew**
University of Victoria
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**Amber Currie**
University of New Brunswick
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**Kristen Rahilly**
Smith College
Sponsored by Dr. John Brady

**Joshua Daniel Field**
Indiana University
Sponsored by Prof. David Bish

**Elizabeth Seibel**
Pennsylvania State University
Sponsored by Dr. Peter Heaney

**Jonathan M. Gates**
Acadia University
Sponsored by Dr. Sandra Barr

**Marcella Hoffman Yant**
Indiana University
Sponsored by Prof. David Bish

**Allison R. Goldberg**
Williams College
Sponsored by Prof. Reinhard Wobus

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**Even if your interests are different than those around you, there is a place for you in MSA.**

Join MSA online at [www.minsocam.org](http://www.minsocam.org).
FIFTIETH ANNIVERSARY OF THE ORGANIC GEOCHEMISTRY DIVISION

The hybrid scientific discipline called organic geochemistry evolved during the early part of the 20th century from the core sciences of organic chemistry and geology, when practitioners in these two disparate fields realized that detailed information on the organic materials in sediments and rocks was of both fundamental and applied interest and importance. It has been suggested that 1930 marked the beginning of organic geochemistry (Kvenvolden 2008). In a seminal paper, Alfred Treibs (1936) demonstrated the power and elegance of the organic geochemical approach by describing free-base and metal-complexed porphyrins in shale, oil, and coal, and by showing the important link between these compounds and their biochemical precursors found in living systems.

For thirty years organic geochemical principles were applied mainly to geological problems in the petroleum field (reviewed by Hunt et al. 2002), and most practitioners at the time were associated with the petroleum industry. In 1959, however, a meeting entitled “General Petroleum Geochemistry Symposium” was held at Fordham University in New York City, in conjunction with the 5th World Petroleum Congress. An academic sponsor of the symposium was a Fordham faculty member named Bart Nagy. Professor Nagy had a strong interest in petroleum geochemistry (see Nagy and Colombo 1967), but he also recognized the need to formally organize organic geochemistry so that workers outside the petroleum industry could be made aware of the potential of this new scientific discipline.

Thus in 1959, besides organizing a symposium, Nagy also worked with the Geochemical Society to establish an Organic Geochemistry Division (OGD), which was formally recognized in 1960 when the division participated in the annual meeting of the Geological Society of America (GSA) in Denver, Colorado. The relationship between OGD and the Geochemical Society continues to the present. To date (2010), forty individuals have served as chairperson. The names of officers of the OGD, since its inception, are listed in the table.

During the past fifty years, the OGD has intermittently sponsored sessions and symposia, commonly at GSA annual meetings, devoted to various aspects of organic geochemistry. In addition, since 1979, the OGD has been active in selecting winners of the Treibs Award for outstanding contributions to organic geochemistry. The first and only honorary recipient was Alfred Treibs. Twenty-four designated awardees have received this honor since 1979.

The year 2010 marks the 50th anniversary of OGD. During the past 50 years, the field of organic geochemistry has evolved into a widely recognized geoscience. It has contributed significantly not only to geology (petroleum formation and occurrence, hydrothermal processes, molecular [amino] stratigraphy, global emissions [seepages] of oil and gas), and biology (biogeochemistry, ecology, microbial processes) but also to other disciplines, such as atmospheric and environmental sciences, soil science, chemical and paleoceanography, hydrology, natural products chemistry, archaeology, and cosmochemistry.

REFERENCES


Keith A. Kvenvolden, Emeritus
U.S. Geological Survey
FROM THE BUSINESS OFFICE

2011 Board Elections
Online elections for the future GS treasurer and secretary positions will be held in November. Visit our website to view the slate of candidates.

Geochemical Career Center
The Geochemical Society’s Geochemical Career Center is a web-based service open to the entire geochemical community, offering an easy-to-use and highly targeted resource for online employment connections.

For job seekers, the Geochemical Career Center is a free service that provides access to employers and geochemistry jobs. In addition to posting résumés, job seekers can browse and view available jobs based on their criteria and save those job notices for later review if they choose. Job seekers can also create a search agent to provide e-mail notifications of jobs that match their criteria. Employers can use the Geochemical Career Center to reach qualified candidates. For a nominal fee, employers can post job openings, search for candidate résumés based on specific job criteria, and create an online résumé agent to e-mail qualified candidates.

If you are looking for a job or have a job you want to post, come to the Geochemical Career Center at www.geochemsoc.org and click on “Career Center.”

GS Events at GSA-Denver
For those attending the GSA meeting, be sure to stop at Booth 921 to renew your GS membership and pick up a fantastic GS lapel pin (free while supplies last)!

The GS Joint Reception with the MSA and the GSA’s new MGPV Division will be on Tuesday, November 2, 2010, from 5:45 to 7:45 pm. Tickets are $10 for professionals and $5 for students and may be purchased at the door (be sure to wear your fantastic GS lapel pin!).

And finally, take in Patricia Dove’s F. Earl Ingerson Lecture titled “Deciphering Carbonates through the Lens of Multiple Pathways to Mineral Formation,” at 8:00 am on Wednesday, November 3.

Thank you to Troy Rasbury and the rest of the 2010 Program Committee, as well as to everyone who volunteered to chair our geochemical sessions.

2010 OGD Best Paper Award
The Organic Geochemistry Division of the Geochemical Society announced in July 2010 that Alon Amrani, Alex Sessions, and Jess Adkins were the recipients of the 2010 Best Paper Award for their paper “Compound-Specific 34S Analysis of Volatile Organics by Coupled GC/Multicollector-ICPMS,” published in 2009 (Analytical Chemistry 81: 9027-9034). The award will be presented during the International Meeting of Organic Geochemistry in 2011 (IMOG 2011).

Geochemical Society Business Office
The business office is available to help Geochemical Society members with any membership issues. If, for example, you need help recovering a damaged subscription issue, are having problems with your online access, or need to change your mailing address, please send us an e-mail letting us know and we will do our best to take care of it in a timely manner.

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Website: www.geochemsoc.org
THE PETROLOGY OF ANORTHOSITES, RELATED GRANITIC ROCKS, AND UHT ASSEMBLAGES: A TRIBUTE TO RONALD F. EMSLIE (1932–2005)

This latest thematic issue of The Canadian Mineralogist is a tribute to the remarkable career of a humble Canadian giant in the field of petrology. Indeed, Ronald Frank Emslie, one of Canada’s outstanding geo-scientists, made immense contributions to the fields of igneous petrology, geochemistry, and mineralogy. Ron dedicated most summers of his more than 35 years with the Geological Survey of Canada carrying out a prodigious amount of difficult field work in remote areas, a task matched only by a sustained level of excellence. His body of work on magmatism in the Grenville, Churchill, and Nain provinces of eastern Canada has been of a vital contribution to our understanding of Proterozoic anorthositic masses, layered intrusions, and related A-type granites.

The issue grew out of a special session held during the Geological Association of Canada–Mineralogical Association of Canada–Society of Economic Geologists–Society for Geology Applied to Mineral Deposits (GAC–MAC–SEG–SGA) meeting in Quebec City in May 2008. The contributions in this issue range in scope from large-scale overviews of how, when, and where Proterozoic anorthosite–mangerite–charnockite–granite (AMCG) suites form to papers dealing with mineral-scale reactions in rocks related to AMCG suites and ultrahigh-temperature (UHT) assemblages. The fifteen papers are grouped broadly by theme, starting with an overview of anorthosites, which is followed by papers that focus on the Adirondack AMCG suites, with implications for their tectonic setting and petrogenesis; a set of papers dealing with geochemical and petrologic aspects of the AMCG suites in the Grenville and Nain provinces of eastern Canada; a group of papers dedicated to providing the field, petrological, geochemical, and geochronological framework of the anorthosite intrusions of the Laramie anorthosite complex in southeastern Wyoming, USA; and papers related to AMCG suites and A-type granites in Baltica (Norway, Finland) and eastern Russia. The final set of papers focuses on the mineralogy and significance of strongly metamorphosed metasedimentary rocks and UHT migmatites.

