

Elements

An International Magazine of Mineralogy, Geochemistry, and Petrology

March 2005
Volume 1, Number 2

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Diamonds

Inclusions in Diamonds

The Origin of Diamond

Strange Diamonds: Carbonado and Framesite

Microdiamonds in Metamorphic Rocks

Meteoritic Nanodiamonds

Changing Color of Gem Diamonds

Growing Better Diamonds



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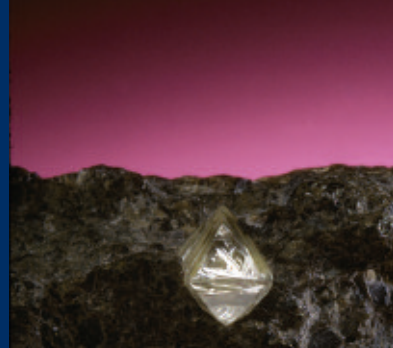
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Elements

An International Magazine of Mineralogy, Geochemistry, and Petrology



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Elements will be published three more times in 2005. Individuals are encouraged to join any one of the participating societies to receive *Elements*. Institutional subscribers to any of the following journals – *American Mineralogist*, *The Canadian Mineralogist*, *Clays and Clay Minerals* – will also receive *Elements* as part of their subscription. Institutional subscriptions are available for US\$100 a year. Contact the managing editor for information.

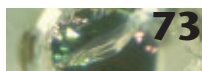
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Diamonds

George E. Harlow and Rondi M. Davies
Guest Editors

Inclusions in Sublithospheric Diamonds: Glimpses of Deep Earth

Thomas Stachel, Gerhard P. Brey, and Jeffrey W. Harris

Stable Isotopes and the Origin of Diamond

Pierre Cartigny

Strange Diamonds: The Mysterious Origins of Carbonado and Framesite

Peter J. Heaney, Edward P. Vicenzi, and Subarnarekha De

Microdiamonds in Ultrahigh-Pressure Metamorphic Rocks

Yoshihide Ogasawara

Meteoritic Nanodiamonds: Messengers from the Stars

Gary R. Huss

High-Pressure and High-Temperature Treatment of Gem Diamonds

James E. Shigley

Growing Diamond Crystals by Chemical Vapor Deposition

Russell J. Hemley, Yu-Chun Chen, and Chih-Shiue Yan

ABOUT THE COVER:

Diamond, the ultrahard cubic form of carbon, is a mineral requiring a long string of superlatives to describe its properties, its technological and commercial importance, and its roots into human culture and our physical world.

Pictured is the Minton diamond octahedron (7 mm across) in kimberlite from the De Beers Mine, Kimberley, South Africa.

PHOTO BY DENIS FINNIN, COURTESY OF AMERICAN MUSEUM OF NATURAL HISTORY.

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The Mineralogical Society of America is composed of individuals interested in mineralogy, crystallography,

petrology, and geochemistry. Founded in 1919, the Society promotes, through education and research, the understanding and application of mineralogy by industry, universities, government, and the public. Membership benefits include special subscription rates for *American Mineralogist* as well as other journals; 25% discount for *Reviews in Mineralogy and Geochemistry* series and *Monographs*; *Elements*, reduced registration fees for MSA meetings and short courses; and participation in a society that supports the many facets of mineralogy. For additional information, contact the MSA Business Office.

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the science of mineralogy and its application to other subjects including crystallography, geochemistry, petrology, environmental science, and economic geology. The Society

further its objects through scientific meetings and the publication of scientific journals, books, and monographs. The Society publishes three journals, *Mineralogical Magazine* (print and online), *Clay Minerals* (print and online) and the e-journal *MINABS Online* (launched in January 2004). For full details on how to join the Society and its events and publications consult the Society's website at www.minersoc.org or contact the General Office.

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The Mineralogical Association of Canada was incorporated in 1955 to promote and advance the knowledge of mineralogy

and the related disciplines of crystallography, petrology, geochemistry, and economic geology. Any person engaged or interested in the fields of mineralogy, crystallography, petrology, geochemistry, and economic geology may become a member of the Association. Membership benefits include a subscription to *Elements*, reduced cost for subscribing to *The Canadian Mineralogist*, a 20% discount on short-course volumes and special publications, and a discount on the registration fee at our annual meeting.

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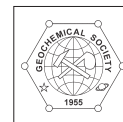
The Clay Minerals Society (CMS) began as the Clay Minerals Committee of the U.S. National Academy of Sciences – National

Research Council in 1952. By 1962, the CMS was incorporated with the primary purpose of stimulating research and disseminating information relating to all aspects of clay science and technology. The membership includes those interested in mineralogy, crystallography, geology, geochemistry, physics, chemistry, biology, agronomy, soils science, engineering, materials science, and industrial science and technology. The CMS holds an annual meeting, workshop, and field trips, and publishes *Clays and Clay Minerals*

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The Geochemical Society is an international non-profit organization for scientists involved in the practice, study,

and teaching of geochemistry. Our principal roles are to provide our members with programs and services that will help them to be better geochemists; to enrich the professional development and careers of geochemists through information, education, relationships, and resources; and to advance the thought and application of geochemistry.

Membership includes a subscription to *Elements*, access to the online quarterly newsletter *Geochemical News*, as well as an optional subscription to *Geochimica et Cosmochimica Acta* (24 issues per year). Members receive discounts on publications (GS Special Publications, MSA, Elsevier and Wiley/Jossey-Bass), and on conference registrations including the V.M. Goldschmidt conference, the fall AGU meeting, and the annual GSA meeting. For more details on our programs or information on how to join, please visit our website at: <https://gs.wustl.edu>

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Institutional subscribers to CMS, MAC, MS, and MSA journals are entitled to electronic access as part of their subscriptions.

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The Canadian Mineralogist Contact mac.amc1@sympatico.ca with your IP address and provide your subscription number.

Clays and Clay Minerals Go to the Ingenta web site, which hosts the electronic journal (www.ingenta.com), or start at The Clay Minerals Society (CMS) website (www.clays.org). You will find further instructions about registering and requesting access.

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Elements: Getting into the Swing

With this second issue of *Elements*, both the editorial team and you, the readers, will sense that we are getting into the swing of a new and exciting enterprise. From now on, each issue will be the responsibility of one of the three scientific editors and a guest editor. This gives me an opportunity to express, I can safely say on behalf of the entire geochemistry–petrology–mineralogy community, heartfelt thanks to the two people, Rod Ewing and Pierrette Tremblay, who more than any others have been responsible for the guiding vision, look, and feel of our magazine. Of course, we have benefited enormously from advice from many sources, but without Rod's clear vision and quiet persuasion, the whole concept would never have moved off the ground and attracted the support of the founding societies. And, as you thumb through this issue, consider the complexity of the production of *Elements*. Thematic articles, society news, various minor pieces, and advertising have to be integrated into an attractive whole, all within a tightly defined space and to an exact deadline. Pierrette does a superb job of piloting the whole ship through the sandbanks and narrows of the publishing business. Thanks too to Alex Speer and the MSA office staff, who took on the considerable task of orchestrating the first mailing of *Elements* to 6140 individuals in 82 countries and to 1258 libraries.

Elements belongs to the members of its supporting societies, and is connected to them through an Executive Committee and an Advisory Board. The Executive Committee is composed of one representative from each society experienced in its workings. It provides financial oversight, acts as a channel of communication between the magazine and the officers and staff of the societies, and approves the appointment of the principal (i.e. scientific) editors and members of the Advisory Board. The Advisory Board has representatives from each society plus some additional members, all chosen for their scientific standing and fields of interest. Their main roles are to propose potential thematic topics and guest editors for consideration by the principal editors, to provide informed

advice and comment as need arises, and to act as reviewers. Thematic topics may also be suggested by interested individuals; a form is available on our website.

The three principal editors are appointed for staggered three-year terms, so that Rod Ewing will serve until the end of 2005, Mike Hochella until 2006, and myself until 2007. Replacements are suggested by the Executive Committee and reviewed by the principal editors for final approval by the Executive Committee. The principal editors intend to meet at least twice a year, and of course we exchange a great deal of e-mail messages. Seeing full-colour pdf files of proofs materialize on my computer screen when I'm working from my cottage in the Scottish Highlands is wonderful—an e-miracle. Guest editors are taking on a substantial task, because they are responsible for getting manuscripts and illustrations up to pre-production standard with fixed deadlines and space restrictions. All papers are reviewed by an independent expert referee, the guest editor, and the principal editor. This procedure ensures quality and gives them all-important 'peer-reviewed' standing with those ever-watchful bean-counters.

Principal editors have an important role in defining the style and content of *Elements*, and in ensuring that articles are pitched at the right level. Authors will find that this is not easy. While we do not aspire to be available to a mass audience like the excellent *Scientific American*, we want to publish papers accessible not only to members of the supporting societies, but also to students, to scientists in adjacent disciplines and to popular science writers and policy makers. Writing for a wider audience means taking off the comfortable old jacket of jargon, buzzwords, acronyms, and notations that we all wear for our technical writing, and putting on something smarter and more outgoing. It's worth the effort—what you write for *Elements* is likely to be read by a far larger audience than even your most-cited technical paper.

Ian Parsons

Thank you very much for the excellent first issue of *Elements*. The choice of theme was excellent, and the articles were very well done. I felt the level of detail was just right for the target audiences described in the initial editorial, "*Elements: Building a New Bridge*". The quality of the production and especially the graphics were outstanding. The authors and all the editorial staff are to be congratulated on a first rate production. If you "will get better and better", my mouth is watering.

Mark J. Logsdon, Geochimica Inc., USA

I arrived back from AGU to find the first issue of *Elements* in my mailbox. What a great first issue! The issue is packed with information, the articles an exciting mix of data, facts, and description of the "state of the field" as it is now. If you go upwards from here, and I am sure that you will, *Elements* will rapidly become a seminal important journal. What a great improvement over the much-too-dry society newsletters (and I know whereof I speak, having produced some of those dry *Geochemical Society Newsletters* in early 1990s!). To mix all that society information with exciting science and to make it available to the seven societies is a master-stroke. My congratulations to all involved in this new journal.

Steven B. Shirey, Carnegie Institution of Washington, USA

The inaugural issue of *Elements* is excellent! My only critique is that the four columns per page used in a couple of items was distracting (and difficult to read because too many rapid eye motions are required). I think two columns per page is best looking and easiest to read. Otherwise, congratulations on a well-designed layout and high-quality content.

Neil Sturchio, University of Illinois at Chicago, USA

It is just great. The color figures are quite nice and helpful for the readers to understand the papers. All figures should be with color if possible. The problem here in Japan is that few students are members of MSA, GS, and so on. They cannot read *Elements*. Copies should be delivered to university libraries so that they have a chance to read *Elements*.

Takashi Murakami, University of Tokyo, Japan

Wow, what a fantastic magazine. For the first time in months if not years, I can see myself reading a magazine from cover to cover. Congratulations on a job well done!

Gregory M. Dipple, University of British Columbia, Canada

In general I heartily approve, although I will definitely miss Canadian-locality articles like Dan Kontak's in the recent MAC Newsletter. I have two suggestions, one positive and one negative; on the positive side: continue the "2005 Preview" page as a rolling item—lets get them anticipating things. On the negative, discontinue the use of bold text for initial figure references; it breaks up the flow of the text since one automatically goes to look to see what was so important.

Douglas Scott, Timmins, Ontario, Canada

I know you all worked really hard on *Elements*, from developing the concept to the final product and it really shows! Really, really good! If we can keep the momentum, I cannot see why *Elements* should not be a sizable force in improving the profile of our fields! Thanks for your hard work.

Susan L. Svane Stipp, University of Copenhagen, Denmark

NOTE FROM THE EDITORS: We are happy to share some of the "flowers" we received following the inaugural issue of *Elements*. Several suggestions from our readers are implemented in this issue or will be in future issues.



The managing editor received real flowers from her fellow editors to celebrate the launch of *Elements* at the GSA meeting. PHOTO BARBARA DUTROW.

I am very impressed! I enjoyed the scientific articles, and I think that the way you laid it out, with a couple of pages for each member society's "news", works very well. I am looking forward to subsequent issues!

Congratulations on a great new geo-science magazine! And best wishes for its successful future.

Sandra Barr, President, Geological Association of Canada

I have just received (and read) the first issue of *Elements*. What a brilliant publication! It really does illustrate how relevant mineralogy and geochemistry are and in a manner that is completely accessible. Congratulations! I will look forward to the next issue on diamonds.

Philippa Black, University of Auckland, New Zealand

My congratulations to you and the rest of the editorial group. I'm very pleased and excited that the societies have a common forum for timely technical and society news. I have two suggestions: (1) Include a section on new web pages that include recent URLs for special reports, technical summaries, activities etc. I suggest you solicit these from readers who want to promote their web-based compilations, typically submitted by individuals and non-profit organizations. (2) Highlight a special graphic from a society member at the very end of the issue. The graphic choice should be selected on aesthetics and not necessarily on technical quality... just a pretty picture. It could include photos of real minerals, molecular models of minerals, phase diagrams, TEM, SEM photomicrographs, field images, etc. Label them "Parting Shot", "Geoimage", "Last Glimpse" etc.

Randall T. Cygan, Sandia National Laboratories, USA

IN THE NEXT ISSUE, READ ABOUT

Genesis: Rocks, Minerals, and the Geochemical Origin of Life

Robert M. Hazen, Guest Editor

Few scientific questions so capture the public imagination, or provoke such lively debate, as how life on Earth emerged. In the next issue of *Elements*, four of the most creative minds in origins research present their original insights on the geochemical origins of life. Each author has studied the field in depth, and each has come to an inescapable conclusion: rocks and minerals must have played a pivotal role in the transition from the blasted, prebiotic Earth to the living world we now inhabit. Rocks and minerals catalyzed the synthesis of key biomolecules; they selected, protected and concentrated those molecules; they jump-started metabolism; and they may even have acted as life's first genetic system.

Rocks and minerals as protective environments for life's origin
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COMING UP

IN SEPTEMBER Toxic Metals: Role of Surfaces

IN DECEMBER Large Igneous Provinces and Environmental Change

Science Societies and the Democratic Process

Peter J. Heaney¹

After Ed Koch was elected mayor of New York City in 1978, he used to stop people on the street and ask, "How am I doing?" This act of populism charmed even the most cynical New Yorkers, who returned him to office for two additional terms.

It's a lot harder to gauge the happiness of your constituency if you work for a scientific society. There are no newspapers that editorialize on the latest initiatives of the Geochemical Society (GS), and cable news completely ignores the adventures of the Mineralogical Association of Canada (MAC). Instead, one is left to look at more indirect indicators. Is the total membership growing or declining? Do the publications attract cutting-edge articles that are widely cited? Are the scientists engaged in society affairs?

To weigh this last question, we can ask another: How many scientists take the 10 minutes required to read the biographical statements of candidates for society positions, check the boxes next to the ones they like, and mail in the pre-addressed envelopes? George Will, political commentator for *Newsweek*, has argued that electorate turnout is a most imperfect measure of voter satisfaction; non-voters may be so at ease with the status quo that their absence should not be construed as discontent. On the other hand, I would note that (a) George Will is wrong about most things; and (b) these are not two-dimensional television personalities who are running for office but our friends and colleagues with whom we went to school and whom we meet at conferences.

I wrote to the presidents of five of the societies that sponsor *Elements* to find out how their leadership is chosen. All responded immediately, and I learned something that surprised me. Only the Mineralogical Society of America offers elections that are actually democratic, meaning that there are more candidates than positions to be filled. The other societies are not in constitutional violation. By-laws for most of the societies are available on the web. Of the five societies polled, MSA alone explicitly requires that its elections shall be contested: "For Councilors there shall be at least twice as many nominees as there are open positions, and there shall be two nominees for Vice President."

This situation provokes a thought: How much democracy do we really need in our scientific societies? Even though MSA calls for contested elections, history shows that most of the membership does not take advantage of that privilege. Alex Speer, Executive Director of MSA, provided me with a list of voter participation going back to 1925. Over the last 10 years, voting rates have averaged only 27%, with a range of 23 to 29%. Interestingly, these figures are consistent with those of the 1930s through the 1950s. The late 1960s and early 1970s saw a surge in the percentage of returned ballots, coincident with slight increases in the levels of membership (in 1971, for example, 41% of 2,674 members voted).

What does it mean when only a quarter of eligible voters cast a ballot? Is MSA structured so adeptly to represent its citizenry that the particulars of the people in the top offices are immaterial? Or does the MSA Council make decisions that are so irrelevant to life's daily routine that the majority of the membership can happily detach from the political process? No one involved in the running of MSA is arrogant enough to assume that the former is true, but neither is the latter. For example, the society is spearheading the development of GeoScienceWorld, which will permit electronic publishing of *American Mineralogist* and the *RiMG* volumes as well as allow full-text web searching on any given topic, and this is exactly the kind of contribution that flies completely below the radar of most members (until they find themselves using it).

It also seems important to note that the period of maximum voter participation coincided with the heady days of the lunar exploration program, when mineralogy, petrology, and geochemistry had a cachet that is less evident in this post-Apollo landscape. One can only conclude that today's anemic voter participation reflects a lack of investment in the direction that MSA is following. That's too bad, because these societies belong as much to the first-year graduate student trying to make sense of Schreinemaker's rule as to the latest winner of the Roebling medal.

And what of the other societies that do not offer even the committed 25% an opportunity to select among multiple candidates for office? Initially, the democrat in me responded to this potential for cronyism with outrage. After all, societies make decisions that can affect some lives pretty profoundly; they all designate the organizers and locations of international meetings, and they all present prestigious awards that can make or cap a career.

But conversations with representatives of those societies have moderated my indignation. The smaller organizations, with their limited membership, sometimes struggle to convince members to add the burdens of office to their already overloaded schedules. In addition, a lack of democracy can paradoxically allow for fairer representation. Though members of MSA are unambiguously committed to gender diversity (no female candidates for office have ever lost), they apparently are more ambivalent regarding international representation (7 of the last 9 foreign candidates for Council have been defeated, despite the fact that roughly half the MSA membership and contributors to *American Mineralogist* are based outside the US). Conversely, MAC explicitly searches for one representative from each of the geographic regions of Canada (as well as one from the US), and GS requires that at least two of its directors reside outside the US.

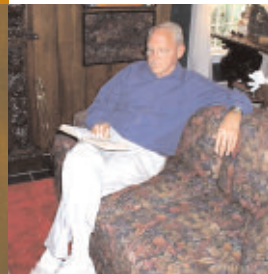
These are complicated issues, and the purpose of this column is not to moralize. But if you're feeling disenfranchised, you can change that. If you belong to MSA, you can vote. If you belong to the other societies, you can read the by-laws. They may not require multiple candidates, but they don't prohibit them either. And they all have mechanisms to allow non-council members to put up nominees. What's beautiful about democratic science societies is also what's terrible about them: they are as successful or as ineffective as the people who participate."

"How much democracy do we really need in our scientific societies?"

"What's beautiful about democratic science societies is also what's terrible about them: they are as successful or as ineffective as the people who participate."

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Paul Ribbe and the Reviews in Mineralogy



"Before and after" the Reviews in Mineralogy! On the left, the picture Paul Ribbe submitted to the University of Cambridge as part of his application in 1959. On the right, Paul enjoying well-earned retirement from editing the RiMG volumes for 30 years.

Paul Ribbe retired from the Series Editor position of the Mineralogical Society of America in 2003, after editing 50 RiMG volumes and five monographs over the past 30 years. This stunning achievement was recognized at the recent meeting of the Geological Society of America, where a special symposium was held in his honor. We gladly accepted his offer to write a brief history of the Reviews in Mineralogy.

Professor Emeritus of Mineralogy at Virginia Tech, Paul served as president of MSA in 1986 and 1987 and was awarded the Distinguished Public Service Medal by MSA in 1993 for his work with the Reviews in Mineralogy. He suspects that he was presented the 1995 Mineralogical Society of Great Britain and Ireland Schlumberger Award for the same undertaking. Paul retired from Virginia Tech in 1996 after 30 years. He and his wife, Elna, live contentedly in Blacksburg, Virginia, where both are heavily involved in Christian ministries.

A BRIEF HISTORY OF MSA'S REVIEWS IN MINERALOGY: FROM MANHATTAN TO THE MOON

Paul H. Ribbe

Alcohol-Soluble Short Course Notes

In the beginning, short courses of mineralogical interest were intended to be held in conjunction with the annual meetings of the Geological Society of America and affiliated societies. Sponsored by the American Geological Institute's Council on Education and directed by Joseph V. Smith, the first short course, *Feldspars*, was held November 1–3, 1965. Notes were produced for the 90 participants by Joe Smith, David Stewart, and myself using state-of-the-art Ditto-Master technology. Tragedy struck when a bottle of Scotch being smuggled in Dave's briefcase into dry Manhattan, Kansas, broke, smearing or completely dissolving the purple ink from most of

his handouts. A surviving fragrant fragment reads: "A discussion of what needs to be known in comparison with what might be determined will be given at the beginning of the lecture." Auspicious beginning!

AGI's Mimeographed Notes

In subsequent years, courses entitled *Pyroxenes and Amphiboles*, *Sheet Silicates*, and *Resonance Spectroscopy* were presented. Lecturers expanded their short course notes into longer chapters. These were mimeographed and compiled in ever-thicker binders for circulation by AGI, which coincidentally (?) ran out of funding for the project in 1968.

MSA's Short Course Notes

Five years passed before J.V. Smith, President of MSA, surveyed the members about the desirability of reviving the short course idea. Thus in 1973 the MSA Councilors appointed a committee to initiate the project that continues to this day. The first of 48 "modern" courses was held the following year with Charlie Prewitt directing. *Sulfide Mineralogy*, a 284-page book, with six authors and six chapters—Short Course Notes, Volume 1—was produced under my editorship in time for presentation at the Miami GSA. (Interestingly, *Sulfides* went through four printings and sold 7600 copies, more than any other single volume.) Three more volumes appeared in subsequent years, with increasing difficulty of scheduling and quality control. Thus, in 1978 Council asked me to assume the role of Series Editor.

Reviews in Mineralogy and the Science Citation Index

In 1980 two significant events took place: MSA changed the name of Short Course Notes to Reviews in Mineralogy and the Institute for Scientific Information asked for permission to reference RiM papers (chapters) in their *Journal of Citation Reports*. Listings in JCR and *Current Contents* since 1984 have helped establish the RiM volumes as significant players in the scientific literature, simultaneously satisfying promotion-and-tenure "bean counters" who insist on knowing the number of citations an author's papers receive in a given year. Furthermore, RiM and RiMG have been provided since 1987 to all libraries that subscribe to *American Mineralogist*, making them accessible to a worldwide audience. (Then there were 1300+ library subscribers, now there are 790.)

Before 1984, all 12 volumes had been typed on an IBM Selectric (5000 pages by one person—Margie Sentelle), pasted up, and submitted as camera-ready manuscripts to the printer. Ed Roedder's *Fluid Inclusions*, our first monograph, moved us into the era of word processors, at which time the average number of pages per volume jumped from 430 to 530. By the late 1990s, size was becoming a problem for paperbound volumes. The average cover-to-cover distance was 630 pages, with the apogee at 1037 pages (*Planetary Materials*). In 1989, the second edition of Volume 2, *Feldspar Mineralogy*, appeared in a Chinese translation, and in 1992 Roedder's *Fluid Inclusions* was published in Russian.

Reviews in Mineralogy and Geochemistry

In the year preceding 2000, MSA, led by Executive Director Alex Speer, and the Geochemical Society, led by President Mike Hochella, negotiated a change of name for the Reviews series: RiM became RiMG—Reviews in Mineralogy and Geochemistry. Jodi Junta Rosso was appointed Series Editor for the Geochemical Society's volumes. The new title better reflected what had been the case for at least 15 years and expanded our horizons significantly.

In 2000, Volume 39 *Transformation Processes in Minerals* became the first RiMG book. The accompanying short course was convened in Cambridge, England—the first outside the continental USA. That year, 1565 pages (3 volumes) were published—not all that remarkable. In 2001—the year the Department of Energy began generous support of student scholarships for select short courses—there were 2196 pages (4 volumes), and in 2002, 3775 (6 volumes!). As editor, I was beginning to feel like a full-time employee of the Society,

Looking Forward to the Past: A Session in Honor of Paul Ribbe and the Reviews in Mineralogy and Geochemistry

Mineralogists young and old from all over the world gathered in Denver last November, at the annual meeting of the Geological Society of America, to contribute to a session in honor of Paul Ribbe. The title of the session reflected the fact that, as reviewed by Michael Hochella (Virginia Tech), Paul Ribbe's career as a teacher and researcher in mineralogy became so intertwined with the development of the Reviews volumes that it is difficult to separate one from the other.

The session was opened by Michael Carpenter (Cambridge), with a picture of Paul Ribbe (reproduced here) that Paul had submitted as part of his application to the University of Cambridge back in 1959. At Cambridge, Paul determined the crystal structures of several feldspars and was the first to show that the structure of low albite had an effectively fully ordered distribution of Al and Si atoms. Throughout Paul's career, the underlying theme of his feldspar research was the connection between the details of the crystal structures at the atomic level and their macroscopic thermodynamic properties and lattice parameters. This was emphasized in a review by Ross Angel (Virginia Tech) of high-pressure crystallographic studies of feldspars that have been made since the feldspar RiM volume was last revised in 1982, and by Ian Parsons (Edinburgh) who discussed the fascinating exsolution microtextures in perthites from the Klokken intrusion, which can only be understood in terms of the coupling between ordering and un-mixing within the feldspars.

The other early volumes in the Short Course Notes series were also devoted to specific mineral groups and built on the same "micro to macro" theme that was to become the subject of a later RiM volume in its own right. Progress in understanding bonding in sulfides through high-pressure crystallographic studies was reviewed by Charlie Prewitt (University of Arizona), a contributor to that first sulfides

volume. "Changing Perspectives" was the very apt title chosen by David Vaughan (University of Manchester) for his presentation that emphasized both the development of studies of the *interactions* of sulfide minerals and the environment over the last 30 years, and the novel experimental tools that have been developed to enable those studies. Having started as critical reviews of the structures and properties of specific mineral groups, the RiM volumes have evolved over the years to encompass "even petrology", as noted by Darrell Henry (Louisiana State) in his talk on Ti in biotite, as well as experimental techniques. Robert Bodnar (Virginia Tech) took up his theme in reviewing the progress in fluid inclusion research since the publication of the only single-authored volume in the RiM series—volume 12 by Edwin Roedder. Novel computational methods have also revolutionized mineralogy on all scales from bonding in minerals (Jerry Gibbs, Virginia Tech) and molecular interactions (Jim Kubicki, Penn State) to km-scale modeling of metamorphism (Barb Dutrow, Louisiana State).

The last part of the session returned to the theme introduced by David Vaughan, that of mineralogy being an integrated study of the interaction of minerals with their environment. Mickey Gunter (University of Idaho) discussed the health issues arising from mineral dusts. Patricia Dove (Virginia Tech), editor of the recent RiMG volume on biomineralization, reviewed

the incredible structures built by various organisms out of calcite that must reflect some "vital" or biological effect. Both she and Jill Pasteris (St. Louis) also emphasized the importance of quantifying such effects so as to be able to use the compositions of biominerals as a proxy for the environment in which the organisms originally lived. Bob Hazen (Carnegie Institution of Washington) looked back to the origin of life and the problem of understanding how life's essential molecules, such as amino acids and sugars, became handed or "chiral." He suggested that chiral mineral surfaces may have played a key role in separating left- from right-handed molecules or in catalyzing chiral synthesis reactions. And he looked forward to the exciting new experimental techniques, borrowed from biochemistry, that are starting to be used to characterize the interactions between mineral surfaces and biomolecules. Bob Downs (University of Arizona) looked even farther forward with his presentation of a recently developed hand-held Raman spectrometer that was straight out of Star Trek!

The breadth of the talks and posters in the session emphasized the influence of the RiM volumes on the careers and thinking of most mineralogists. Jim Kubicki (Penn State) reflected the feelings of many in saying that being asked to edit a RiM volume was one of the highest honors he had received in his career. Several speakers concluded their talks with either news of forthcoming volumes in the series or informal proposals for new volumes, clearly demonstrating that the series Paul Ribbe founded and developed over thirty years remains a vital endeavor and a valuable resource for mineralogists. While all participants at the session expressed their thanks in various ways to Paul Ribbe for his service to the mineralogy community and for his incredible patience with authors and editors, the last slide of Bob Hazen's talk said it best. It simply read, in large friendly letters, "Thank you Paul".

Ross Angel and Nancy Ross
Virginia Tech
Blacksburg, November 2004

even though Jodi Rosso had assisted with several volumes and edited 2.5 of the 13. With my wife's gentle encouragement, I retired, knowing that Jodi would accept the job of Series Editor for both GS and MSA beginning with Volume 54.

RiMG in Cyberspace

By 2003 MSA had joined GSW (GeoScience World), an aggregate of Earth science societies bonded together to market their electronic publications, all of which are designed to exploit the search capabilities of AGI's GeoRef.

Although the means of individual access to RiMG has not yet been determined, the five volumes printed in 2003 and 2004 are already online through GSW, thanks to Jodi and Alex. The plan is to continue electronic publication of RiMG and in the near future to post volumes dating back to 2000 and earlier.

RiMG in Orbit?

The next volume to appear will be Volume 57 *A New View of the Moon* to be published in cooperation with NASA.

Conclusion

It would be false modesty to underestimate the impact on the disciplines of mineralogy, petrology, and geochemistry of the work of 963 different authors of 716 chapters (30,314 pages) in 56 volumes. For the curious: the entire series occupies nearly 6 feet (1.8 m) of shelf space and weighs 103 pounds (46.8 kg). More than 170,000 books have been sold to individuals over 30 years; about 40,000 are in libraries, and more than 42,000 are in inventory. Now that the number of books in print has exceeded the number of miles from Manhattan to the Moon, RiMG would appear to have a solar if not a stellar future.

International Gemmological Conference, Wuhan, China

The 29th International Gemmological Conference (IGC) was held at the China University of Geosciences in Wuhan, China, September 13–17, 2004. The conference, founded in 1951 by Dr. Edouard Gübelin and a number of his fellows, is designed to bring together professional research gemmologists worldwide to discuss the latest developments in gemmological research and other items of gemmological interest. It is held every two years, in the odd years, and usually alternates between venues in Europe and the other continents. The 29th conference was deferred until 2004 because of the SARS scare in China in 2003.

Attendance is by invitation and is limited to two delegates per country (though there may be extra observers). The 29th IGC welcomed delegates from Australia, Bahrain, Canada, China, Czech Republic, Germany, Holland, India, Indonesia, Japan, Korea, Russia, Singapore, Spain, Sri Lanka, Switzerland, Taiwan, Thailand, UK, and USA.

Delegates to the conference are expected to deliver papers on their current research. Papers given at the 29th session covered such diverse topics as “Study of Crystal Defects in Synthetic Diamond with Synchrotron Radiation X-ray Diffraction Topography” (Dr. Chen Tao) and “Trace-element geochemistry of gem corundum from various gem fields of Madagascar” (Dr. T. Thanasuthipitak). Willow Wight, research associate at the Canadian Museum of Nature and editor of the *Canadian Gemmologist*, spoke on her recent work on the non-nacreous pearls of *Placopecten magellanicus* scallops from Digby, Nova Scotia, Canada.



The Mengyin diamond mine, China

Although the conference itself lasts for one week, there are both pre- and post-conference tours. For the 29th session, the pre-conference tour included the Jurong Shi pearl farms and the Ma'anshan turquoise mine. The post-conference tours covered the Changle sapphire deposits, the Mengyin diamond mine, and the Damaping peridot mine.

The Ma'anshan turquoise mine lies some 30 km southwest of the city of Nanjing. Turquoise was discovered here in the 1960s as a result of examination of iron deposits in a Mesozoic volcanic sequence. The major item of interest during our visit was a

single, 20-tonne slab of turquoise that had just been mined and was being crated for shipment.