There is no igneous rock more difficult to explain than anorthosite. Its petrogenesis challenged Norman L. Bowen a century ago, and it challenged another top-notch Canadian petrologist, Ronald Emslie, throughout his long and productive career. The volume contains contributions to the petrogenesis of AMCG suites from a veritable who’s who in this challenging field.

CANADIAN MINERALOLOGIST, Volume 48, Part 4, 336 pages

Check the table of contents at www.canmin.org or www.canmin.geoscienceworld.org.
looking forward to the GAC-MAC meeting in Ottawa next year!

...of sheet silicates, part of which I presented at GeoCanada 2010. I am... "Q UANTIFYING ROCK TEXTURE (MICROSTRUCTURE) AND WHAT IT CAN BRING... "PLAN TO ATTEND OTTAWA 2011 – 25–27 MAY

Ottawa will host the 2011 joint annual meeting of the Geological Association of Canada, the Mineralogical Association of Canada, the Society of Economic Geologists, and the Society for Geology Applied to Mineral Deposits. Canada’s capital city offers a unique blend of culture, history, and natural beauty. It lies at the junction of the rocky edge of the Canadian Shield and the Cambrian and Ordovician deposits of an ancient sea, and is ideally situated for its two universities and the Geological Survey of Canada. As Ottawa is home to Canada’s parliament, the meeting will provide an opportunity to showcase the societal relevance of the Earth sciences to federal decision makers. Committed to exploring both the scientific and the societal aspects of Earth sciences, Ottawa 2011 will feature symposia and sessions that revolve around the theme "Navigating Past and Future Change." Join us on 25–27 May 2011 at the University of Ottawa!

Extend your stay in our beautiful city and enjoy its many landmarks and events. Ottawa is abloom with millions of tulips during the first weeks of May, and the world-famous Canadian Tulip Festival attracts hundreds of thousands of visitors. Ottawa Race Weekend takes place the weekend immediately following our meeting—make sure to register early for this popular event and run through the streets of Ottawa and along the Rideau Canal, a UNESCO World Heritage Site! These events will ensure that Ottawa hotels will be busy at the time of our meeting, so please reserve your accommodation for Ottawa 2011 now! Special rates have been arranged with several nearby hotels; please see our web page for details.

Here is a sampling of the sessions being organized:

- EARTh CLIMATE: PAST, PRESENT, FUTURE – Andrew Miall
- PRECAMBRIAN METALLOGENY: A CANADIAN ARCHEAN AND PROTEROZOIC PERSPECTIVE – Benoît Dubé et al.
- GEONENVIRONMENTAL ORE DEPOSIT MODELS – Alexandre Desbarats, Michael Parsons
- NEW METHODS IN DETECTION OF HIDDEN MINERAL DEPOSITS – Neil Rogers
- EMERGING TECHNIQUES AND ISSUES RELATED TO GEOLOGY AND HEALTH – Suzanne Beauchemin, Heather Jameson, Jeanne Percival
- RARE ELEMENTS: MOBILITY AND CONCENTRATION PROCESSES – Iain Samson, Anthony Williams-Jones, Robert Linnen
- ALKALI PORPHYRY Cu-Au-PGE DEPOSITS: REVISED MODELS, EXPLORATION TOOLS AND LINKS TO OTHER ORE DEPOSITS ASSOCIATED WITH ALKALIC MAGMATISM – Joel Gagnon, Simon Jackson
- ELEMENTAL AND ISOTOPIC ANALYSIS BY LA–ICPMS: ADVANCES AND APPLICATIONS – Joel Gagnon, Simon Jackson
- ENVIRONMENTAL GEOMICROBIOLOGY: MICROBIAL INFLUENCES AND MOLECULAR-SCALE INTERACTIONS WITH MINERALS – Chris Weisener, Danielle Fortin
- GENESIS OF URANIUM DEPOSITS: GEOLOGICAL CONTROLS AND PROSPECTIVE TERRAINS – Eric Potter, Kurt Kyser, Gerard Zaluski, Rebecca Hunter
- MAGMATIC-HYDROTHERMAL EVOLUTION IN FELSPIC MAGMAS – Daniel J. Kontak, Jaroslav Dostal, Susan Karl
- HYDROCARBONS AND METALS – Liz Turner, Rob Rainbird
- ECONOMIC POTENTIAL OF NORTHERN CANADIAN SEDIMENTARY BASINS: HYDROCARBONS AND METALS – Liz Turner, Rob Rainbird
- QUANTIFYING ROCK TEXTURE (MICROSTRUCTURE) AND WHAT IT CAN BRING TO PETROLOGY – Michael Higgins, James Scoates

Abstract submission deadline is January 15, 2011.

Details on registration, programs, and events are available on our website: www.gacmacottawa2011.ca.

Yulia Uvarova
IMA MEDAL – CALL FOR NOMINATIONS

Frank C. Hawthorne, recipient of the 2010 IMA Medal, was honoured during the 20th General Meeting of the IMA in Budapest, Hungary. Frank follows Charles Prewitt as the second distinguished scientist to be internationally acclaimed in this way.

The IMA Medal is awarded every two years for excellence in mineralogical research and is considered as one of the pre-eminent awards in this discipline. The recipient is chosen for scientific eminence as represented primarily by scientific publications of outstanding original research in mineralogy. The medal represents a lifetime achievement award. Service to mineralogy, teaching, and administrative accomplishment are not primary considerations for the award.

As chairman of the IMA Medal Committee, I am sending out a call for nominations for the IMA Medal for 2012, which should reach me before the deadline of April 1, 2011. Details of the nomination procedure and the requirements for the nomination package are given on the IMA website at www.ima-mineralogy.org/. The salient points are as follows:

- Mineralogy is broadly defined and the candidate need not qualify as a mineralogist. Rather, his or her published record should be related to the mineralogical sciences and should make some outstanding contribution to them. Several disciplines are equally suitable for the award: mineralogy, geochemistry, petrology, crystallography, and applied mineralogy.

- The award is made without regard to nationality.

- Membership in a mineralogical society is not a prerequisite to receive the award.

- Nominators, either a member of a mineralogical society or group or a national representative of a mineralogical society or group, must submit complete nomination packages by April 1, 2011, to the Chair of the IMA Medal Committee.

- The recipient of the IMA Medal will present a lecture on a topic related to the award at an international meeting. The lecture will be published in an international journal of mineralogy.

This is a great honour! Let’s identify and nominate those colleagues who have led the way in the mineralogical sciences!

Walter V. Maresch
Chair, IMA Medal Committee
E-mail: walter.maresch@rub.de
Mail: Institute for Geology, Mineralogy and Geophysics, Ruhr-University Bochum, D-44780 Bochum, Germany

IMA BUSINESS MEETINGS HELD AT IMA 2010

Two formal IMA business meetings, three Council meetings and many business meetings of commissions and working groups were held during the IMA 2010 General Meeting in Budapest, Hungary. At the first business meeting, President Takamitsu Yamanaka thanked the Organizing Committee and all helpers for such an excellent conference; with 1700 delegates it was the largest IMA conference so far. The organization was headed by Tamás Weiszburg from Hungary (Chairman of the International Organizing Committee), Ekkehart Tillmanns from Austria (General Chairman and Chairman of the Scientific Programme Committee) and Dana Pop from Romania (Secretary General), together with many colleagues from central Europe.