After the conference, we flew to Jinan and drove from there to Changle, 150 km to the east. Sapphire occurs in Changle county in two types of deposit. Primary sapphires are obtained as megacrysts in specific layers in alkalic basalts 16–17 million years in age; secondary sapphires are recovered from ancient stream beds buried beneath 10–12 metres of alluvial soil. The sapphire-producing area covers 420 km², and is basically agricultural.

The Mengyin diamond mine is also some 150 km from Jinan, to the south-east. Diamonds were discovered here in 1965, and subsequent exploration located the kimberlite (micaceous peridotite) pipes and veins. The age of the kimberlite intrusion is estimated at around 80 million years, although the diamonds themselves are probably more than 450 million years old.



Sorting diamonds by hand

Mining first took place as an open-pit operation, but the work went underground in 2001 and now reaches a depth of 210 metres. The kimberlite “carrot” divided at depth, and reached the surface as two separate entities, the larger of which is 75 × 45 metres, and the smaller 75 × 20 metres. The smaller pipe is the more productive of the two. The kimberlite, apparently controlled in a NE to NW fan by the Tanlu fault, also occurs in small veins that are generally short (10–100 metres) and range in width from 0.5 to 2 metres. Other exposures are known in the area.

The mine produces an average of 300 carats per day, for an annual gross of 100,000 carats, 20% of

which are gem quality. On the day of our arrival, they had already found 800 carats, much to the delight of the mine manager, who insisted that we had brought them luck. The primary habit is octahedral, and the colours range from black through brown and yellow to completely colourless. A tiny percentage of very small crystals are pink, but no blue diamonds have been seen to date. The largest diamond recovered from the area (in 1977) was a 158.79-carat yellowish crystal. The largest one found directly in the pipe was a 119.01-carat rounded octahedron (in 1983).

The mine shaft and buildings are at the edge of a small village and, apart from the incredible noise, have a very casual air about them. Ore brought from the shaft first goes through a jaw crusher, then a cone crusher, before being delivered to the grease belts. The fines recovered from the grease are sorted by hand by five or six very sharp-eyed young women who can spot a diamond of infinitesimal size with ease.

In the crushing house, the noise is deafening, there is water everywhere, and the entire building vibrates. In fact, it may be vibrating to pieces: there were holes in the walls. Interestingly, two-thousand-year-old technology works well. The crushed material is moved to an upper level by a huge Archimedes screw.

The final stop on the tour (besides the Great Wall, which is *de rigueur* for everyone) followed a flight to Beijing and a 240-km drive northwest from there to Zhangjiakou. The Damaping peridot mine is a further 30 km north of Zhangjiakou, in a series of Miocene alkaline basalt flows. As in Changle, there are alluvial and in situ deposits. One area of the hillside on the long climb up to the mine appears to be covered by fine, green peridot sand. The peridot is essentially 90% forsterite. Development in the area is slowing because of weaker markets, but the resources have not been exhausted.

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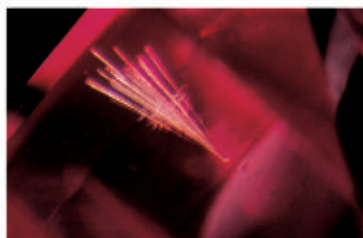
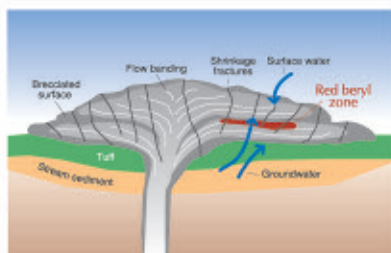
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Diamonds



Tiffany diamond, 287.42 ct, canary, from Kimberley, South Africa. PHOTO COURTESY OF TIFFANY & CO. ARCHIVES

George E. Harlow and Rondi M. Davies¹

Active research on diamond, a carbon mineral with superlative properties, extends into many realms of natural and material sciences. Extreme hardness and transparency make diamond a valuable gem and a high-pressure research tool, as well as a superabrasive. Natural formation at high pressure and resistance to weathering make diamonds our most informative messengers from Earth's mantle. A review of diamond's character and forms leads into the topics of the articles in this issue of *Elements*.

KEYWORDS: diamond, gem, high pressure, mantle, carbon

Diamond, the ultrahard cubic form of carbon, is a mineral requiring a long string of superlatives to describe its properties, its technological and commercial importance, and its roots into human culture and our physical world. Diamond is the hardest known substance, a strategic mineral critical to the market in superabrasives—over 800 million carats (160 metric tons) and about US\$10⁹ annually (Olson 2002), just for abrasive. Diamond, the king of gems, is at the heart of the most lucrative part of the gem industry, with an unmatched combination of brilliance, fire, hardness, and value (~US\$2 × 10¹⁰ annually for stones alone; Olson 2003). Natural diamonds are probably the oldest and deepest-sourced objects we will ever touch, and provide direct information about the mantle. The superlative character of diamond—linking technology, commerce, glamour, natural science, and material science—provides great impetus for ever-advancing scientific investigation. Consequently, when asked if diamond might serve as an inaugural topic for *Elements*, the answer had to be “yes.”

One of us has plowed the furrows of diamond subjects while creating a well-travelled exhibition entitled *The Nature of Diamonds*, accompanied by a book with the same name (Harlow 1998), while the other has cut her teeth studying inclusions in diamonds. Thus, we are both certified diamond junkies who find irresistible the attraction of diamond crystals, science, and personalities. And the activity relating to diamonds is abundant. Diamond is probably one of the only minerals on which several journals focus: *Diamond and Related Materials*, *Industrial Diamond Review*, *Industrie Diamanten Rundschau*, *New York Diamonds*. So, we had to restrain ourselves to invite only seven investigators or research groups to write articles on advancements in diamond-related science, with a geoscience connection of course, for this issue of *Elements*. The topics presented, however, do provide a view into the diversity and wealth of research on, and interest in, the densest form of element six.

Red chromian pyrope and green chromian diopside inclusions in a diamond octahedron from the Mir pipe, Sakha Republic, Russia (each about 0.2 mm across).

COURTESY UIGGM, SIBERIAN BRANCH OF RUSSIAN ACADEMY OF SCIENCES, NOVOSIBIRSK. PHOTO: GEORGE HARLOW

Diamond is a beautiful substance in many ways. Its simple but elegant crystal structure (FIG. 1), in which each carbon atom is bonded to four other atoms in a tetrahedral arrangement, yields a strong rigid framework. Combining this structural arrangement, which coincides with the hybrid sp^3 orbitals of carbon, with the unmatched strength of the C–C bond, explains most of diamond's properties, many of which are presented in TABLE 1.

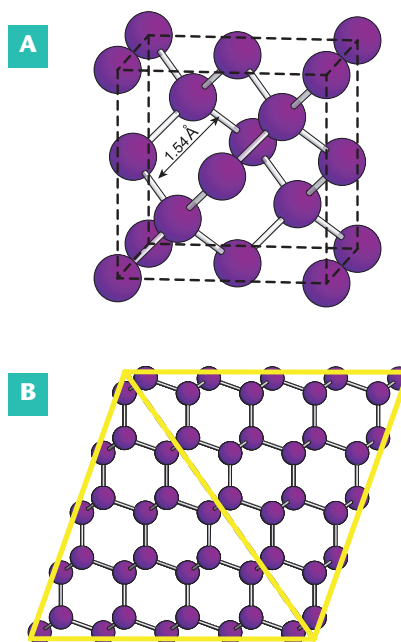


FIGURE 1 Ball and stick models of the diamond structure showing (A) the unit cell with the C–C distance indicated and (B) a projection with the boundaries of an octahedron, the archetypal “diamond” shape.

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TABLE 1

DIAMONDS: VITAL STATISTICS

Composition	C (carbon)
Crystallographic class	Cubic – hexoctahedral (highest of symmetries)
Space group	<i>Fd3m</i> $a = 3.57 \text{ \AA}$ (cell edge)
Common crystal forms (and indices)	Octahedron {111}, cube {100}, dodecahedron {110}, rounded variations due to etching
Twins	Spinel-law common, yielding the flat triangular “macle”
Hardness	10 on Mohs’ scale, 56–115 Knoop hardness number (GPa), 10,000 Brook’s indenter scale, octahedral face hardest, cube face softest
Moduli	Bulk modulus: ~500 GPa; Young’s modulus: ~1050 GPa
Cleavage	Excellent parallel to octahedron face {111}
Density	3.51 g cm ⁻³ (or specific gravity = 3.51)
Luster	Adamantine (the definition for this kind of luster)
Colors	Colorless, yellow, blue, green, and many others
Refractive index	2.4175 (in the yellow light of a sodium lamp)
Dispersion	Large (0.0437 – the difference in index at G and B Fraunhofer wavelengths), leading to rainbow colors on refraction
Optical transmission	Transparent over a broad range of the electromagnetic spectrum; an excellent material for optical windows
Thermal conductivity	Superb, 5 to 25 watts centimeter ⁻¹ °C ⁻¹ (at 300K); 4 times greater than copper; an excellent thermal conductor
Electrical conductivity	0 to ~100 ohm cm ⁻¹ (resistivity at 300K); an insulator

The rigid bonding leads to great hardness, incompressibility, and extraordinary thermal conductivity. Diamonds are called “ice” because of their ability to conduct heat so well; they feel icy cold because they rob heat from your diamond-touched lip. The uniform covalent bonding causes a large band gap, 5.5 eV, and makes diamond an electrical insulator and transparent over a broad portion of the electromagnetic spectrum. The dense packing of electrons yields a high refractive index (the ratio of light’s velocity in a vacuum to that in the material) of 2.42, quite remarkable for a material with such a low average atomic number. The list goes on, and the significance of these extraordinary properties will become evident in the articles in this issue of *Elements*.

The high density of diamond (3.51 g cm⁻³) as compared to that of graphite (2.20 g cm⁻³), the other common polymorph of carbon, is a clear indication that diamond is a high-pressure mineral, formed mostly in Earth’s interior. Thus, diamond is a key indicator and recorder of events deep within our planet, in part because its extreme strength

and refractory nature permits it to survive exhumation to Earth’s surface and subsequent weathering (another aspect is the extraordinary volcanic style of kimberlites and lamproites, which act as express elevators to raise diamonds quickly from depth, but that is a different story). Moreover, inclusions captured in a diamond growing in the mantle are protected by its adamantite embrace, so diamonds have become our “space missions” to inner Earth, providing our most important samples for understanding the chemistry of the deep mantle. By extracting inclusions (yes, diamonds get busted, burned, and ground away) and analyzing them, researchers have discovered the association of diamond with peridotite and eclogite assemblages from the roots of ancient cratons. More recently, transition-zone and lower-mantle signature minerals have been identified. The contribution by Stachel, Brey, and Harris reviews the status of these, the deepest samples of Earth that we have at our finger tips. Diamonds, while essentially pure carbon, allow us to investigate their carbon source through isotopic analysis of C and the minor contained N. Cartigny presents the available isotopic data and shows how diamonds reveal the hallmarks of primitive Earth, recycled crustal sources, and crystallization processes.

Two lesser known and understood varieties of diamond are, first, natural polycrystalline diamond—carbonado and framesite—and, second, microdiamonds discovered over the last 20 years associated with metamorphic rocks. Heaney, Vicenzi, and De review the characteristics of carbonado and framesite and help unravel some of the mystery around these enigmatic materials. As a high-pressure mineral, diamond is an important indicator for recognizing portions of Earth’s crust that have been buried to ultrahigh-pressure (UHP) conditions (for crustal rocks, that is) and, more remarkably, returned to the surface with diamonds intact. Search for UHP terranes by recognizing diamond or coesite (a high-pressure form of SiO₂) has become an exciting direction in metamorphic petrology, with important implications for how the Earth works. However, only recently have studies focused on the small UHP diamonds themselves. Ogasawara reviews the UHP occurrences of diamond and the ideas behind the processes by which they are formed before focusing on the Kokchetav Massif, Kazakhstan, where the most varied and abundant microdiamonds have been found.

One of the most remarkable diamond discoveries in the last decades is that of the nanometer-sized diamonds in meteorites. Meteoritic diamonds are hardly new, since they were described in the Canyon Diablo iron meteorite in 1891 (Foote 1891). These were later interpreted as the conversion of graphite to diamond by shock metamorphism upon the meteorite’s impact with Earth. On the other hand, diamonds in the Nova Urei (Ringwood 1960; Carter et al. 1964) and Kenna (Berkley et al. 1976) ureilites formed by shock on the meteorite parent body. Searching for the most primitive materials and reservoirs of noble gases in primitive meteorites, such as carbonaceous chondrites, led Ed Anders and colleagues to seek the last moieties in meteorites that could not be dissolved by aggressive acid or base—diamond, graphite, and silicon carbide. Huss reviews the results of research on these “nanodiamonds” and their possible origin in supernovae prior to the formation of our solar system (we really get goose bumps thinking about the possibility that the carbon in our bodies arrived on Earth as diamond and later will be recycled by subduction, in a while of course, to make more diamond).

Diamond science owes much to the fact that it is the most desired of gemstones. Its great value has led to some very secretive research on how to carry out an alchemy reminiscent of turning lead into gold—turning brown diamonds colorless, and more. Pure diamond is colorless carbon, so



World map showing diamond sources cited in this issue. Colored areas demark “Archons”—cratons older than 2.5 Ga, “Protons”—cratons 1.6-2.5 Ga, and “Tectons”—0.8-1.6 Ga, important in prospecting for mantle-derived diamonds (see Stachel et al., this

issue). Black diamond symbols are used for mantle-derived sources and red diamonds for ultrahigh-pressure (UHP) metamorphic sources. (ADAPTED FROM LEVINSON 1998)

color is the product of trace amounts of another element, such as N or B, or defects, or some combination of these. Treatments have been developed to remove color or enhance color, and Shigley provides this story and describes the challenge to the gem industry. After all, people value the color nature has bestowed on a diamond far more than colors produced in the lab, so the industry must strive to maintain confidence by developing methods to distinguish the natural from the enhanced.

Our modern technological society owes much to the prowess of diamond as an abrasive and superhard material. In geoscience, the diamond anvil cell (DAC) has permitted experimentation at pressures above 100 GPa to better understand the interiors of planets and the basic properties

of matter. And, if only diamonds were large and common enough, we might all have watches with faces that could not be scratched, computers with diamond guts to extract the heat from much smaller and denser electronic microdevices, and DACs on our lab bench. Hemley, Chen, and Yan describe advances in growing diamonds by chemical vapor deposition (CVD), so that such possibilities, and more, are not just a dream.

These are just a few windows into the exciting science spanned by diamond research. We hope you will appreciate how much more this extraordinary mineral is than merely corresponding to 10 on the Mohs scale of hardness or being the featured bauble in an engagement ring. ■

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Olson DW (2003) *Gemstones*. US Geological Survey Minerals Yearbook (<http://minerals.usgs.gov/minerals/pubs/commodity/gemstones/gemstmyb03.pdf>) and based on US representing ~ 60% of the world market (Harlow 1998).

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Glossary for Diamond Science

Solid carbon in nature

Diamond – is the cubic form of carbon in which every carbon atom bonds with four other carbon atoms in a rigid tetrahedral framework. Its high density (3.51 g/cm³) requires high pressure for thermodynamic stability (see Fig. 1 in Cartigny, this issue, which shows diamond stability in relationship to the conditions interpreted to exist, on average, below old continents and young ocean floor).

Graphite – is the hexagonal form in which each carbon atom bonds with three others to form sheets weakly connected by residual (Van der Waals) forces.

Lonsdaleite – is a diamond-like structure with hexagonal symmetry and appears to be metastable.

Amorphous carbon – is non-crystalline carbon as found in soot. Buckey-balls or buckminsterfullerenes are an organized but non-crystalline (in the traditional sense) form.

Earth structure and mantle rocks

Lithosphere – the relatively rigid shallow solid Earth, consisting of the crust and the non-convecting portion of the mantle immediately beneath.

Asthenosphere – the relatively weak, convecting portion of Earth's upper mantle, with low seismic velocities and located essentially between the lithosphere and the transition zone.

Transition zone – a layer in the mantle from ~410 to 660 km depth, where olivine converts to wadsleyite and ringwoodite (see below). Below the transition zone, silicate perovskite plus ferro-periclase replace ringwoodite.