Delegates approved the IMA officers’ reports and voted in the new Council for terms of office varying between two and four years. They also voted to approve some important revisions to the IMA constitution (see New Rules below) and discussed and voted on the venues for future meetings. IMA will encourage commissions and working groups to propose sessions at the Goldschmidt Conference in Prague next year, and Council will meet during this conference. The following year, the business meeting, which delegates from all member societies may attend, will be at the first European Mineralogical Conference; this meeting will be held at Johann Wolfgang Goethe-University, Frankfurt, Germany, on 9–13 September 2012 (see http://jmc2012.uni-frankfurt.de/). The next IMA General Meeting will be in South Africa in 2014. The theme will be ‘delving deeper’, and the conference will feature much applied mineralogy and field trips to famous mining areas, as well as the usual wide array of topics, ranging from historical mineralogy to environmental science.

Outgoing President Takamitsu Yamanaka thanked all the other outgoing officers and Council members, and in particular he highlighted the long and invaluable service to IMA by retiring Secretary, Maryse Ohnenstetter. Council presented Maryse with a bowl made from precious Pannonian serpentine (chlorite to be mineralogically correct) from Bernstein, Burgenland, Austria. Another long-serving member of IMA Council who finally ‘escaped’ at the Budapest conference is Ian Parsons, who served 12 years, including terms as Vice President, President and Past President (read his account of IMA 2010 on page 344).

New Rules

The presidential term of office has been reduced from four to two years. Thus the plan is to elect a future president at each biennial business meeting. This person will serve as 1st Vice President for two years, President for two years and then Retiring President for two years. Presidents need not be the chair of an IMA conference, as has recently been the custom, and this should also give more flexibility in finding really good people to lead IMA. The chairperson of the Organizing Committee of the forthcoming General Meeting will be the 2nd Vice President, to ensure good communications with Council and recognize their contribution to IMA activities.

Frances Wall, IMA Communication Officer, f.wall@exeter.ac.uk
Mineralogy museums, which are becoming more and more attractive to a broad public, have common rules and aims to preserve scientific and systematic mineralogy. The mission of the IMA Commission on Museums (CM), which counts national representatives from 37 countries, all members of IMA, is to foster recognition of mineral science collections as essential scientific, educational and cultural resources; promote support for growth, maintenance and use of collections and exhibits; and finally advance museum practice through cooperation in the development, review and dissemination of information. The CM keeps the catalogue of type minerals, in close contact with the IMA Commission on New Minerals, Nomenclature and Classification. The CM meets officially every two years, at the IMA General Meeting and at the International Conference on Mineralogy and Museums. During the IMA General Meeting in Budapest, CM held a session on the history of mineralogy, ‘Mineral Museums and Historical Mineralogy’, which was well attended. The next conference is MM 7 in 2012, to be held in Freiberg, Germany.

In addition, members meet several times a year at the world’s largest mineral shows, such as in Tucson (Arizona, USA) in February and München (Germany) in November. This gives an opportunity for curators to meet with university mineralologists and others with related interests. In 2001 a group of mineral museum curators meeting at the Munich Show established a European branch of the Commission.

A catalogue of type mineral specimens – a complete listing of type minerals and their depositories – is now currently available on the Internet (www.smmp.net/IMA-CM). The Commission on Museums welcomes participation from anyone interested in the preservation and attractive display of the Earth’s treasures.

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**NO-NAME MINERALS!**

At the open meeting of the Commission on New Minerals, Nomenclature and Classification (CNMNC) held at the recent, highly successful IMA meeting in Budapest, Hungary, Dorian Smith reviewed the official IMA unnamed mineral codes and their usage. There are now more than 1600 entries on the Valid list and nearly 1850 on the Invalid list. These lists, which are on the CNMNC website (http://pubsites.uws.edu.au/ima-cnmnc) in pdf format, can be searched using the facilities built into the freely available Adobe Reader® software. Unnamed minerals on both lists are arranged first by year of publication, next (the Valid list) by a trivial (i.e. unique) number within that year, and then (both lists) by alphabetically ordered codes.

Authors submitting new minerals to the IMA (CNMNC) for approval must now indicate that they have checked these lists to see whether the new mineral has been previously reported with an “Unnamed” status. Authors reporting new unnamed minerals should, wherever possible, use the format indicated by Smith and Nickel (2007). Such new unnamed minerals will be added to the lists most quickly if authors themselves draw the reports to the attention of the Sub-Committee on Unnamed Minerals. An e-mail giving their interim code and the reference for the publication can be sent to Dorian.Smith@ualberta.ca. Anyone interested in working on this IMA CNMNC sub-committee should contact either Peter Williams (P Williams@uws.edu.au), Stuart Mills (smills@eos.ubc.ca) or Dorian Smith.

Dorian Smith


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**TEACHING EARTH SCIENCES IN THE FIELD**

Students, their supervisors, and field guides discussing phenomena along the contact between a mafic dyke and its granodioritic host at Onion Valley, California.

Doctoral students and their supervisors from Swiss universities studied plutonic rocks and their contact metamorphic aureoles in the Sierra Nevada and Quaternary volcanic rocks in the southern Cascades, California, in September 2010. The field school was led by geologists from the USGS (Thomas W. Sisson) and MIT (Tim Grove and Christy Till) and was attended by eighteen doctoral students and their supervisors from the Swiss universities of Lausanne, Geneva, Fribourg and ETH Zürich, most of them members of the Swiss Society of Mineralogy and Petrology. Exchanges between the students and these leading scientists were beneficial to all. Long discussions were held on the outcrops and during the evenings on fundamental issues of magmatism, batholith formation and metamorphism.

Field schools are an integral part of Earth science education at the PhD level in Switzerland, enhancing scientific exchange on orogenic processes. In the California field school, the participating students were an interdisciplinary group whose PhD topics included numerical modeling, magmatic and metamorphic petrology, and isotope geoscience. The school was part of the doctoral program “4D Adamello”, which is supported by the Swiss National Science Foundation and the rectorates of the Swiss universities and includes nine PhD projects. Other attending PhD candidates are working on related projects in Europe and South America. This and other doctoral programs and schools at Swiss universities have identified field workshops as a powerful and efficient tool for teaching forefront science to doctoral candidates. Future field schools on magmatism will be held at Quaternary volcanoes in Chile, in Miocene magmatic rocks and their country rocks in Patagonia, and in ultrahigh-grade metamorphic rocks and Tertiary intrusions in the Alps.

For further information, visit www.unil.ch/img/page72459_en.html (4D Adamello; Doctoral School ProDoc) and http://mineral.cuso.ch (Doctoral Program in Mineral Sciences).

Urs Schaltegger
Université de Genève
The conference buildings on the campus of Eötvös Loránd University

The 20th General Meeting of the International Mineralogical Association took place between 21 and 27 August in Budapest, Hungary. It was a great success, and I and everyone I spoke to seem to have thoroughly enjoyed themselves, not least because of the high standard of many of the presentations. The IMA General Meetings take place in different, interesting cities every four years, and the organizers always make a genuine effort to be truly international. These meetings have a feel that is different, more characterful, than many of the other big meetings I’ve attended. IMA 2010 was the biggest mineralogical meeting ever, with about 1700 participants from 74 countries. The organization was headed by Tamás Weiszburg from Hungary (Chairman of the International Organizing Committee), Ekkehart Tillmanns from Austria (General Chairman and Chairman of the Scientific Programme Committee) and Dana Pop from Romania (Secretary General). They orchestrated a consortium representing the mineralogical or geological societies of Austria, Bulgaria, Croatia, Czech Republic, Hungary, Poland, Romania, Serbia, Slovakia and Slovenia. That in itself was a considerable feat of organization, and it’s good to see that mineralogy is thriving in countries that until not long ago had the misfortune to be behind the Iron Curtain.