Pyrolite – coined by A.E. Ringwood for a model composition of Earth's primitive or "fertile" mantle, originally consisting of 1 part basalt (e.g., as from the mid-ocean ridge—MORB) and up to 4 parts anhydrous peridotite. There are many versions depending on whether the composition is used to model the seismological or melting properties of the upper mantle. (The term "fertile" and related words are a hot-bed of meanings and interpretations too rich to go into here beyond the simple sense of permitting the described rock to produce a melt of desired composition on adiabatic decompression).

Eclogite – a rock consisting of roughly equal parts green omphacitic *clinopyroxene* [nominally CaNa(Mg,Fe)AlSi₄O₁₂] and orange *garnet* [(Ca,Fe,Mg)₃Al₂Si₃O₁₂]. It is essentially the high-pressure metamorphic equivalent of basalt, the major constituent of the ocean floor.

Peridotite – is the principal rock in Earth's mantle. It is dominated by olivine (the gem variety is peridot), and is often subdivided into types containing *spinel* [(MgFe)(Al,Cr)₂O₄], indicating a shallower origin, or *garnet* [red and rich in *pyrope* (Mg₃Al₂Si₃O₁₂)], indicating deeper origin. The other important constituents are orthopyroxene and clinopyroxene.

Harzburgite – a peridotite essentially free (<5%) of clinopyroxene and thus depleted in elements like Na, Ca, and Al relative to pyrolite; it is interpreted to be the residue after extraction of a melt fraction.

Lherzolite – a peridotite with 2–10% clinopyroxene, considered to be representative of primitive or fertile mantle, since no melt has been extracted from it.

Wehrlite – a type of peridotite in which clinopyroxene is more abundant than orthopyroxene; it is thus thought to be overly "fertile," perhaps because it has been enriched by the addition of fluid or melt.

Minerals of the mantle

Olivine, wadsleyite, and ringwoodite – are (Mg,Fe)₂SiO₄ phases. Olivine is the orthosilicate α -form stable in rocks from Earth's surface to a depth of ~410 km where wadsleyite (the β -form) a denser di-silicate is stable, and at ~520 km ringwoodite (the γ -form with spinel structure) becomes stable (see Stachel et al.).

Pyroxene – a rock-forming, chain-silicate, mineral family with formula $M\text{SiO}_3$ – where M is usually a divalent metal or metals and Si is in tetrahedral coordination with oxygen.

Clinopyroxenes – have monoclinic symmetry and are generally rich in Ca + Mg + Fe and/or Na + Al.

Orthopyroxenes – are orthorhombic and have a formula close to (Mg,Fe)SiO₃.

Garnet – a rock-forming, orthosilicate, mineral family with formula $M^{2+}_3N^{3+}_2\text{Si}_3\text{O}_{12}$; M can be Ca, Mg, or Fe²⁺ and N is generally Al, Cr, or Fe³⁺

Majorite – is a form (polymorph) of silicate garnet in which Si resides in the 6-coordinated site (e.g., symbolized as ⁶Si) as well as the tetrahedral site: Mg₃⁶(MgSi)⁴Si₃O₁₂.

Ferropericlase – (or *magnesiowüstite*) is (Mg,Fe)O and significant in the deep mantle as a dense phase formed as a reaction product with MgSiO₃-perovskite in the reaction $\text{Mg}_2\text{SiO}_4 = \text{MgSiO}_3 + \text{MgO}$. IMA suggests ferroan periclase.

Perovskites – a structure type with potentially diverse compositions and with the same formula as pyroxene but different coordination: $^{12}M^{6}XO_3$. Perovskite itself is CaTiO₃ and is stable at low pressures, but silicate perovskites, MgSiO₃ and CaSiO₃, are the main minerals of the lower mantle.

Isotope ratios and notations

Delta notation – isotope ratios are often reported in "delta notation", which gives the deviation of the measured ratio from the standard ratio in parts per thousand [$\delta^{13}\text{C} = ((^{13}\text{C}/^{12}\text{C})_{\text{meas}} / (^{13}\text{C}/^{12}\text{C})_{\text{std}}) - 1) \times 1000$] The standard for C is PDB, a fossil belemnite, for which the notation is sometimes presented as $\delta^{13}\text{C}_{\text{PDB}}$. In the case of oxygen, the formulation is based on ¹⁸O/¹⁶O with the standard being Standard Mean Ocean Water (SMOW); for sulfur it is ³⁴S/³²S with standard Canyon Diablo Troilite (CDT or a synthetic equivalent VCDT).

Noble Gases

³He/⁴He ratios – are used to measure the relative contributions from mantle and crustal sources in the production of a rock. Since ³He is primordial in origin but most ⁴He is radiogenic, low ³He/⁴He ratios suggest a strong input from the crust, where radionuclides are concentrated.

Meet the Authors



Gerhard P. Brey received a Diploma in mineralogy at the Friedrich Alexander-Universität of Erlangen in 1973 and a PhD in geochemistry from the Australian National University (Canberra) in

1976. From 1978 to 1994, he was a research assistant at the Max-Planck-Institut für Chemie in Mainz in the Division of Cosmochemistry. He taught at the Technische Universität Darmstadt where he fulfilled the requirements for the degree of Habilitation in 1990. Since 1995, he has been professor of petrology at the Johann Wolfgang Goethe-Universität in Frankfurt, where he continues his experimental work on geothermobarometry and the application to mantle xenolith suites and inclusions in diamonds from the upper and lower mantle. In January 2004 he was elected as Dr. *honoris causa* by the Russian Academy of Sciences in Moscow.



Pierre Cartigny obtained his PhD in 1997 at the Institut de Physique du Globe de Paris. After two years as a postdoc at the University of Göttingen (Germany), he joined the Stable Isotope Laboratory of

IPG-Paris as a CNRS researcher. His main interests focus on the geodynamic cycle of nitrogen and on the origin of the isotopic variability within Earth's mantle.



Yu-Chun Chen is a PhD student in the Department of Electrical and Computer Engineering at Auburn University and a predoctoral fellow at the Carnegie Institution of Washington. His fields of research include

fabrication and microelectronic applications of carbon nanotubes, microelectronics manufacturing, and CVD single-crystal diamond. He was born in Chang-Hua, Taiwan. He received his BS degree from the Department of Electronics Engineering at Feng-Chia University prior to entering the graduate program at Auburn in 2001. He has been a graduate research and teaching assistant and was selected as an Auburn University Graduate Research Fellow in 2004. His PhD advisor is Professor Yonhua Tzeng.



Rondi M. Davies is a postdoctoral fellow in the Department of Earth and Planetary Sciences at the American Museum of Natural History. She was educated in Papua New Guinea and Australia, where her benchmark

study of the origin of eastern Australian diamonds earned her the prestigious Voisey Medal. Rondi also studied the origins of deep-sourced ancient diamonds from the Slave craton, Canada. She is now researching the nature and history of Earth's mantle using high-pressure experimental techniques and is involved in the Museum's educational and outreach programs.



Subarnarekha De examined natural polycrystalline diamonds (PCD) using transmission electron microscopy for her PhD research at Princeton University. She has also performed high-pressure synthesis of

polycrystalline diamonds at the Geophysical Laboratory, Carnegie Institution of Washington, and she has contrasted synthetic compacts to natural PCD using various microscopic techniques. More recently, as an NRC Post-Doctoral Fellow at the NASA Ames Research Center, De investigated terrestrial carbonates and compared them to globules from Martian meteorite ALH84001 to shed light on the "life on Mars" question.



Jeffrey W. Harris, based at the University of Glasgow, has played an outstanding role in the development of research on diamond, making significant contributions in the fields of diamond

classification, inclusion identification and geochemistry, and age-determination techniques. He is author or coauthor of 109 peer-reviewed papers. He has acted as a diamond consultant to DeBeers Consolidated Mines Ltd for 29 years and on their behalf, coordinates, facilitates, and participates in joint research projects with other universities and research centres throughout the world. Currently this includes over 30 projects in Australia, Britain and other European centres, Canada, South Africa, and the United States. He is an Associate Editor of the *Journal of Gemmology*.



George E. Harlow is curator of minerals and gems in the Department of Earth and Planetary Sciences at the American Museum of Natural History. His research focuses on the chemistry

and structure of minerals as tools for understanding their origin and the record of geological processes they contain. Projects inspired by the museum's collections include the origin of jadeite rock (jade) in Guatemala and elsewhere, and the mineralogy of the Mogok Stone Tract, Myanmar, famous for rubies, spinels, and a complex mineralogy. Diamond inclusions led to study of and experiments on K-rich clinopyroxene and the behavior of large-ion lithophiles and volatile components in minerals at upper mantle conditions. He has curated the exhibitions *It's Gold* (1979–80), *Tiffany: 150 Years of Gems and Jewelry* (1988), *Global Warming* (1992), and *The Nature of Diamonds* (1997).



Peter J. Heaney received his PhD from Johns Hopkins University in 1989. He is currently an associate professor in the Department of Geosciences and the Materials Research

Institute at Penn State. Heaney has focused his research on mechanisms of mineral growth and transformation as revealed by real-time X-ray and electron diffraction techniques. His recent areas of interest include the origin of naturally occurring polycrystalline diamonds, the effects that atomic exchange exerts on mineral phase transition behavior, and the formation pathways followed by the many varieties of microcrystalline silica.



Russell J. Hemley is a staff scientist at the Geophysical Laboratory, Carnegie Institution of Washington. His research explores the behavior of materials over a broad range of thermodynamic

conditions from low to very high pressures and how this relates to problems in Earth and planetary science, physics, chemistry, materials science, and biology. He obtained degrees in chemistry (Wesleyan University, BA 1977; Harvard University, MA 1980, PhD 1983) before joining the Carnegie Institution in 1984. He is a fellow of the American Physical Society, the American Geophysical Union, and the American Academy of Arts and Sciences, and a member of the National Academy of Sciences.



Gary R. Huss is professor at the Hawai'i Institute of Geophysics and Planetology at the University of Hawai'i. He received his Bachelor's degree in geology at Rice University, his Master's degree in geology at the

University of New Mexico, and his PhD in geology at the University of Minnesota. He joined the laboratory of Edward Anders at the

University of Chicago in 1988 to study the newly discovered nanodiamonds in meteorites. Since, his research has covered many aspects of the early solar system, including nanodiamonds, various types of presolar grains, short-lived radionuclides, the timing of events in the early solar system, and the processes that led to the meteorites, asteroids, and planets.



Yoshihide Ogasawara, Dr. Eng., is professor of petrology at the Department of Earth Sciences, Waseda University, Tokyo. Since his doctoral dissertation, he has worked on low-pressure type dolomitic marbles and carried out related computer-assisted thermodynamic studies. In 1993, he began studying ultrahigh-pressure metamorphic rocks, with a focus on UHP carbonate rocks. Recently he has concentrated on the evolution of deeply subducted carbonate rocks and the formation of diamond in the metamorphic rocks of the Kokchetav Massif, northern Kazakhstan.



James E. Shigley is director of research at the Gemological Institute of America (GIA) in Carlsbad, California. Prior to joining GIA in 1982, Dr. Shigley studied geology as an undergraduate at the University of

California at Berkeley and later received his doctorate in geology from Stanford University. He is the author of various articles on diamonds and other gemstones and is a well-known speaker on gemological topics to both professional and general audiences. Dr. Shigley directs GIA's research activities, which include the identification of natural, synthetic, and treated diamonds, colored stones and pearls, and the evaluation of various characterization techniques for identifying gems.



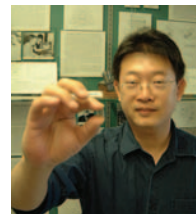
Thomas Stachel is professor and Canada Research Chair in Diamonds at the University of Alberta in Edmonton. He completed his PhD in 1991 at Würzburg University, Germany, on the

volcanology and petrology of the Ellendale lamproites, Western Australia. A first postdoctoral research project on the Gross Brückaros Caldera in Namibia still kept him in the field of volcanology. With a Marie Curie Fellowship of the European Union, he joined Jeff Harris at the University of Glasgow in 1994, where he became involved in research on diamonds and their inclusions. From 1996 to 2001 he was a lecturer at the Institute for Mineralogy at Frankfurt University where he completed his "habilitation" on diamond research in 1999. In the same year he was awarded the

Victor Moritz Goldschmidt Award of the German Mineralogical Society. He joined the University of Alberta in 2001.



Ed Vicenzi is a research geochemist and the director of the analytical laboratories in the Smithsonian Institution's Department of Mineral Sciences. He is actively involved in the application of electron and ion microbeam methods to Earth and planetary research. His current interests include mining information from combined Time of Flight-Secondary Ion Mass Spectrometry, X-ray microanalysis, and cathodoluminescence datasets. Before joining the National Museum of Natural History in 1999, he spent six years at the Princeton Materials Institute. Prior to this, he spent two years as a postdoc at Macquarie University in Australia. He received his PhD from Rensselaer Polytechnic Institute, a Master's degree from the University of Oregon, and a BSc from McGill University, all in Earth sciences.



Chih-Shiue Yan is a research scientist at the Geophysical Laboratory, Carnegie Institution of Washington. He was born and raised in Taiwan. In 1995, he began graduate work on CVD diamond under the direction of Professor Yogesh Vohra (University of Alabama at Birmingham, UAB) and Russell J. Hemley and Ho-kwang Mao (Carnegie Institution). During this period he developed techniques for the fabrication of single-crystal diamond by CVD and received his PhD in physics from UAB in 1999. He then became a research fellow and associate at Carnegie before assuming his current position in 2004.



The Clay Minerals Society will hold its Annual Meeting in Burlington, Vermont, U.S.A. June 11-15. Burlington is situated on the shores of Lake Champlain, located between the Green Mountains to the east and the Adirondack Mountains to the west. The meeting's theme "Green Mountain Clays", reflects both the ancient tectonic processes responsible for forming metamorphic chlorite, serpentine, talc and muscovite in deformed Paleozoic rocks of the Green Mountains, as well as the Pleistocene glaciation and deglaciation that led to the deposition of lacustrine and marine clay-rich deposits in the Champlain Valley.

IMPORTANT DEADLINES

Abstract Submission:
APRIL 1, 2005
Pre-registration: May 15, 2005
Hotel: May 20, 2005
For more information, see www.middlebury.edu/cms, or contact the conference chairs:

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One of the highlights of the 2005 meeting will be field trips that take advantage of these geological resources. One field trip will be to the Adirondack Mountains to examine glacial till spodosols and their associated weathering reactions and clay mineralogy (June 11), and the other will be to serpentinized peridotites in the Green Mountains to examine tectonic, mineralogical and environmental issues (June 15).

The conference will host numerous theme sessions and symposia, covering topics such as soil mineralogy and geochemistry, links between soils and sediments, clays and the environment, ceramic science, stable isotopes and clays, structural modeling and quantitative analysis, clays and climate, and a special session devoted to the pioneering research of Robert C. Reynolds in the areas of sedimentary basin analysis, hydrocarbon geology and structural analysis of clays.

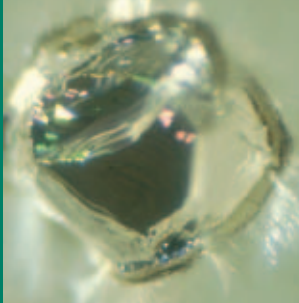
The CMS Workshop "Characterization of Solid-Water Interface Reactions of Metals and Actinides on Clays and Clay Minerals" will be held on June 11 and is being organized by Andreas Bauer of Forschungszentrum Karlsruhe, Institut für Nukleare Entsorgung (INE), Karlsruhe, Germany; bauer@ine.fzk.de



Burlington is a small city of 40,000 inhabitants and is home to the University of Vermont, a thriving pedestrian-friendly downtown, museums and natural areas, and a working agricultural landscape renowned for world-class cheeses. The meeting will be held at the Wyndham hotel on the Burlington waterfront, a venue that is ideally-suited for a CMS meeting. We encourage you to attend, to meet old colleagues and friends, to strike up new professional relationships, to share knowledge and ideas, and to enjoy early summer on the shores of Lake Champlain.