The meeting took place in two huge, comfortable, modern buildings of the Eötvös Loránd University, on the west bank of the Danube (Duna in Hungarian). They were close together and it was easy to commute between them. The meeting was very efficiently run and had a number of special touches that made it memorable. Name badges to hang round your neck that were double-sided were a touch of genius. There was a small army of students, from many countries, in yellow ‘Can I help you?’ T-shirts, and the poster sessions were accompanied, not only by beer, but by live musicians. A young man played Bach and (I think) Bartok on the piano beautifully, and there was a wonderful soprano. An IMA 2010 Conference Choir performed at the ceremonies, and participants were invited to join them. On each day a very professionally produced full-colour news-sheet was handed out, commenting on the events of the previous day and highlighting the day’s forthcoming events. There were all manner of sporting events to attend and a big programme of popular field trips.

High spots of the scientific parts of the meeting were the two daily plenary lectures, all of which were well attended. Six were ‘Elements S’ talks, to mark this magazine’s fifth year of publication. Five of these were given by young(ish) guest editors or contributors to successful issues, the sixth by Rod Ewing, the founding father and prime mover of Elements. A contingent of distinguished American mineralogists greeted his ascent to the rostrum with an outburst of whistles and whoops, which added to the festive feel. A second series of IMA plenaries, by household names in the world of mineralogy, included the presentation of the 2009 IMA Medal to Frank Hawthorne and the EMU Research Excellence Medal to Max Wilke. Olgeir Sigmarsson gave a beautifully illustrated account of the 2010 Eyjafjallajökull eruption, which caused much disruption in European airspace but obligingly went back to sleep in time for IMA.

As a one-time president of IMA, I would like to end by thanking all the organizers, and their yellow-shirted helpers, for their immense amount of hard work and for providing us with such an imaginative, well-run meeting. As a past Elements editor, I’d like to thank them also for giving our plenary lecture series such prominence. As I write, the delicate swallows and house martins in my garden are swooping about, preparing to make their great autumn journey to South Africa. In 2014 we can make the same journey, in our clumsy jets, to the next IMA meeting. If I’m spared, I’ll be there!

Ian Parsons
University of Edinburgh, UK
11th INTERNATIONAL PLATINUM SYMPOSIUM

Every 4 years or so since 1970, academic researchers, government geologists, and industry geologists have gathered to discuss current research on the geology, mineralogy, geochemistry, and origin of platinum group element (PGE) and nickel–copper–(PGE) deposits. Past meetings have been held in Melbourne and Perth (Australia), Denver and Billings (USA), Pretoria and Rustenberg (South Africa), Toronto (Canada), Espoo and Oulu (Finland), and Moscow (Russia).

The 11th International Platinum Symposium (IPS) was held in June 2010 on the Laurentian University campus in Sudbury, Ontario (Canada) and was attended by 295 participants (244 professionals and 51 students) from 26 countries. It was hosted by the Mineral Exploration Research Centre and Department of Earth Sciences at Laurentian University (LU) and by the Ontario Geological Survey (OGS).

Three premeeting workshops were held: PGE in Mantle Melts, organized by Steve Barnes (CSIRO) and Marco Fiorentini (U Western Australia); PGE–Chromite Connection, organized by Jim Mungall (U Toronto); and Layered Intrusions, organized by Jim Miller (U Minnesota Duluth) and James Scoates (U British Columbia).

The three and a half days of technical sessions included 86 morning and afternoon oral presentations and 57 late-afternoon poster presentations. They were arranged according to the following themes: PGE Deposits (organized by Dave Peck, Consultant, and Gordon Chunnnett, U Witwatersrand); Ni–Cu–(PGE) Deposits (Michael Lesher, LU, and Peter Lightfoot, Vale); PGE Geochemistry (Sarah-Jane Barnes, UQAC, and James Brenan, U Toronto); and PGE Mineralogy and Beneficiation (Michelle Huminicki, Brandon U, and Paul Sylvester, Memorial U). The meeting was opened by Christine Kaszyczki (Ontario Assistant Deputy Minister of Mines and Minerals), and keynote speakers included Tony Naldrett (U Toronto/U Witwatersrand), Jean-Pierre Lorand (CNRS-Paris), Ed Ripley (Indiana U), and Louis Cabri (Consultant). Ray Goldie (Salman Partners) gave an evening public lecture. The meeting was dedicated in honour of Reid Keays, who coorganized the first IPS in Melbourne and who has been a world leader in PGE research.

Nine pre- and post-meeting field trips, organized by Michael Easton (Ontario Geological Survey) and Dave King (Quadrant-FNX), were held: Levack Mine and North Range of the Sudbury Intrusive Complex (SIC), led by Steve Dunlop, Steven Gregory, and Renée Parry (Quadrant-FNX) and Walter Peredery (Consultant); McCreedy West Mine and North Range SIC, led by Roger Lichty, Mynyr Hoxha, and Thomas Maxwell (Quadrant-FNX) and Walter Peredery (Consultant); Podolsky Mine and Whistle Offset, led by Judd Fee and Chelsey Protulipac (Quadrant-FNX); Sudbury Footwall Deposits, planned by Jake Hanley (St Mary’s) and led by Mike Sweeney (Xstrata) and Attila Pénart (Wallbridge); Sudbury Contact and Offset Deposits, led by Paul Golightly (Consultant) and Ed Pattison (Consultant); Abitibi Komatiites and Ni–Cu–(PGE) Mineralization, led by Michel Houlé (Geological Survey of Canada), Sonia Préfontaine (OGS), and Brian Atkinson (OGS); Lake Superior Ni–Cu–(PGE) and PGE–Cu–Ni, led by Jim Miller (U Minnesota Duluth) and Mark Smyk (OGS); and River Valley PGE–Cu–Ni, led by Mike Easton (OGS), Richard James (LU), and Scott Jobin-Bevans (Caracle Creek).

Laboratory tours were also given: Ontario Geoscience Laboratories (OGL), led by Dr. Romain Millot (BRGM, Orléans, France, r.millot@brgm.fr) and Dr. Pr. David Polya (University of Manchester, United Kingdom, david.polya@manchester.ac.uk) and By the AquaTRAIN project, funded by the European Union, focuses on geogenic chemicals. These elements are naturally found in groundwaters and soils. Despite their “natural” origin, the concentrations of these geogenic chemicals, notably arsenic, selenium, fluoride, and manganese, can be high enough to cause significant environmental and health risks. For example, in many parts of circum-Himalayan Asia, over one hundred million people have been chronically exposed to arsenic-bearing groundwater, used extensively for drinking, irrigation, and cooking, with devastating health consequences. In Europe, exposures are generally lower but there are still significant concerns. It is important, therefore, to understand the occurrence, and the controls on the occurrence, of geogenic chemicals and to explore remediation options and the implications for policymakers and regulators. These key aspects fall within four major work areas within the AquaTRAIN Marie Curie Research Training Network as well as other groups in Europe and elsewhere.

The objectives of this international conference, incorporating the final AquaTRAIN workshop, were:

1 To present state-of-the-art developments in these 4 aspects of geogenic chemicals in groundwaters and soils: speciation, occurrence, remediation and implications for policy
2 To enable exchange of ideas between European- and non-European-based researchers, for example, to see how remediation, mapping, microbiological and speciation methods developed in Europe can potentially be applied to other areas, and to explore how studies of highly impacted aquifers in Asia can inform studies in Europe
3 To identify key research questions and objectives and explore potential for collaborative research to address these objectives.

Dr. Romain Millot (BRGM, Orléans, France, r.millot@brgm.fr)
Pr. David Polya (University of Manchester, United Kingdom, david.polya@manchester.ac.uk)
Pr. Laurent Charlet (Université J. Fourier, Grenoble, France, laurent.charlet@obs.ujf-grenoble.fr)
A CENSUS OF MINERAL SPECIES IN 2010

Michael D. Higgins¹ and Dorian G. W. Smith²

Our census is an instantaneous view of the state of the population of mineral species. As in the case of a demographic census, it is necessarily subject to minor errors and omissions, but these do not change the overall picture. The census includes both unnamed minerals (new minerals but not sufficiently well documented to be officially named) and named species—those approved by the Commission of New Minerals, Nomenclature and Classification (CNMNC) of the International Mineralogical Association (http://pubsites.uws.edu.au/ima-cnmnc/). This community of unnamed minerals and named species has over 6000 members now, but it is continually growing and changing: new unnamed mineral species are validated; existing unnamed minerals are promoted by receiving a name; and existing minerals are renamed or discredited. The physical and chemical properties of each species also evolve as more data are added and the higher-level classifications of minerals are changed. The availability of databases of mineral properties puts us in a position to see a broad view of mineral properties and their variations much more easily and more accurately than at any time in the past. This census is based on the very substantial MinIdent-Win database (http://micronex.ca).

The development of mineralogy is mirrored by the discovery rate of new minerals (Fig. 1). The number of minerals known in antiquity (~30) had not increased substantially by 1760. During the next 50 years the discovery rate climbed to about 10 new minerals per year and stayed there until the end of the 1950s when analysis by electron beam instruments became possible. From then on, the discovery rate climbed rapidly, rising to about 100 per year, or one every 4 days, in the 1980s and has diminished only slightly since that peak. The growth of mineral numbers also reflects the advances in crystallographic techniques and instrumentation and in particular our new ability to determine site occupancies accurately. Another effect may be the relative ease of the modern two-stage process of mineral identification: first, definition as a valid, unnamed species and, second, promotion to a named species when more complete data become available. Currently about 25% of mineral species remain unnamed.

In a general way, the chemical compositions of minerals can be explored by looking at the elements in their formulae. O is the most common element, occurring in 76% of formulae, followed by H (53%), Fe (32%), Si (31%), Ca (27%), S (24%) and Al (23%). It is known that mineral formulae do not always reflect the actual composition of minerals, but how common is this? One way to explore this is to compare the number of minerals with an element in their formula with the number of minerals with that element as a significant component—here taken for simplicity as a mean analyzed composition greater than 1%. There is a very good 1:1 correlation between these measures, except for the rare earth elements heavier that Nd, which are commonly omitted from formulae. Another way of looking at mineral compositions is by means of a graph of the number of minerals with the element in the formula versus crustal abundance (Fig. 2). More than two-thirds of the elements lie in a broad band across the diagram, indicating that the number of minerals that contain each element is correlated with the crustal abundance. That is, silicates are numerous because Si and O are abundant; minerals with Au are less numerous because this element is rare. This correlation also suggests that there are many more minerals of the less abundant elements waiting to be described. Within the correlation band, the non-metals (H, O, S, As and Te) are generally in more mineral formulae than metals, which is comforting as the broad classification of minerals is partly based on these elements (silicates, oxides, sulfides, etc.).

But what about the elements that lie beneath this band? They appear to lack their fair share of minerals. Some elements just below the correlation band form their own minerals, but these are not numerous: Mo, W, Th and N. Also, the presence of a number of rare earth elements in this part of the graph partly reflects the discrimination in formulae mentioned above, but it is also due to the great difficulty in determining REE accurately by microbeam techniques, resulting in their absence from many reported analyses. However, even if this is taken into account, REE minerals do seem to be less numerous than expected. The other elements below the band are a mixed bunch that seem to be genuinely camouflaged by similar but more abundant elements: Re, Hf, Nb, Ga, Sc, Br, I, In, Cs, Ge, Cd and Tl.

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Cosmochemistry is an exciting, new and rapidly growing interdisciplinary field. A student of cosmochemistry is expected to have some knowledge of chemistry, physics, astronomy, mineralogy and geology. A scholarly presentation of all these aspects in a single publication has been lacking for many years. Charles Cowley’s Introduction to Cosmochemistry, published in 2005, is too heavily biased towards astrophysics to qualify as a comprehensive cosmochemistry book. The new book by Hap McSween and Gary Huss entitled Cosmochemistry is to a large extent devoted to the chemical and isotopic composition of solar system materials, but it also contains sections on nucleosynthesis and solar physics and an appendix on analytical techniques. It provides an excellent introduction to the multidisciplinary field of cosmochemistry.

A comparison with Ross Taylor’s Solar System Evolution (1992) reveals the enormous progress achieved during the last 18 years of cosmochemical research: (1) Advances in instrumentation for analyzing trace elements and stable and radioactive isotopes in meteorites and components of meteorites down to the micro- and nanometer scales have produced an incredibly precise chronology of the early solar system. (2) New dating tools, such as the $^{182}$Hf–$^{182}$W system, have opened the way for the spectacular discovery that iron meteorites are older than stony meteorites. (3) Completely new types of meteorites have been identified. (4) A wealth of data from new missions to Mars, the Moon, the asteroids and comets has led to a quantum leap in our understanding of the formation and evolution of the solar system. All of this is competently and extensively reviewed in the McSween and Huss book.

The book begins with a definition of cosmochemistry as “the study of the chemical composition of the universe and the processes that produced these compositions.” During the second half of the 20th century, cosmochemistry evolved as an offshoot of geochemistry. Extraterrestrial materials were simply analyzed with instruments commonly used in geochemistry. This has completely changed. Following McSween and Huss, geochemistry may now be considered a branch of cosmochemistry. One can view cosmochemistry as the materials science of the universe. As McSween and Huss point out, the generally small size of valuable extraterrestrial materials has been and will be a driving force for improvement in analytical tools, which will provide collateral benefits to geochemistry, as exemplified, for example, in stable isotope cosmochemistry. Sophisticated procedures specifically developed for measuring tiny variations in stable isotopes among solar system materials find increasing applications in low-temperature geochemistry. Also, many of the isotope systems used for dating Earth rocks were first developed for the analysis of extraterrestrial samples and only later applied to the chronology of terrestrial samples. Examples include the Ar–Ar, Sm–Nd, Lu–Hf, and Re–Os systems.

Following the introduction, some basic nuclear physics and chemistry are presented, apparently addressed to a readership at the undergraduate level. With these tools at hand the origin of elements is discussed in some detail. This sequence highlights the procedure adopted by the authors for the entire book. Basic physics, chemistry and mineralogy are explained to the extent required for understanding the more complicated issues. A didactic approach is visible throughout the book. Each of the fourteen chapters is arranged in the same way, with an overview at the beginning and a summary after the main text; this is followed by a section with questions about the main message of the chapter and suggestions for further reading and references. The text is divided into many smaller units, sections and subsections with appropriate headings. I find this helpful as many readers will use the book mostly as a source of information on specific cosmochemical issues and problems.

Before discussing meteorites, the authors provide a detailed account of presolar grains; this excellent chapter is based on the extensive experience of the second author in this subject. In the following chapters, the authors stress processes of formation of meteorites and their parent bodies and avoid extensive discussions about naming and classifying meteorites and their components.