Inclusions in Sublithospheric Diamonds: Glimpses of Deep Earth

Thomas Stachel¹, Gerhard P. Brey², and Jeffrey W. Harris³



A 400-micron wide ferropericase inclusion in a diamond from the São Luiz alluvial deposits of Brazil. PHOTO BY JEFFREY W. HARRIS.

Diamonds originate in the deep roots of ancient continental blocks (cratons) that extend into the diamond stability field beneath about 140 km. Over the last two decades, rare diamonds derived from even greater depths—the deep upper mantle, the transition zone (410–660 km), and the lower mantle—have been recognized. Inclusions in diamonds from the deep upper mantle and the transition zone document sources of basaltic composition, possibly related to subduction of old oceanic crust back into Earth’s mantle. Diamonds from the lower mantle carry inclusions that largely confirm predictions of the composition and mineralogy of the deep mantle based on a “pyrolite” (primitive peridotitic) composition of silicate Earth. For some inclusions, however, the chemical evidence again points to a connection with subducting oceanic slabs, possibly ponding at the top of the lower mantle.

Keywords: diamond inclusion, majorite, perovskite, phase transition, transition zone, lower mantle, subduction, megalith

INTRODUCTION

The vast majority of diamonds mined from primary deposits in kimberlite and lamproite pipes and from secondary deposits derived through erosion and redeposition originated from a narrow depth window between about 140 and 200 km, as indicated by calculations of temperature and pressure of formation of their silicate inclusions. The top end of this depth range corresponds to the transition of graphite to diamond at conditions in Earth’s mantle; the bottom end appears to coincide with the “normal” maximum thickness of lithosphere, the non-convecting uppermost portion of our planet (FIG. 1). Such substantial thicknesses of lithosphere are only achieved beneath the oldest parts of continents, the cratons; this explains the observation that primary diamond deposits are generally limited to areas where the last major tectonothermal event occurred at least 2.5 billion years ago—this is the essence of the so-called “Clifford’s Rule”.

Mineral inclusions in diamonds are overwhelmingly derived from the two principal rock types occurring in the deep lithosphere, peridotite and eclogite (e.g., Meyer 1987). Although peridotitic diamonds dominate, the relative abundance of eclogitic diamonds generally increases with larger stone sizes, giving them great economic importance. The study of lithospheric diamonds has proven to be a valuable tool complementary to similar research on fragments of mantle rocks

(xenoliths) found in volcanic rocks of deep origin. The inclusions are typically 0.1–0.2 mm in size, rarely 0.5 mm, and are found using an optical microscope. If necessary, they can be identified in situ using Raman spectroscopy and characterized structurally using X-ray diffraction. For chemical analysis, mineral inclusions are released by crushing or burning their diamond hosts. The inert nature and presumed old ages of diamonds make their inclusions particularly useful for studying the origin and evolution of ancient lithosphere.

Important observations over the last two decades have shown that hidden among the dominant lithospheric diamonds are samples

derived from even greater depths, extending to at least 700 km. Xenoliths of mantle material from beneath the lithosphere are extremely rare, and the few examples appear to have equilibrated to lithospheric conditions (e.g., Sautter et al. 1991). Our knowledge of the mineralogy and chemical composition of the sublithospheric mantle, therefore, is derived indirectly, using high-pressure experiments, seismic data, and cosmochemical and isotopic constraints. Mineral inclusions in ultradeep diamonds are the only direct samples from the deep mantle available for study and allow us to test the models derived from geophysical and experimental studies.

Discontinuities in the velocity of compressional and shear waves discovered in seismic studies point to layering in Earth’s mantle. High-pressure experiments by A.E. Ringwood and coworkers (including W.O. Hibberson, T. Irifune, L. Liu, and A. Major) showed that these seismic discontinuities coincide with phase transitions affecting important mantle minerals. Based on these data, the mantle is subdivided into three major layers (see FIGS. 1 AND 2):

1 The upper mantle (<410 km) It is thought to consist predominantly of olivine and low-Ca pyroxene. In the present paper, we use the term “asthenosphere” for the entire convecting upper mantle beneath the lithosphere (see glossary p. 70).

2 The transition zone (410–660 km) The 410-km seismic discontinuity coincides with the experimentally observed conversion of olivine (α -phase) into spinel-like wadsleyite (β -phase), with roughly an 8% increase in mineral density. A further 100 km down, wadsleyite transforms to ringwoodite (γ -phase), which has a true spinel structure and is another 2% denser. This latter phase transition has been linked to a mild seismic discontinuity in the mid-transition zone (at about 520 km).

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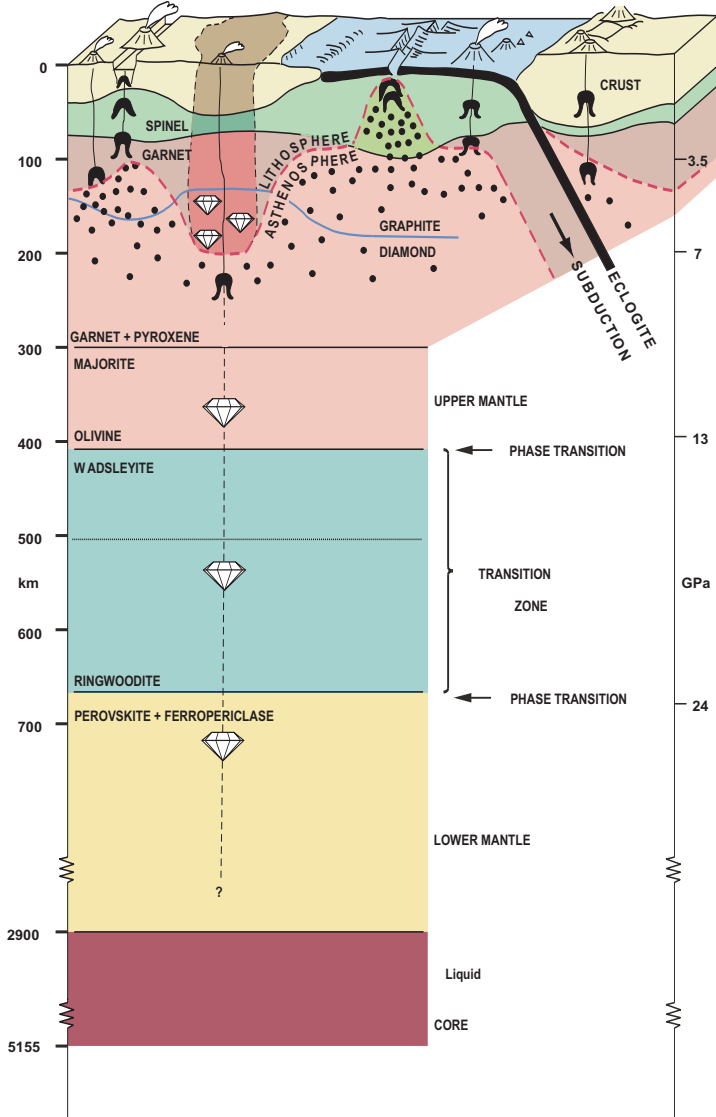


FIGURE 1 Vertical section through Earth's crust, mantle and core. The upper mantle, underlying the crust (shown in light yellow) is separated into two main mineralogical layers, spinel facies (green) and garnet facies (pink). The uppermost, non-convecting portion of Earth including the crust and part of the upper mantle is called the lithosphere, and the underlying convecting part the asthenosphere. Beneath ancient cratons the lithosphere may extend to about 200 km depth. In cooler regions of Earth's mantle the graphite/diamond transition occurs at shallower depth. Beneath cratons, therefore, there is a region where lithosphere and diamond stability overlap and this is the main source region of diamonds worldwide. Rare ultradeep diamonds may come from (i) the deep upper mantle, where majorite garnet becomes stable, (ii) the transition zone, characterized by the stepwise isochemical conversion of olivine first to wadsleyite and then to ringwoodite, and (iii) the lower mantle. These ultradeep diamonds are the only direct samples available from the deep interior of our planet.

3 The lower mantle (660–2900 km) In contrast to the upper mantle, which is made up of silicate minerals based on various combinations of SiO_4 -tetrahedra, silicon is octahedrally coordinated with oxygen in the lower mantle. The dominant phases are CaSi- and MgSi-perovskites, in addition to the oxide phase ferropericlase. The nature of the 660-km discontinuity is still not fully understood, with conflicting experimental, geochemical, and geophysical evidence as to whether it represents an impediment to whole mantle convection or not (cf. Agee 1998).

The discovery of ultradeep inclusions in diamonds was not a stepwise recognition of increasingly deeper origins. Rather, it began unexpectedly in 1984 with a small paragraph in a paper by Scott Smith et al. (1984) on kimberlite dikes near Orrorroo in South Australia. These authors noted that if ferropericlase (see glossary p. 70) inclusions in diamonds from this occurrence and the Koffiefontein Mine in South Africa were indeed syngenetic, then, because of an apparent association with inclusions of orthopyroxene chemistry, they may indicate diamond formation in “deeper levels of the mantle” (i.e., the lower mantle). Not much attention was given to this discovery till more compelling evidence for lower-mantle diamonds was found at Rio São Luiz in the Juina area of Brazil (reviewed in Harte et al. 1999).

The next stage was the recognition of inclusions of majorite garnet (see glossary p. 70) in diamonds from the Monastery mine, South Africa (Moore and Gurney 1985), which indicated formation in the asthenosphere and the transition zone. The most recent discoveries of ultradeep inclusions came from Snap Lake (Canada), in the form of subcalcic, high-Cr majoritic garnet (Pokhilenko et al. 2001) and from Yubileynaya (Siberia), where Sobolev et al. (2004) report wehrlitic, high-Cr majorite garnet.

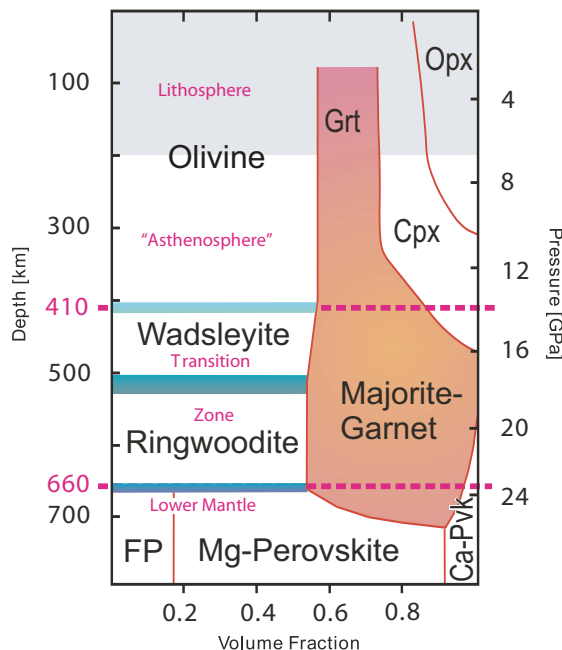


FIGURE 2 Relative mineral proportions and phase transitions in Earth's mantle (after Ringwood 1991; Agee 1998; Wood 2000). FP: ferropericlase; Grt: garnet; Cpx: clinopyroxene; Opx: orthopyroxene; Mg-perovskite: MgSi-perovskite; Ca-Pvk: CaSi-perovskite.

Although individual inclusions of “ultradeep” origin are by now quite common, so far only five localities have yielded many sublithospheric diamonds. Of these five localities, four have yielded diamonds with majoritic garnet inclusions: Monastery, Jagersfontein (both South African), Juina (Rio São Luiz, Brazil), and Kankan (Guinea). The principal sources of diamonds with lower-mantle parageneses are Juina, Kankan, and the Lac de Gras region of Canada. Studies on diamonds from these five occurrences (for references see Stachel 2001) form the basis of the review given here.

ASTHENOSPHERE AND TRANSITION ZONE

Important Phase Transitions

All four major minerals occurring in peridotite, the principal rock type in the upper mantle, are affected by phase transitions and reactions over the depth range in this zone. First, at around 300 km depth, orthopyroxene is eliminated by a structural conversion to monoclinic low-Ca pyroxene. At similar depths, garnet increasingly dissolves pyroxene as a majorite component to give a garnet-structured, high-pressure form with pyroxene stoichiometry. For a predicted primitive composition of the Earth's mantle ("pyrolite" of Ringwood 1962a and 1962b), all pyroxene would be dissolved in majorite garnet at about 450 km depth (Fig. 2). At about 550 km depth, the majorite component of garnet begins to decrease through exsolution of CaSi-perovskite. Magnesium-rich olivine, the most important constituent of the upper mantle, is eliminated at the top of the transition zone through conversion to wadsleyite, which in turn converts to spinel-structured ringwoodite in the middle of the transition zone. So, in the mid-transition zone, the typical four-phase peridotite of the upper mantle will have converted to a two-phase rock composed of silicate spinel and majorite garnet.

The Problem of Retrograde Phase Transitions

Based on these phase transitions, it might be expected that recognition of inclusions in diamonds from the deep asthenosphere and transition zone would be fairly straightforward and could be based on phase identification (X-ray diffraction, Raman spectroscopy). In fact, exhumation converts these high-pressure minerals to lower-pressure phases or assemblages. This happens because diamond deforms plastically at the high temperatures of the Earth's mantle, and thus high internal pressure on inclusions is relaxed during ascent. Even rapid ascent from the point of diamond formation is not sufficient to prevent retrograde conversion of ringwoodite or wadsleyite to olivine and of low-Ca clinopyroxene to orthopyroxene. The only exception is the retrograde reaction of majorite to "normal" garnet plus pyroxene, as this conversion is not an isochemical phase transition and leaves the telltale signature of an extra phase if reequilibration proceeds. The onset of pyroxene exsolution from majorite garnet has been documented for inclusions in diamonds from Juina by Wilding (1990).

Because of the polymorphic transitions, chemical fingerprinting appears to be the only way to detect former single-phase low-Ca clinopyroxene, wadsleyite, and ringwoodite inclusions. High-pressure experiments on pyrolite compositions show elevated Al contents in wadsleyite and (even more so) in ringwoodite relative to olivine (Akaogi and Akimoto 1979). From experiments, wadsleyite in equilibrium with a primitive mantle contains ≥ 0.3 wt% Al_2O_3 , which is also true for ringwoodite. As 0.1 wt% is the highest Al_2O_3 content for all of the 700 olivine inclusions analyzed from diamonds worldwide, we can exclude wadsleyite or ringwoodite as precursors.

Majorite Garnet

The only samples recognized so far as being from the asthenosphere and transition zone are inclusions of majoritic garnet. Experimental studies have found a near linear increase in "excess" silicon with increasing pressure for the pressure range of about 7–15 GPa, thus suggesting the possibility of using the majorite component in garnet as a geobarometer. Here we provide an interpretation using the 1200°C experimental data of Akaogi and Akimoto (1979) and Irifune (1987) for pressure estimates, though bulk chemical effects are not accounted for and experi-

mental data sets of other authors would lead to somewhat different results. FIGURE 3 shows the compositional spread of majorite inclusions in diamonds from worldwide sources. The bulk of the inclusions show majorite contents that translate to an asthenospheric depth of origin of about 250–350 km. A few majorites, however, come from greater depths, probably extending even into the transition zone. For the one inclusion from Jagersfontein showing the highest majorite component yet observed, even the most conservative pressure estimates (e.g., Gasparik 2002) imply an origin beneath the 410-km discontinuity.

Diamond Growth in the Transition Zone

A surprising feature of majoritic garnet inclusions is their paragenetic association with eclogite as inferred from their major-element composition. Earth's mantle is generally assumed to have a chemistry matching primitive peridotite ("pyrolite") with a very minor component (probably <1%, cf. Schulze 1989) of eclogite, the high-pressure metamorphic equivalent of basalt. Yet, only 10% of the about 90 majoritic garnet inclusions analyzed so far belong to the peridotitic suite. These peridotitic majorites are so high in chromium (up to 14 wt% Cr_2O_3) that they do not correspond chemically to pyrolitic mantle but to non-convecting lithospheric mantle with a history of melt extraction (cf. Pokhilenko et al. 2004). The Cr-rich majorites show that at some stage during Earth's history, the lithosphere may have locally extended to a depth of about 300 km, which is significantly deeper than what we observe today based on the record from mantle xenoliths.