A full chapter is devoted to geochemical and cosmochemical fractionations – a very useful and informative section highlighting the similarities and differences of geochemical and cosmochemical processes. A first-order observation about the result of a typical cosmochemical process is the depletion of volatile elements in almost all solar system objects. In this and later sections, the authors emphasize evaporation of chondritic matter as their preferred model for producing the low volatile-element contents of most meteorites and planets. The authors consider the famous Ca–Al–rich inclusions (CAIs) as residues of episodic heating processes. Low temperatures prevailed throughout the formation of the solar system except for local heating events that produced chondrules. This point of view is not universally accepted. There is evidence in meteorites for condensation processes. Here the authors could have provided a more balanced discussion by mentioning alternative possibilities. Other chapters deal with chronometers and the chronology of the early solar system, and there is a chapter on highly volatile elements, mainly rare gases and organic matter.

The remainder of the book is devoted to the larger objects of the solar system: asteroids (as meteorite parent bodies), comets and the terrestrial planets. Included are discussions of the composition and evolution of the Earth, Mars, the Moon and Vesta. We have samples of all four of these. Early in their history they differentiated into a core, mantle and crust, but each of them has had a somewhat different evolution. Similarities and differences among the planets are subsumed in what is today called comparative planetology, a completely new area of research. The final chapter deals with the description of analytical tools and their applications, a worthwhile addition for scientists from other disciplines.

Despite the 550 pages of text, one will always miss one aspect or another, depending on one’s personal preferences. I, for example, regret the absence of a presentation on recent modeling of the formation of the Earth and the other terrestrial planets, which has been done by Wetherill and later Stewart, Morbidelli and others. Impact enthusiasts will miss a section on impacts and terrestrial craters. It is, however, virtually impossible to cover all aspects of cosmochemistry in a single book.

The book is very well written. It goes into great detail when necessary and succeeds in explaining even complex facts with simple words, avoiding technical jargon. Most of the figures are excellent and focus on the main message. This is a style that the senior author has successfully applied in his earlier books on meteorites and the solar system. The book is complemented by tables with element abundances in some meteorites, condensation temperatures and other items.

In summary, Cosmochemistry gives a comprehensive survey of the present state of the science. I highly recommend it for undergraduate and graduate students. Researchers in other fields with some interest in cosmochemistry will also find this book extremely useful.

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THEORETICAL AND COMPUTATIONAL METHODS IN MINERAL PHYSICS: GEOPHYSICAL APPLICATIONS

In the foreword to Reviews in Mineralogy and Geochemistry volume 71, entitled *Theoretical and Computational Methods in Mineral Physics: Geophysical Applications*, the editors, Renata Wentzcovitch and Lars Stixrude, note that the influence of computational mineral physics to the Earth sciences has been "transformative and was unimaginable at the onset." Just how much the use of atomistic model calculations in the mineral sciences has changed in the last 25 years becomes clear by comparing volume 71 with volume 14 of the series, published in 1985 (*Microscopic to Macroscopic Atomic Environments to Mineral Thermodynamics*; S.W. Kieffer and J. Gale, editors). While atomistic model calculations have long been employed to study structure–property relations of a few minerals (e.g. by Born and Zeman in 1963 for garnets), in the mid-1980s atomistic modeling of minerals emerged as a tool to understand and predict structures, stabilities, and elastic, vibrational, and thermodynamic properties of silicates and related compounds. Volume 14 includes a paper by Burnham, entitled "Mineral Structure Energetics and Modeling Using the Ionic Model," which describes the state of the art at that time.

Volume 71 shows that models based on empirical potential (force field) are still employed to give fundamental insight that cannot be obtained by models based on quantum mechanics, either in terms of the number of atoms required in the simulation or to the requirement for very fast calculations. For example, in molecular dynamics simulations, millions of time steps may be required. Twenty years ago a simple geometric optimization of an ionic model of garnet on a microVax using one of the few established codes at that time took a few days. Nowadays, the same calculation takes a few seconds on a PC. These advancements are due not only to improvements in the hardware but also to the development of very efficient codes, such as the widely used "General Utility Lattice Program" (GULP), written by J. Gale. The capabilities of this program are introduced in a chapter by J. Gale and K. Wright. In other chapters (Carrez and Cordier on dislocation modeling, Vinograd and Winkler on modeling of the thermodynamics of solid solutions), applications of atomistic modeling studies performed with the GULP code are presented; in these applications, rather complex structural models are required, thus preventing the brute-force approach used with quantum mechanical models. The usefulness of force field calculations is also discussed by Ghiorso and Spera, who employ models with several thousand atoms, running for long times, to study transport properties.

So, while more mature, user-friendly, and efficient codes, in conjunction with faster computers, have transformed the field of empirical potential–based modeling, this development could have been anticipated 25 years ago. The most fundamental change, which was not foreseeable 25 years ago, was the impact that density functional theory (DFT)–based calculations have nowadays. DFT-based calculations of structures and their properties are currently the most widely used quantum mechanical models for solids, and they have provided new insight into all fields concerned with the understanding of structure–property relations of condensed matter. Consequently, the book provides overviews to the theoretical groundwork of DFT (by Perdew and Russwuzinsky) and to density functional perturbation theory (by Baroni et al.). The latter is an extension of "standard" DFT that allows an efficient calculation of the lattice dynamics, and hence of thermodynamic properties, in the quasi-harmonic approximation. These two chapters provide a good entry point for researchers interested in the foundation of modern atomistic simulation approaches. A chapter entitled "Minnesota Density Functionals" (by Zhao and Truhlar) is addressed more to the advanced specialist as, to the best of my knowledge, their functionals have not yet been implemented in DFT codes commonly used in mineral physics studies.

After introducing the theoretical basis, emphasis is placed on studies showing state-of-the-art developments of approaches needed to compute thermodynamic and thermoelastic properties (chapters by Wentzcovitch at al.; Alfe; and Stixrude and Lithgow-Bertelloni), diffusion (Amman et al.), thermal conductivity (Stackhouse and Stixrude), structure prediction (Oganov et al.), and phase transition in ice and at multi-megabar pressures (chapters by Umemoto and Umemoto et al.). It is worthwhile noting that the studies of dislocations and solid solutions mentioned above also employed density functional theory–based calculations at some stages, e.g. for validating empirical potentials. The ability to compute structural and properties at elevated temperatures, and not only in the athermal limit, is of fundamental importance for the applicability of first-principles calculations to the Earth sciences, and the book conveys in an outstanding manner the achievements of the last years.

In addition to the studies mentioned above, which are mostly concerned with crystalline phases, DFT studies also allow the simulation of melts (chapter by Karki). A comparison with the Ghiorso and Spera contribution highlights the difference between force field–based models and parameter-free DFT simulations with respect to accessible ensemble sizes and simulation times. The comparatively small ensembles that can be studied by quantum mechanical methods require extensive tests to exclude size effects, i.e., the dependence of the results on the number of atoms used in the model. On the other hand, the predictive power of force fields is limited to the pressure range for which they were derived, and the applicability of such models in simulations of the behavior of minerals at extreme conditions requires extensive validation studies, so that parameter-free models become a more attractive choice. It will be interesting to see how far and how fast the gap between force field and quantum mechanical dynamics simulations and ab initio calculations will be closed by the evolution of new hardware concepts, such as the use of graphical processing units, in conjunction with new parallelization techniques.

While the above-mentioned chapters convincingly show that with "standard" DFT numerous problems can be addressed, this approach has several shortcomings, many of which are related to our ignorance of the exact form of the exchange-correlation functional. This lack of knowledge forces us to use approximations such as the generalized gradient approximation. It is therefore of great interest to develop alternative methods that do not rely on approximations. One such approach is based on quantum Monte Carlo (QMC) techniques, introduced in the contributions by Ceperley and Mitas and Kolooreh. There is, of course, the caveat "Given sufficient computer resources...," which is a subtle hint to the adventurous reader who is considering trying this approach, that these calculations can be computationally very expensive, and the codes are certainly not as easy to use as some of the mature DFT codes available in the public domain.

Alternatively, some shortcomings of standard DFT approaches can be overcome by an extension of standard DFT, and one such extension, the so-called LDA+U approach, is reviewed by Cococcini. In the Earth sciences, this approach, which better describes the interaction of localized electrons, is required for accurate studies of several important iron-containing phases, such as wüstite and fayalite, and specifically for studies of spin transitions of lower-mantle minerals (chapter by Hsu et al.).

As is obvious from this long list of topics, volume 71 provides a comprehensive overview of recent developments in atomistic modeling approaches in mineral physics. The editors have very carefully selected complementary contributions from leaders in the field, which cover the general topic from a variety of viewpoints. There is very little redundancy. The contributions are balanced, although other approaches, such as the calculation of phonons from finite displacements instead of perturbation theory, could have been included. It probably would have been helpful for some readers to have a list of Internet resources, as many codes are in the public domain, and excellent tutorials are available on the web. But these are minor shortcomings, as the extended bibliographies contain all the necessary information.

In conclusion, volume 71 of Reviews in Mineralogy & Geochemistry offers a representative snapshot of the current state-of-the-art computational methods in mineral physics. Comparing volume 14 to volume 71 leads me to wonder about the unforeseen developments that volume 137, to be published around 2035, will contain.

Björn Winkler
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**ICAM 2011**

**First Circular Call for Papers and Workshops**

**01-05 August 2011**

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10th ICAM International Congress for Applied Mineralogy, Trondheim, Norway. Details: Maarten A.T.M. Broekmans; e-mail: maarten.broekmans@rug.nl; website: www.icam2011.org

**August 6 – 9**


**August 7 – 11**


**August 7 – 11**

European Association of Geochemistry (EAG) Workshop: Tools in Environmental Biogeochemistry – Opportunities and Limitations, Tubingen, Germany. Details: Andreas Kappler, e-mail: andreas.kappler@uni-tuebingen.de; web page: www.eag.eu/EAG_Workshop.html

**August 8 – 12**

74th Annual Meeting of the Meteoritical Society, Greenwich, England. Details: Gretchen Benedix, e-mail: greb@nmhm.ac.uk; web page: www.metsoc2011.org

**August 8 – 14**

2011 Goldschmidt Conference, Prague, Czech Republic. E-mail: helpdesk@goldschmidt2011.org; web page: www.goldschmidt2011.org

**August 14 – 19**


**August 22 – 26**


**August 22 – 29**


**August 28 – September 1**

American Chemical Society (ACS) National Meeting & Exposition, Denver, CO, USA. Web page: www.acs.org

**August 30 – September 2**


**September 4 – 7**

7th European Conference on Mineralogy and Spectroscopy (ECMS 2011), Potsdam, Germany. Details: Prof. Dr. Monika Koch-Mueller; e-mail: mkoch@gfs-potsdam.de; web page: www.physchemgeo/ecms/index.html

**September 4 – 7**

FRAGILE EARTH: Geophysical Processes from Global to Local Scales and Associated Hazards, Munich, Germany. Webpage: www.geosociety.org/meetings/2011munch

**September 20 – 24**

4th Hemispheric Conference on Geology, Bari, Italy. Details: Saviero Fiore, e-mail: fiore@m3a.cn.it; web page: www.geomed2011.it

**September 26 – 29**

11th Biennial Society for Geology Applied to Mineral Deposits (SAGA) Meeting, Antofagasta, Chile. E-mail: sgaa2011@ucn.cl; web page: www.sgaa2011.ucn.cl

**October 9 – 12**

Geological Society of America Annual Meeting, Minneapolis, MN, USA. E-mail: meetings@geosociety.org; web page: www.geosociety.org/meetings/2011

**October 16 – 20**

Materials Science & Technology 2011 Conference and Exhibition – MS&T’11 combined with the ACS’ 113th Annual Meeting, Columbus, OH, USA. Web page: www.tms.org/Meetings/meetings.asp

**November 21 – 24**

Conference on Arsenic in Groundwater in South Asia, Hanoi, Vietnam. E-mail: vietctasad53@yahoo.com; web page: vietas.erd.dtu.dk

**November 28 – December 2**

MRS (Materials Research Society) Fall Meeting, Boston, MA, USA. Web page: www.mrs.org/s_mrs/index.asp

**2012**

**March 11 – 15**

The Minerals Metals & Materials Society (TMS) TMS 2012: Linking Science and Technology for Global Solutions, Orlando, FL, USA. E-mail: mtsgserv@tms.org; web page: www.tms.org/meetings/annual-12/AM12/home

**March 25 – 29**

243rd American Chemical Society (ACS) National Meeting & Exposition, San Diego, CA, USA. Web page: www.acs.org

**April 9 – 13**


**April 22 – 25**

AAPG Annual Convention & Exhibition, Long Beach, CA, USA. Web page: www.aapg.org/meetings

**May 28 – 30**


**May 31 – June 10**


**July 15 – 19**

International Congress on Ceramics (ICCA), Chicago, IL, USA. Web page: ceramics.org/4th-internationalcongress-on-ceramics-icc4

**July 28 – August 2**

American Crystallographic Association (ACA) Annual Meeting, Boston, MA, USA. Web page: www.AmerCrystalAsn.org

**July 29 – August 2**


**August**

Annual meeting of the Meteoritical Society, Cairns, Queensland, Australia. Details: Trevor Ireland; e-mail: trevor.ireland@anu.edu.au; web page: www.meteoriticalsociety.org

**August 27 – 31**


**August 28 – 30**

34th International Geological Congress, Brisbane, Australia. E-mail: info@34igc.org; web page: www.34igc.org

**September 19 – 23**

244th ACS National Meeting & Exposition, Philadelphia, PA, USA. Web page: www.acs.org

**September 9 – 13**

First European Mineralogical Conference, Johann Wolfgang Goethe-University, Frankfurt, Germany. Website: http://emc2012.uni-frankfurt.de

**September 17 – 20**


**November 4 – 7**

Geological Society of America (GSA) Annual Meeting, Charlotte, NC, USA. Web page: www.geosociety.org/meetings

**November 26 – 30**

MRS Fall Meeting, Boston, MA, USA. Web page: www.mrs.org/s_mrs/index.asp

**2013**

**April 7 – 11**

245th American Chemical Society (ACS) National Meeting & Exposition, New Orleans, LA, USA. Web page: www.acs.org

**May 19 – 22**

AAPG Annual Convention & Exhibition, Pittsburgh, PA, USA. Web page: www.aapg.org

**May 22 – 24**


**July 3 – 10**

IAVCEI General assembly 2013: Forecasting Volcanic Activity, Kagoshima, Japan. Details: Masato Iguchi, e-mail: iguchi@iho.dpri.kyoto-u.ac.jp; web page: www.iavcei.org/IAVCEI.htm

**August**

ECM-28 – XXVIII European Crystallographic Meeting, Warwick, UK. Details forthcoming

**August 4 – 8**

Microscopy & Microanalysis 2013, Indianapolis, IN, USA. Web page: www.microprobe.org/events

**September 8 – 12**

246th American Chemical Society National Meeting & Exposition, Indianapolis, IN, USA. Web page: www.acs.org

**October**

MSS&T’13: Materials Science & Technology Conference and Exhibition, Montreal, Quebec, Canada. Details forthcoming

**October 27 – 30**

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

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The meetings convened by the societies participating in Elements are highlighted in yellow. This meetings calendar was compiled by Andrea Koziol. To get meeting information listed, please contact Andrea at Andrea.Koziol@notes.udayton.edu.
It is strange how sometimes a striking and unusual family name seems to attract our attention repeatedly, linking apparently unrelated places, events and activities. The name Agassiz is extremely rare but turns up in all manner of contexts. The family originated from a village near Lake Neuchâtel in Switzerland and has produced an extraordinary number of high-achievers. Most Elements readers will have heard of Louis Agassiz (1807–1873), and perhaps his son Alexander (1835–1910), because they both made important contributions to Earth sciences. But what of Auguste, who founded the Longines watch firm? Or James, who commanded a ship in Lord Nelson’s fleet during the Napoleonic wars and was praised for his act of sending fire ships into the French lines. Or James’s son, Lewis, who as a British Royal Marine led a firing party into Washington, DC, during the Anglo-American war of 1812–1815? National boundaries appear not to have existed for the Agassiz clan.