There is considerable compositional overlap between eclogitic majorite garnet inclusions and lithospheric eclogitic garnet inclusions. This suggests that diamonds with eclogitic inclusions from within and beneath the cratonic lithosphere grew in similar source rocks. This compositional overlap seems to support the extreme view that the sublithospheric upper mantle is composed of eclogite (cf.

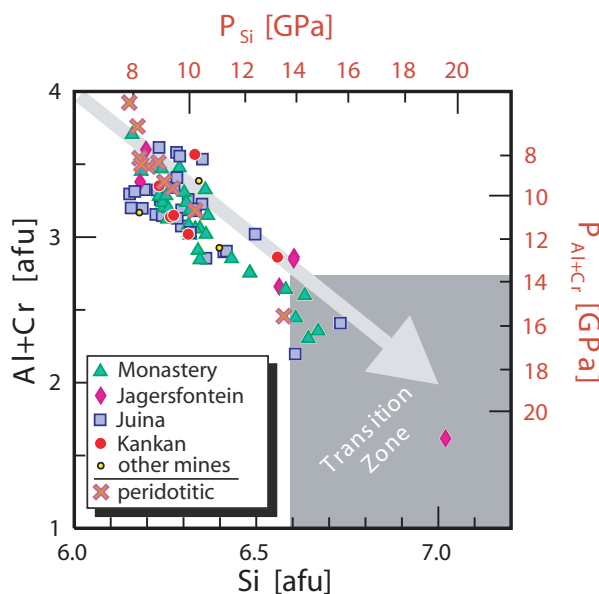


FIGURE 3 Majoritic garnet inclusions in diamonds from worldwide sources. An increasing majorite component with increasing pressure corresponds to increasing Si and decreasing Al+Cr. P_{Si} and $P_{\text{Al+Cr}}$ (given in giga-Pascal) are obtained via linear regression of experimental data (1200°C) of Akaogi and Akimoto (1979) and Irifune (1987) and are approximate values only. The transition zone, beginning at about 410 km (or 13.7 GPa) is indicated in grey. Except for crosses, which have peridotitic sources, all majorites shown are eclogitic in paragenesis. [afu] is atoms per formula unit.

Gasparik 2002). However, plate tectonics, the standard model in Earth sciences, provides a mechanism in accord with the petrological, geochemical, and geophysical constraints on the composition of Earth's mantle and the evidence against the long-term survival of extreme compositional stratification. Plate tectonics predicts that old and therefore dense oceanic lithosphere is subducted back into the mantle (Fig. 1) where it sinks through the asthenosphere and transition zone to the top of the lower mantle and in part even farther, to the core–mantle boundary, as seen from seismic tomography. The former basaltic oceanic crust in such sinking slabs could well be the source of eclogitic majorite inclusions in diamonds.

But why would diamond formation in the asthenosphere and transition zone be restricted to down-going slabs? Carbon is a trace element in a peridotitic mantle (≤ 0.04 wt%). For the growth of macrodiamonds, a local enrichment mechanism for carbon is needed. Within the lithosphere, this is probably accomplished by redox fronts, where reducing fluids encounter oxidized rocks or vice versa. The deep asthenosphere and transition zone are expected to be fairly well mixed and more reduced than the lithospheric mantle, making the presence of redox fronts unlikely. A sinking oceanic slab, however, will at least locally be oxidized through seawater alteration and provide redox gradients where reduced hydrocarbon-bearing fluids may precipitate diamond. In addition, thermally stable carbonates in subducting slabs may become reduced to diamond by virtue of a crystal chemistry-induced decrease in oxygen fugacity with increasing pressure. Strong support for a subduction model comes from the rare-earth elements in some majoritic garnets where europium is depleted relative to its neighboring rare-earth elements (REEs). Eu (as Eu^{2+}), unlike the other REEs, follows calcium and fractionates into the low-pressure mineral plagioclase. It is removed from the basaltic rocks during crystal–melt fractionation prior to being transformed into eclogite during subduction.

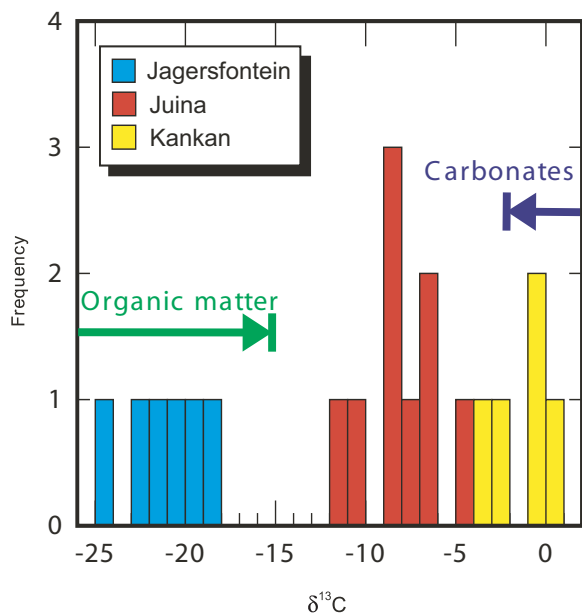


FIGURE 4 Carbon isotopic composition of diamonds with majoritic inclusions (all mines with less than two analyses were excluded). Kankan diamonds with majorites show similarities to the carbon isotopic composition of carbonates, Jagersfontein diamonds (Deines et al. 1991) resemble organic matter. At Juina (Hutchison et al. 1999) the carbon isotopic composition extends from the mantle value (about -5‰) to more negative values (i.e. isotopically lighter compositions), which may be due to a fractionation process affecting a primordial fluid.

Carbon isotopic data on diamonds containing majorite garnet inclusions (Fig. 4) exist for only three occurrences, Jagersfontein, Juina, and Kankan, and appear to support multiple origins for ultradeep diamonds: (i) subducted carbonates (high $\delta^{13}\text{C}$, Kankan), (ii) mantle fluids (at about -5‰) combined with minor isotopic fractionation (Juina), and (iii) subducted organic matter or strong isotopic fractionation (low $\delta^{13}\text{C}$, Jagersfontein) (see glossary p. 70).

LOWER MANTLE

Phase Transitions at the 660-km Discontinuity

The present understanding of Earth predicts that mantle of the deep transition zone should be approximately 60 vol% ringwoodite and 40 vol% majorite. At about 660 km, ringwoodite breaks down to an Al-poor MgSi-perovskite and ferropericlase (FIGS. 1 AND 2). Majorite garnet begins to exsolve CaSi-perovskite at a depth of ~ 550 km, and from the 660-km discontinuity down to ~ 700 km, the garnet gradually reacts to form aluminous MgSi-perovskite and expels some more CaSi-perovskite. If the lower mantle is richer in iron than assumed by the pyrolite model, stishovite, the high density polymorph of SiO_2 , would also be present.

Diamond Inclusions from the Lower Mantle

Ferropericlase: The most prominent lower-mantle inclusion mineral in diamond is ferropericlase [(Mg,Fe)O]. It is easy to recognize by its peacock-like play of colors under the microscope. Ferropericlase is preserved during exhumation because it is stable over the entire pressure range of the mantle. However, when raised above the depths of the lower mantle and in the presence of low-Ca pyroxene, ferropericlase should react to form olivine (or wadsleyite or ringwoodite). The absence of ferropericlase from “normal” upper mantle rocks, therefore, appears to indicate that all ferropericlase inclusions in diamonds are of lower-mantle origin. However, there is evidence that local regions within the upper mantle have low silica abundances; thus, the presence of single inclusions of ferropericlase in diamonds does not automatically prove a lower-mantle origin. It is only the coexistence in the same diamond of ferropericlase with non-touching inclusions of perovskite chemistry that unarguably reveals a lower-mantle origin.

Experimental studies on pyrolite compositions predict that ferropericlase in the lower mantle should have an Mg-number [$100\text{Mg}/(\text{Mg}+\text{Fe})$] of 84–85. Ferropericlase inclusions recovered from diamonds show a prominent mode in Mg-number at 85–88, indicating either a slightly more depleted or a slightly hotter source than modelled in experiments. Ferropericlase inclusions from Juina differ significantly from this fairly uniform picture by showing a very large range in Mg-numbers, from 36 to 87, and a polymodal distribution, with the majority of analyses falling between 60 and 82. The ferrous nature of the inclusions from Juina (in this case, correctly termed magnesio-wüstite) led Harte et al. (1999) to speculate about a possible origin from Fe-enriched mantle regions near the core–mantle boundary (2900 km). Alternatively, these inclusions may reflect much shallower but non-pyrolitic lower-mantle sources, for example ancient subducted oceanic crust.

Stishovite: This high-pressure SiO_2 -phase should be stable together with ferropericlase in the lower mantle at elevated iron contents (and possibly also in the transition zone at unusually high T); otherwise the two phases would combine to form MgSi-perovskite. Harte et al. (1999) constrained the magnesium-iron ratio for this reaction using the compositions of inclusions in diamonds from Juina and

found that stishovite coexists with ferropericlase and MgSi-perovskite at Mg-numbers as high as 70 for the former and 86 for the latter. Compared with high-pressure experiments, these ferropericlase and perovskite Mg-numbers are relatively high. The other four occurrences of stishovite plus ferropericlase in diamonds worldwide all reflect even more magnesian compositions and, therefore, should not exist in equilibrium. Disequilibrium seems the most straightforward explanation, but considering the relative “abundance” of these samples, some doubts are justified.

TAPP: One of the surprising discoveries made by the Edinburgh-Glasgow group on Juina diamonds was the occurrence of inclusions with a garnet-like composition but a tetragonal structure, hence called “TAPP” for Tetragonal Almandine–Pyrope Phase. TAPP is chemically distinct from “normal” peridotitic garnet because it is essentially Ca free (≤ 0.1 wt% CaO) (FIG. 5). Because TAPP is less dense than garnet at appropriate pressure–temperature conditions, it was suggested that TAPP represents a retrograde phase, possibly stabilized by high $\text{Fe}^{3+}/\text{Fe}^{2+}$ ratios. This explanation is supported by a TAPP sample in a lower-mantle diamond from Kankan, which clearly resulted from a reaction that occurred during ascent through the mid-transition zone.

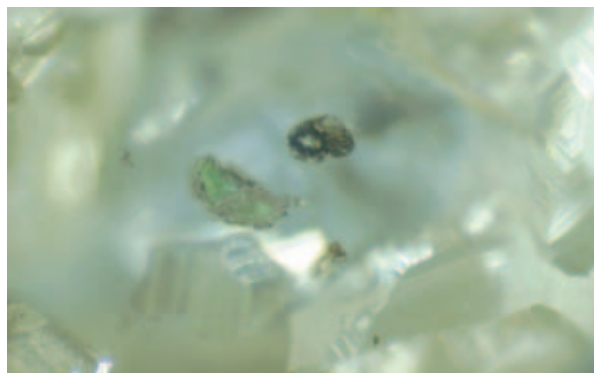


FIGURE 5 150 micron-long green tetragonal-structured garnet known as TAPP (tetragonal almandine–pyrope phase), in a diamond from the São Luiz alluvial deposits, Brazil. PHOTO BY JEFFREY W. HARRIS

MgSi-perovskite: Compositionally, MgSi-perovskite is a high-pressure equivalent of orthopyroxene. Crystallographic studies of inclusions show that presumed perovskites inverted to pyroxene during exhumation. Nickel content is the chemical indicator used to determine whether an inclusion originally formed as orthopyroxene or MgSi-perovskite. In the lower mantle, all nickel is partitioned into ferropericlase, and MgSi-perovskite consequently has less than 300 ppm NiO, as opposed to typical orthopyroxene from the upper mantle which has >1000 ppm NiO.

Seventeen out of 20 MgSi-perovskite inclusions discovered worldwide have Al_2O_3 contents below 3 wt%. As discussed above, experiments indicate that garnet dissolves gradually into MgSi-perovskite in the uppermost 50 km of the lower mantle, as the solubility of Al in perovskite increases with pressure. If models for the composition of the lower mantle are correct, then MgSi-perovskite with such low Al contents should occur only in the topmost ~20 km of the lower mantle. Only three MgSi-perovskites from Juina show high Al contents (about 10 wt% Al_2O_3) and thus may be derived from the deeper lower mantle.

CaSi-perovskite: Being almost pure CaSiO_3 , CaSi-perovskite is compositionally distinct from minerals occurring in typical upper-mantle and transition zone rocks. It should

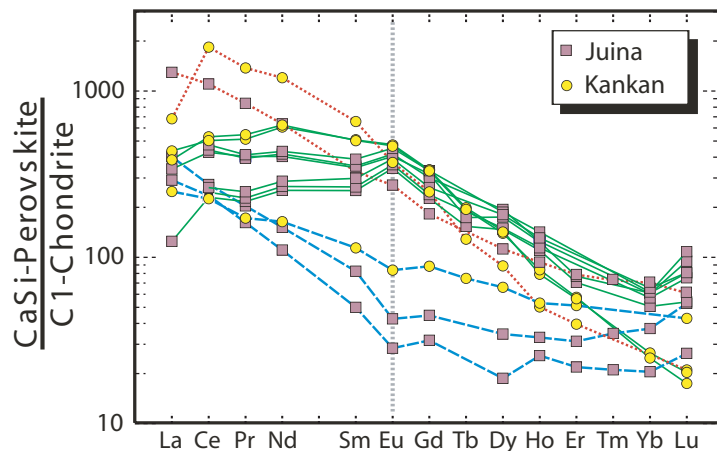


FIGURE 6 The concentrations of rare-earth elements (REEs) in CaSi-perovskite inclusions in diamonds from Juina and Kankan normalized to C1-chondrite as a “primitive” reference material. CaSi-perovskites generally show high concentrations in light REEs (left side of figure). Different types of REE patterns may be distinguished (shown as green, red and blue lines). The three groups also differ in the behavior of Eu, which shows positive spikes for the “green group”, negative spikes for the “blue group” and normal behavior for the “red group”. Negative Eu-anomalies are usually attributed to feldspar fractionation and positive anomalies to feldspar accumulation, making former oceanic crust that subsequently became subducted into the lower mantle a likely protolith.

be a high-pressure phase in both peridotitic and eclogitic parageneses. Despite the fact that the perovskite structure is never preserved—primary CaSi-perovskite inclusions are either amorphous or converted to the less dense walstromite structure—the discovery of CaSiO_3 inclusions was a crucial piece of evidence at Juina that established for the first time a lower-mantle origin for some diamonds.

CaSi-perovskite is particularly interesting among lower-mantle phases because it acts as a sink for incompatible trace elements e.g., strontium (0.03–0.73 wt%), zirconium (0.01–0.22 wt%), and total REEs (0.03–0.22 wt%). FIGURE 6 is a concentration diagram (normalized to C1-chondrite as a “primitive” reference material) for the REEs in CaSi-perovskites from Juina and Kankan. The analysed perovskites fall into three groups (see different line colors) with contrasting REE distributions. For each of these groups, the behaviour of Eu is different, with positive Eu anomalies with fairly flat slopes from La to Sm and negative anomalies for the three perovskites with the lowest total REEs. As discussed before, differences in the behaviour of Eu relative to neighbouring Sm and Gd are interpreted as a response of protolith composition to addition or extraction of plagioclase (which readily accommodates Eu^{2+} compared to the other trivalent REEs, including Eu^{3+}) at low pressure.