The graceful mountain which dominates my first picture is the Finsteraarhorn (4274 m), the highest peak in the Bernese Oberland. The first point on the long ridge leading from the summit is the Agassizhorn, named after Louis Agassiz. He was born in Switzerland and his first post was professor of natural history in Neuchâtel. He worked initially on living fish, before studying fossils and more general palaeontology. Louis became interested in glaciers and built a hut on one of the Aar glaciers in which he lived for some time, observing their behaviour. He was the first person to suggest that large areas of Europe had been covered by ice sheets like the one in present-day Greenland. After moving to Harvard University in 1846, he became one of the best-known scientists in the world. Glacial Lake Agassiz is central North America is also named after him.

But Louis had what many would now regard as a dark side. He never accepted Darwin’s view of evolution, and rather than seeing all of humankind as having common origins, he advanced the view that the individual races were created separately and, more controversially, that the black races were intrinsically inferior. He illustrated this supposed inferiority in 1850 with a photograph of a slave from the Congo, called Renty, whom he found in South Carolina. An organization called the ‘De-mounting Louis Agassiz’ committee has been organizing a petition to change the name Agassizhorn to Rentryhorn, which has recently been refused by the three Swiss communities in whose territory the mountain stands. Louis based his ideas on race on what he perceived as scientific facts, and although he was wrong, it seems to me that Louis deserves his minor peak as a reward for his glaciological insights. You may not agree.

In 1840 Louis visited Scotland, and on being shown grooves on an exposure of andesite forming one of the numerous volcanic necks that give Edinburgh its dramatic skyline, declared that they were produced by ice. The ‘Agassiz Rock’, as it is now known, has a seminal position in our modern view that all of Scotland owes its landforms to glaciation. The Rock is somewhat overhanging, and being conveniently close to the Edinburgh University science campus, is used by rock climbers, who are responsible for the film of white powder you can see in the photograph. On my lunchtime walks I often pass lithe young men standing contemplating their route up, although curiously I have never seen one actually climbing. There is even a detailed guide to the climbs. Here are the instructions for getting up a route called The Wizard, rated Br 5c/6a Font 6a: F12, G12 (jugs), LH-I9 (slope pinch), RH-K9 (edge)... I could go on. It reminds me somewhat of the knitting patterns my grandmother used to generate multicoloured Shetland sweaters.

I encountered another Agassiz when, about ten years ago, I visited Michigan Tech in Houghton as an MSA Lecturer. Houghton is at the base of the Keweenaw Peninsula, which sticks out into Lake Superior and is notable for its amazing snowfall, hitting a recorded maximum of 9.92 m in 1978–79. It also has the world’s largest deposits of native copper, which have been mined for around 7000 years, up to 1968. In the 19th century, miners arrived from Finland and from Cornwall, in southwest England, and you can still enjoy a sauna and a Cornish pasty. The copper was precipitated from warm brines circulating in Proterozoic conglomerates and amygdaloidal basalts. The lump in my picture weighs 4.26 tonnes and is worth about US$32,000 at today’s prices. Like his father Louis, Alexander Agassiz started his career as an expert on fish and always maintained his interest in marine biology, but through a web of family connections became involved in the copper mining, which in 1867 was beginning to falter, partly because of the inaccessibility of the region. With great determination Alexander developed the mines, eventually amassing a considerable fortune of which he gave US$500,000 to Harvard to found its museum of comparative zoology. His statue can be seen in the town of Calumet, Michigan, looking more academic than mining tycoon.

Ian Parsons
University of Edinburgh, UK
The Department of Earth Sciences (ES) at IUPUI invites applicants for two tenured/tenure track positions in geochemistry and hydrology—rank open. Candidates should have a Ph.D., strong research records, an interest in multidisciplinary research and commitment to undergraduate and graduate education. A Ph.D., received prior to August 2011 in geology, hydrology, limnology, geochemistry, or a closely related field, is required. ES is a growing and evolving department that embraces an Earth Systems approach to research and teaching as we adopt a new interdisciplinary Ph.D. degree program in Applied Earth Sciences. This new program is built on the research strengths of two centers that reside in the department: the Center for Earth and Environmental Science, recognized for excellence in water resources research, and the Center for Urban Health with a focus on earth science-based solutions for improving human health. Efforts will be supported by a number of existing interdisciplinary efforts, state-of-the-art laboratories, instrumented field research stations and information technology resources.

**Hydrology/Hydrogeology.** We seek an individual with experience in either hydrology or hydrogeology as applied to natural systems and/or environmental geosciences, including water quality and human health. Field-based research and teaching programs are important to the program and preference will be given to individuals who can interface with interdisciplinary research teams, including collaboration with other ES faculty and those in chemistry, biology and public health.

**Geochemistry.** We will consider individuals with experience in the broad field of low temperature geochemistry, and who can effectively apply their techniques and expertise towards natural, (paleo-) environmental and/or societal issues. Disciplines might include, but are not limited to, aqueous geochemistry, hydrogeochemistry, biogeochemistry, water/mineral/microbe interactions and stable isotope geochemistry. Preference will be given to individuals who can interface with interdisciplinary research and teaching programs, including collaboration with faculty in hydrology, sedimentology, petrology, and remote sensing. Opportunities also exist for collaboration with faculty in other departments of IUPUI, Indiana University, and Purdue University.

Applicants should submit a letter of application, curriculum vitae, statement of research interests, statement of teaching interests and philosophy, and the names and contact information (including e-mail) of at least four (4) references. Review of applications will begin December 15, 2010 but the position will remain open until filled. Interested individuals are encouraged to submit their application electronically to department chair, Kevin Mandernack, at kevinman@iupui.edu, specifying either the Hydrology or Geochemistry Search Committee. Mailed applications can be sent to: Department of Earth Sciences, Indiana University-Purdue University at Indianapolis, 723 West Michigan Street, SL118, Indianapolis, Indiana, 46202-5132. Questions regarding the hydrology/hydrogeology position should be directed to Lenore Tedesco (ltedesco@iupui.edu) and those for the Geochemistry position to Andrew Barth (ibsz100@iupui.edu). Prospective candidates can also learn more about these positions at the fall AGU meeting in San Francisco where ES faculty will be in attendance and available for consultation. Competitive start-up award and salary are available. Consideration will be given to mid-rank professionals in addition to entry-level candidates.

IUPUI is Indiana’s Urban Research and Academic Health Sciences Campus, and the focal point of IU’s Life Sciences Initiative. IUPUI is an Equal Opportunity, Affirmative-Action Employer.
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