Formation of Lower-Mantle Diamonds

From the low Al contents of the MgSi-perovskites, it appears that the bulk of the lower-mantle diamonds are derived from the topmost ~20 km of the lower mantle. This characteristic, combined with the trace-element composition of CaSi-perovskites (with their positive or negative Eu anomalies), suggests that the diamonds were not derived from primitive mantle but from former oceanic slabs that accumulated at the top of the lower mantle (the “megalith model” of Ringwood 1991, see FIG. 7). As in the asthenosphere and transition zone, redox conditions in the lower mantle may generally be too reducing for the formation of

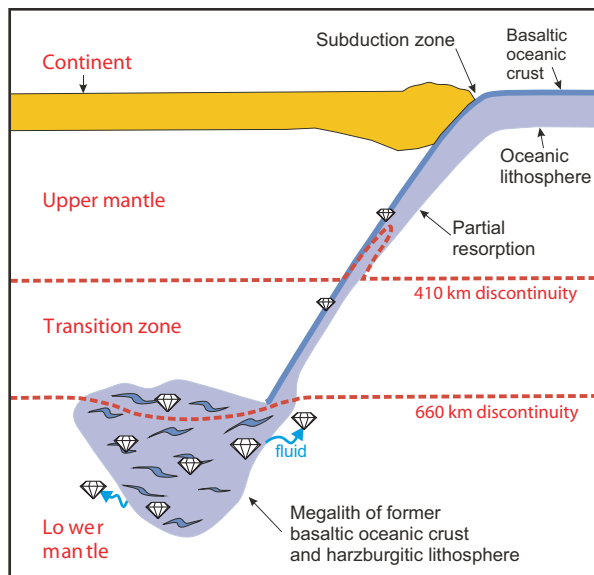


FIGURE 7 According to the “megalith model” of Ringwood (1991), subducting oceanic slabs may become buoyant at the top of the lower mantle. The resulting pile of subducted lithosphere is called a “megalith”. The evidence for diamond formation at the top of the lower mantle, in combination with crustal signatures in lower-mantle diamonds containing CaSi-perovskite, suggests that megaliths may well be the primary source. Oxidizing fluids coming out of the subducted lithosphere may cause diamond formation in highly reducing “normal” lower mantle. The formation of diamonds with inclusions of majoritic garnet may occur earlier during the subduction process, in the deep upper mantle and transition zone. Exhumation of ultradeep diamonds may occur through mantle plumes or in the course of normal mantle convection.

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macrodiamonds without the assistance of oxidized slab material or oxidizing fluids emanating from subducted material (Fig. 7) to provide the necessary redox gradients.

In conclusion, inclusions in ultradeep diamonds have turned out to be an excellent tool for testing mantle models based on high-pressure experiments and geophysical data. We have gained glimpses of the fate of subducting slabs passing through the asthenosphere and transition zone, and overall we observe good consistency with compositional models for the lower mantle. However, no studies involving radiogenic isotopes have yet been undertaken on ultradeep diamonds, and our knowledge of lower-mantle diamonds is largely based on only two occurrences. The search for more ultradeep material is therefore guaranteed to continue.

ACKNOWLEDGMENTS

In order to produce an easy-to-read overview on sublithospheric diamonds, the authors have attempted to keep references to a reasonable minimum. We would like to acknowledge that the information reviewed here is based on the efforts of people like Frank Brenker, Rondi Davies, Peter Deines, John Gurney, Ben Harte, Mark Hutchison, Felix Kaminsky, Rory Moore, Nick Sobolev, Ralf Tappert, and Martin Wilding. ■

Stable Isotopes and the Origin of Diamond

Pierre Cartigny¹

Most diamonds form in a relatively narrow depth interval of Earth's subcontinental mantle between 150 and 250 km. From carbon isotope analyses of diamond obtained in the 1970s, it was first proposed that eclogitic diamonds form from crustal carbon recycled into the mantle by subduction and that the more abundant peridotitic diamonds formed from mantle carbon. More recent stable isotope studies using nitrogen, oxygen, and sulfur, as well as carbon, combined with studies of mineral inclusions within diamonds, have strengthened arguments supporting and opposing the early proposal. The conflicting evidence is reconciled if mantle carbon is introduced via fluid into mantle eclogites and peridotites, some of which represent subducted oceanic crust.

KEYWORDS: diamond, stable isotopes, mantle, metasomatism

INTRODUCTION

Natural diamonds crystallize only at high pressures and temperatures. These conditions occur in the upper mantle, at depths exceeding ~150 km and temperatures above 950°C (FIG. 1). Diamonds are brought from the mantle to the surface as xenocrysts (foreign crystals) within volumetrically rare volcanic rocks called kimberlites and lamproites. These magmas not only form deep enough to pick up diamond, but also ascend to the surface fast enough to prevent transformation of diamond to graphite or its dissolution in the magma. The occurrence of diamond on the Earth's surface is thus both accidental and the result of the unique resistance of diamond to dissolution. For Earth scientists, the study of diamond and its impurities not only provides important insights into the conditions prevailing in the very deep mantle, but also helps us to understand the evolution of our planet.

Over the last twenty-five years, studies of diamonds from occurrences worldwide have yielded an enormous amount of data. It is now generally accepted that most natural diamonds are old and xenocrystic, and come from ancient lithosphere. In spite of major advances, the remaining questions about their formation are profound and complex. In particular, the source of carbon from which diamonds formed is still a hotly debated subject. This article reviews available stable isotopic data on diamonds, with a focus on the potential source(s) of carbon. The current models for the origin of diamonds in Earth's mantle will be presented and discussed in the light of stable isotope data on carbon and nitrogen from diamonds and on sulfur and oxygen from mineral inclusions found in diamonds.

CARBON ISOTOPES IN DIAMONDS

Carbon has two stable isotopes, ¹²C and ¹³C, with abundances of 98.9% and 1.1%, respectively. The ¹³C/¹²C ratio of most terrestrial samples varies little, from ~0.010956 to

~0.011237. ¹³C/¹²C ratios are expressed in terms of how they deviate in ‰ (parts per thousand) relative to the Pee Dee Belemnite, an internationally accepted standard (see glossary p. 70).

Carbon isotopic compositions are available from more than four thousand diamonds worldwide. Major sources include Siberia, Canada, Australia, Brazil, and West, East, and southern Africa (Botswana and South Africa). Data are also available from (1) impact-diamonds grown at high temperatures over an extremely short time period, (2) metamorphic diamonds formed within crustal rocks buried at high pressure and temperature along subduction/collision zones (Ogasawara this issue), and (3) diamond types that are less well understood, e.g., carbonados (Heaney et al. this issue).

Variation in Carbon Isotopes

The distribution of δ¹³C values in diamonds formed in Earth's mantle (FIG. 2A) can be divided into distinct populations on the basis of the mineralogy and chemistry of inclusions of silicate minerals. These are usually about 200 μm in maximum dimension and define two principal groups referred to as 'peridotitic' or P-type and 'eclogitic' or E-type. The P-type reflects the mineral assemblage of a peridotite, a four-phase assemblage of olivine, enstatite, garnet, and clinopyroxene. The E-type is related to eclogite, a rarer rock consisting principally of garnet and clinopyroxene. Sulfides are also common as inclusions and have P- or E-type affinities. Peridotitic and eclogitic diamonds can

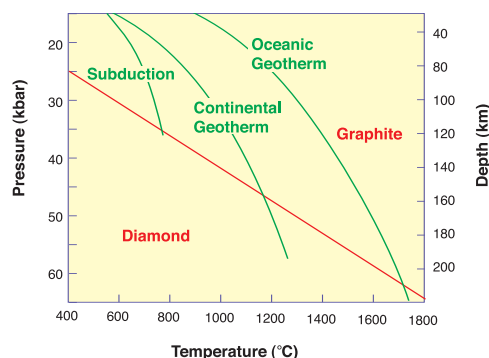


FIGURE 1 P-T phase diagram for elemental carbon. The different geotherms illustrate that diamond is stable in continental settings at pressures of ~45 kbar (corresponding to depths of 150 km) and in oceanic settings at ~60 kbar. In subduction zones, as illustrated here by a 'warm' subduction gradient, diamond is stable at lower pressures (~35 kbar). With a steeper geothermal gradient (not shown), diamond is stable at pressures of ~30 kbar (i.e., 100 km depth).

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have diamond overgrowths, and these are usually referred to as fibrous, cubic, or coated diamond. Hereafter, such overgrowths will be referred to as “coated/fibrous diamonds”. They may be related to kimberlite magmatism (Boyd et al. 1994) and record the date of kimberlite emplacement (less than 350 Ma ago), making them genetically different from their cores, which vary in age from 1 to 3 Ga (Shirey et al. 2002).

While most macrocryst diamonds sampled by kimberlites and related rocks originate from the base of ancient lithosphere known as cratons (~100–250 km depth), they can also form at much greater depths including Earth’s lower mantle (≥ 660 km depth) (see Stachel et al. this issue). Over the depth range of 330 to 660 km, macrocryst diamonds belong mostly to the eclogitic growth environment, as indicated by the present eclogite/peridotite abundance ratio of about 8 to 1 (Stachel et al. this issue).

Worldwide diamonds have a carbon isotopic composition ($\delta^{13}\text{C}$) ranging from -38.5 to $+5.0$ ‰ (FIG. 2A). Of these, approximately 72% are contained within a narrow interval between -8 and -2 ‰, which is within the range of mantle values. The distribution is continuous, with a clear decrease in frequency on either side of a peak $\delta^{13}\text{C}$ value of about -5 ± 1 ‰.

The $\delta^{13}\text{C}$ distributions of the two principal diamond types are significantly different (Sobolev et al. 1979). P-type diamonds (FIG. 2B) exhibit a narrower range of $\delta^{13}\text{C}$ values (from -26.4 to $+0.2$ ‰) than E-type (FIG. 2C) (from -38.5 to $+2.7$ ‰), while both fibrous/coated (FIG. 2D) and lower-mantle diamonds (FIG. 2E) show narrow ranges of values: -8.1 to -4.9 ‰ and -8.5 to -0.5 ‰, respectively. A much greater proportion of E-type diamonds than P-type diamonds (34 and 2%, respectively) have very negative $\delta^{13}\text{C}$ values (defined here as < -10 ‰). $\delta^{13}\text{C}$ values for diamond formed in crustal rocks—represented by microdiamonds formed in subducted metamorphic rocks—range from -30 to -3 ‰ (FIG. 2F). See FIG. 1 in Heaney et al., this issue, for $\delta^{13}\text{C}$ data from impact-related diamonds ($\delta^{13}\text{C}$ from -22 to -8 ‰) and carbonados ($\delta^{13}\text{C}$ from -32 to -25 ‰). Sedimentary carbon is divided between a concentration near 0‰ and a scatter of light values between about -40 and -15 ‰ (average about -25 ‰, FIG. 2G).

The distributions shown in figures 2a to 2d are based on diamond analyses from worldwide kimberlites, lamproites, and their placer deposits. A comparison of the carbon isotope values from individual localities, using the example of Venetia, South Africa (FIG. 3A) shows that more than 90% of individual locations have a similar range and distribution of values. However, there are several striking exceptions. Diamonds from the Guaniamo kimberlites (Venezuela, FIG. 3B), from the Argyle lamproite (western Australia, FIG. 3C), and from the New South Wales placer deposits (eastern Australia, FIG. 3D) show $\delta^{13}\text{C}$ distributions for eclogitic diamonds centered at approximately -15 ‰, -11 ‰, and $+2$ ‰, respectively. Rare peridotitic diamonds analyzed so far from these sources show typical mantle $\delta^{13}\text{C}$ values of about -5 ‰. In addition, locations such as Orapa (Botswana) and Jagersfontein (South Africa) (FIG. 3E) show a strong E-type, bimodal $\delta^{13}\text{C}$ distribution with a peak at about -5 ‰ and another at about -20 ‰. For both sources, the $\delta^{13}\text{C}$ range for P- and E-type diamonds is nearly identical.

Intradiamond Variability

Intradiamond carbon isotope variability is studied by comparing results of the combustion of several fragments from a single stone. Such a method detects $\delta^{13}\text{C}$ zonation only on a scale of up to 1 mm and will not detect any oscillato-

ry zonation on a scale of 10–100 μm . Although large $\delta^{13}\text{C}$ variations of up to 15‰ have been measured within a single diamond, most stones show little $\delta^{13}\text{C}$ variability across growth zones, more than 95% of analyses varying by less than 3‰. When large variations are found, they usually correspond to distinct growth episodes such as the formation of a coat over a pre-existing diamond core.

Within the small range of internal $\delta^{13}\text{C}$ variations, no systematic trend of increasing or decreasing $\delta^{13}\text{C}$ values from core to rim is recorded for either E- or P-type diamonds. Within the coats of fibrous/coated diamonds, a systematic trend of increasing $\delta^{13}\text{C}$ values (from -8 to -5 ‰) from core to rim has been detected (Boyd et al. 1994). Sufficiently detailed data are not available from which to determine the scale of $\delta^{13}\text{C}$ variability in diamonds formed in the lower mantle or other environments (see above).

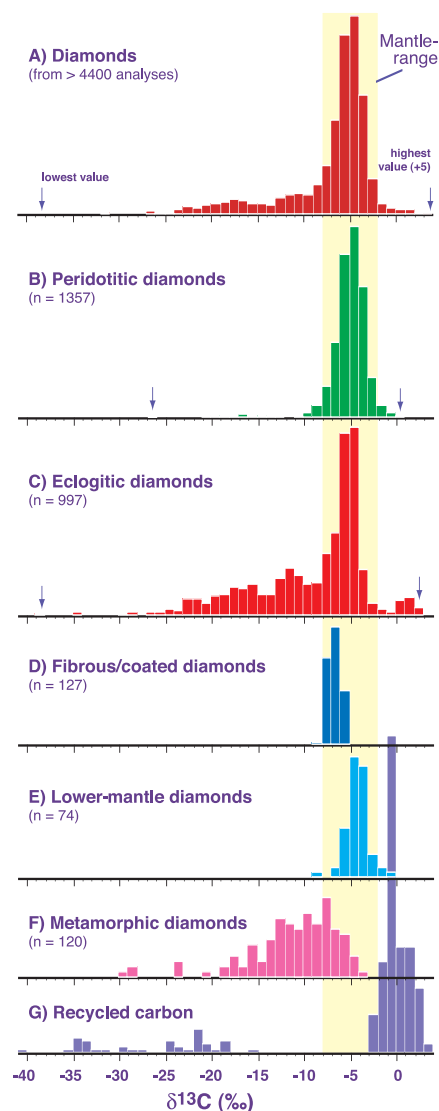


FIGURE 2 Comparative histograms of $\delta^{13}\text{C}$ values for (A) worldwide diamonds of known and unknown paragenesis, (B) peridotitic diamonds, (C) eclogitic diamonds, (D) fibrous/coated diamonds, (E) diamonds from the lower mantle, (F) metamorphic diamonds, and (G) sedimentary carbon represented by carbonates and organic matter. The mantle range (vertical yellow band) defined by the study of mid-ocean ridge basalts, carbonatites, and kimberlites is also indicated. For A to C, each diamond locality has been weighted, because more than 10% of all published data on eclogitic diamonds are from Argyle, and without weighting these data would cause a false second peak at about 11‰ in B.

Origin of Carbon Variability

Carbon isotope data combined with the study of inclusions in diamonds have led to the emergence of three main models to explain the variability of carbon isotope compositions.

Model 1 – Distinct carbon sources: Low $\delta^{13}\text{C}$ values within some eclogitic diamonds led many scientists to suggest that such diamonds formed from distinct carbon sources, unlike their peridotitic counterparts (Kirkley et al. 1991). This model suggests that eclogitic diamonds are derived from sedimentary carbon recycled into the mantle via subduction zones, whereas peridotitic diamonds formed from mantle-derived carbon. Metasedimentary carbon consists of mixtures of organic matter and carbonates with end member $\delta^{13}\text{C}$ values averaging -25 ‰ and 0‰, respectively

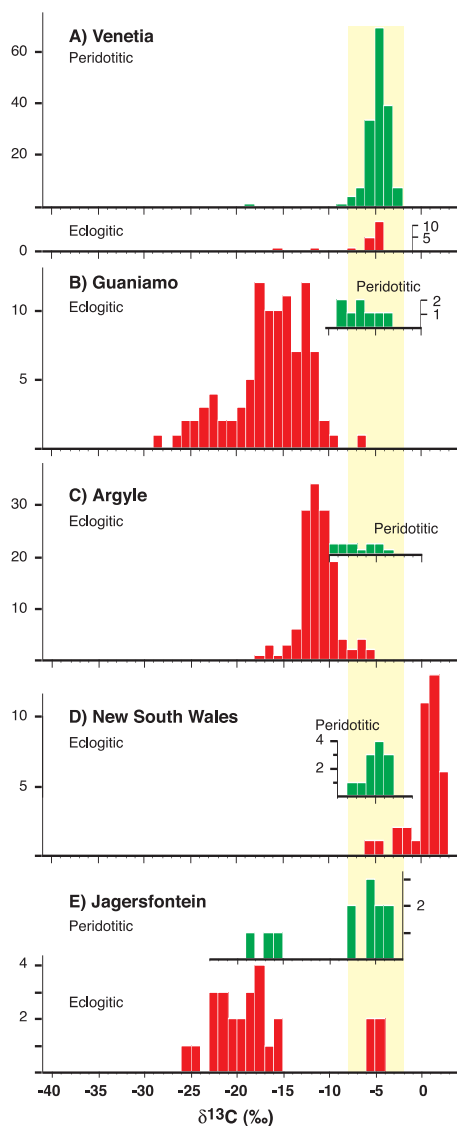


FIGURE 3 Comparative histograms of $\delta^{13}\text{C}$ values for diamonds from individual localities. (A) Venetia (South Africa) represents a typical locality, while (B) Guaniamo (Venezuela), (C) Argyle (Australia), (D) New South Wales (Australia), and (E) Jagersfontein (South Africa) are atypical localities. Vertical axis is number of diamonds.

During subduction, the carbon isotope compositions of organic matter and carbonates re-equilibrate as temperature increases, the fractionation factor for $\delta^{13}\text{C}_{\text{carbonate}} - \delta^{13}\text{C}_{\text{graphite}}$ being $4.5 \pm 1.5\text{‰}$ at 700°C (Satish-Kumar et al. 2002). Thus the isotopic compositions of metasediments will be homogenized if they maintain chemical connectivity, and extreme variability should not be present within the diamond stability field. A comparison of true metamorphic diamonds (formed in crustal rocks) with eclogitic diamonds (cf. Figs. 2c and 2f) shows some general similarities in their $\delta^{13}\text{C}$ range, but the $\delta^{13}\text{C}$ distributions differ principally because there is a near-complete absence of $\delta^{13}\text{C}$ values around -5‰ for metamorphic diamonds.

Model 2 – Primordial isotopic variability: A statistical analysis of carbon isotopes in diamond with respect to diamond shape, size, color, nitrogen content and speciation, type and chemical composition of the mineral inclusions, and the occurrence of plastic deformation led to the unambiguous conclusion that a single kimberlite can sample sev-

(FIG. 2G), values which have remained fairly constant through geological time. From the present data, about 54% of E-type diamonds have $\delta^{13}\text{C}$ values of about $-5 \pm 3\text{‰}$. If these diamonds were the product of recycled carbon, mass-balance considerations indicate the need to recycle a mixture composed of 20% organic matter (average $\delta^{13}\text{C}$ value of about -25‰) and 80% of carbonates (average $\delta^{13}\text{C}$ value of about 0‰) (FIG. 2G). One would accordingly expect a majority of E-type diamonds with $\delta^{13}\text{C}$ values between -5 and 0‰ , in contrast to the observation that most eclogitic diamonds have a $\delta^{13}\text{C}$ range between -5 and -25‰ (FIG. 2C). Thus the $\delta^{13}\text{C}$ distribution produced by mixing carbonate and organic matter does not match that of eclogitic diamond. High $\delta^{13}\text{C}$ values (i.e., $1 \pm 2\text{‰}$) are actually extremely rare among macrodiamonds and are largely restricted to the alluvial diamonds from New South Wales.

eral diamond subpopulations (Deines et al. 1993). As these distinct diamond subpopulations are not related by any of the above criteria, the authors suggested that the observed isotopic heterogeneity was primordial, acquired during Earth's accretion and not homogenized by mantle convection. This model would be supported, for instance, by the $\delta^{13}\text{C}$ range defined by carbon in meteorites, which is indeed broadly similar to that of eclogitic diamonds (Deines 1980).

The preservation of primordial carbon isotope heterogeneity in Earth's mantle, however, is not supported by data from other fields of mantle isotope geochemistry, which show almost no evidence for preservation of primitive mantle compositions. In addition, methods used to identify diamond subpopulations are not robust. Identification by morphological features such as shape, color, size, and plastic deformation often associates primary and postgrowth diamond formation features (Harris 1992). Defining diamond subpopulations according to the chemical composition (or nature) of mineral inclusion(s) implicitly assumes fixed chemical compositions but fails to account for multiple inclusions from a single diamond spanning almost the entire known range of chemical compositions (e.g., Sobolev et al. 1998). Nitrogen contents have been assumed to reflect the diamond growth environment (high/low nitrogen contents within the diamond being derived from nitrogen rich/poor parts of the mantle), although other processes, such as growth rate, may control the incorporation of nitrogen into the crystal structure.

Model 3 – Fractionation of stable isotopes at mantle temperatures:

A unique property of stable isotopes is that coexisting compounds in equilibrium will display distinct stable isotopic compositions. This fractionation depends chiefly on temperature and the phases involved. For temperatures of 1000°C , the carbon isotope fractionation between coexisting C-bearing species is small—less than 4‰ (Bottinga 1969). However, the formation of carbon-bearing species in an open system, where minute amounts of material are removed continuously under conditions of a constant fractionation factor, can lead to very significant $\delta^{13}\text{C}$ ranges, in some cases in excess of 40‰ . For example, the $\delta^{13}\text{C}$ compositions of carbonates from a peridotite xenolith spanned a range from -5‰ to $+24\text{‰}$ (Deines 1968). As the most positive $\delta^{13}\text{C}$ values are higher than metasedimentary carbon in this example, mixing involving metasedimentary carbon can be ruled out to explain the isotopically heavy end-member. Such $\delta^{13}\text{C}$ variations are best explained by the precipitation of carbonates from CO_2 .

Although the range of $\delta^{13}\text{C}$ produced by isotopic fractionation in an open system can be large, the mode(s) and the shape(s) of the resulting distribution(s) are not random. A step towards identifying the composition of the C-bearing phase(s) (e.g., CO_2 , carbonate, methane, carbide) in the diamond growth medium/media is to examine the $\delta^{13}\text{C}$ distribution(s) for diamond (Deines 1980). As an example, FIGURE 4 shows the model $\delta^{13}\text{C}$ frequency distributions produced by fractionally precipitating diamond from CO_2 and methane. The worldwide diamond $\delta^{13}\text{C}$ compositions (FIG. 2a) are actually compatible with such an open-system fractionation process in which diamonds grow from different gaseous species. It has therefore been suggested that both eclogitic and peridotitic diamonds precipitated from mantle-derived carbon with an initial $\delta^{13}\text{C}$ value of about -5‰ (Javoy et al. 1986; Galimov 1991). The main strength of this model is that it accounts for the strong overlap of both eclogitic and peridotitic diamonds in the $\delta^{13}\text{C}$ range of -8 to -2‰ .

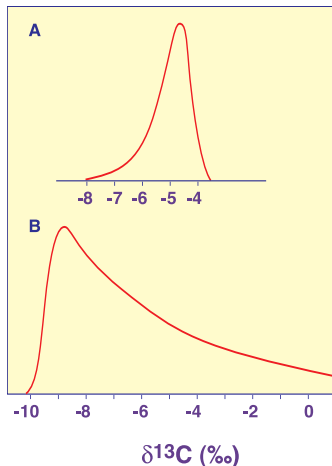


FIGURE 4 The $\delta^{13}\text{C}$ distribution produced by the precipitation of diamond from (A) CO_2 and (B) methane (modified from Deines 1980). In both cases, the initial $\delta^{13}\text{C}$ value was -5‰ .

ADDITIONAL TRACERS

Because the isotopic compositions of mantle-derived and metasedimentary carbon overlap, carbon isotopes alone will not resolve the origin of diamond. An alternative approach consists of analyzing major and trace elements (Stachel et al. 2004) and radiogenic and stable isotopes of inclusions in diamond. Radiogenic isotopes have been used to decipher the history of diamond formation in the mantle, in particular to demonstrate the Archean to Proterozoic formation age of most peridotitic and eclogitic diamonds (Shirey et al. 2002). The oxygen and sulfur isotopes of silicate and sulfide inclusions are described in the present article.

A second approach consists of analyzing the elements trapped within the diamond matrix. More than 80 elements have been detected in the crystal structure of diamonds, of which nitrogen, boron, oxygen, and hydrogen (ppm levels) are the most abundant. Nitrogen, the main impurity in diamond (Kaiser and Bond 1959), is the only element that has been systematically studied.

Oxygen and Sulfur Isotopes

For both oxygen and sulfur isotopes, Earth's mantle is assumed to be homogeneous with $\delta^{18}\text{O}$ values from $+5$ to $+6\text{‰}$ relative to SMOW and $\delta^{34}\text{S}$ from -1 to $+1\text{‰}$ relative to CDT (see glossary p. 70). In contrast, the igneous oceanic crust, altered by seawater and including accompanying sediments, shows values deviating greatly from the mantle range. Fairly limited oxygen and sulfur isotope data are currently available from silicate (less than 20 analyses) and sulfide (less than 50 analyses) inclusions in diamond. The $\delta^{18}\text{O}$ values (from $+4$ to $+16\text{‰}$) and $\delta^{34}\text{S}$ (from -11 to $+14\text{‰}$) (Fig. 5) obtained respectively from silicate and sulfide eclogitic inclusions clearly fall outside the mantle range, and such evidence has been taken to support a subduction-related origin (Chaussidon et al. 1987; Lowry et al. 1999; Taylor and Anand 2004). In addition, the identification of mass-independent fractionation of sulfur isotopes ($\delta^{33}\text{S} \neq 0.5 \times \delta^{34}\text{S}$) within eclogitic sulfide inclusions in diamonds (Farquhar et al. 2002) is key evidence that eclogite and eclogitic inclusions in diamonds are fragments of subducted Archean oceanic crust. This is because, on Earth, mass-independent fractionations were produced only in the anoxic Archean atmosphere. Thus, oxygen and sulfur isotopes data from inclusions in diamonds link them to subducted oceanic crust. Whether oxygen and sulfur iso-

tope data can be used to constrain the source of the carbon from which the diamonds formed relies heavily on the assumption that the carbon in diamond came from the same source as the hosting eclogite.

Nitrogen Content and Isotopic Composition

In diamonds, nitrogen present within the crystal structure substitutes for, and is strongly bonded to, carbon atoms. Nitrogen concentrations in diamonds range widely, from traces up to 3500 ppm, and average ~ 200 ppm and ~ 300 ppm in peridotitic and eclogitic diamonds, respectively (Figs. 6A and 6B, Deines et al. 1993). In contrast to an early suggestion from Dyer et al. (1965) that 98% of all diamonds would be nitrogen bearing (i.e., Type I), a survey of recent publications

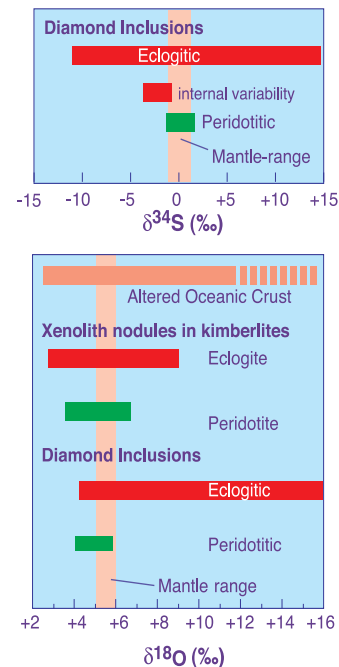


FIGURE 5 Ranges of $\delta^{34}\text{S}$ and $\delta^{18}\text{O}$ values measured from sulfide and silicate inclusions in diamonds. The mantle ranges, as defined by mid-ocean ridge basalts, are indicated for comparison. The range of $\delta^{18}\text{O}$ values for eclogite and peridotite xenolith nodules from kimberlites are also shown.

shows that, in the investigated size of crystals (~ 2 to ~ 4 mm, i.e. <0.02 carat), a value of $\sim 70\%$ is more appropriate. Diamonds of different types show distinctly different N contents. Fibrous/coated diamonds have, on average, high N contents, while those from the lower mantle (not shown in Fig. 6) include a high proportion of diamonds with low N contents (Type II; <20 ppm). Metamorphic diamonds (Fig. 6b) are unique in their range of very high N contents. The distributions of nitrogen contents shown in Figures 6a and 6c are representative of diamonds from most kimberlite occurrences, with only subtle differences in the abundance of Type II diamonds and average N contents.

Within a single diamond growth zone, sharp variations or oscillations of more than several hundred ppm of nitrogen are readily identified between layers using Fourier-transform infrared or cathodoluminescence mapping (Mendelsohn and Milledge 1995; Harte et al. 1999). Such abrupt changes or oscillations probably reflect changing growth conditions. Their preservation over billions of years of storage in the mantle demonstrates that nitrogen cannot diffuse out of the crystal structure—the observed distance of diffusion is about $30 \mu\text{m}$. Recent experiments by Koga et al. (2003) further support this premise.

Nitrogen has two stable isotopes, ^{14}N and ^{15}N ($\sim 99.6\%$ and $\sim 0.4\%$, respectively). Unlike C isotopes, upper mantle-derived samples and (meta)sediments show distinct isotopic signatures for nitrogen. Nitrogen in sediments is present as ammonium ions. Because of similarities in charge and ionic radius, nitrogen follows potassium and enters potassic minerals such as illite, smectite, and phengite (the first two minerals being clays, the last a mica). Most sediments show positive $\delta^{15}\text{N}$ values, with an average of about $+6\text{‰}$ relative to air. With increasing metamorphism, devolatilization leads to a decrease in N content and relative enrichment in ^{15}N (Haendel et al. 1986). Accordingly,

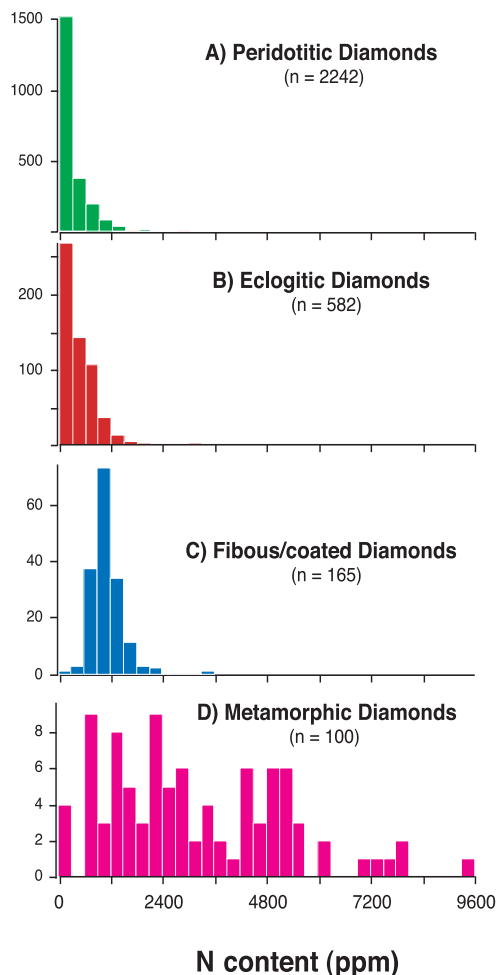


FIGURE 6 Comparative histograms of nitrogen contents of diamonds. Lower-mantle diamonds, usually with N contents less than 50 ppm, are not shown here.

metasedimentary nitrogen is characterized by $\delta^{15}\text{N}$ values that are invariably positive (Fig. 7A), from the Archean to recent geological periods.

The isotopic composition of nitrogen in the upper mantle has been estimated from the study of fibrous/coated diamonds, mid-ocean ridge basalts, and diamonds associated with peridotite (Figs. 7C to 7E). The $\delta^{15}\text{N}$ values for these samples are spread over a large range, from -25‰ to $+15\text{‰}$, with most values being negative ($\sim 65\text{‰}$) and centered around $-5 \pm 3\text{‰}$. Because of the relative ^{15}N enrichment during subduction, we would expect to find positive $\delta^{15}\text{N}$ values in eclogitic diamonds if they were formed solely from crustal carbon and nitrogen. In support of this statement, metamorphic diamonds show $\delta^{15}\text{N}$ values from -1.8 to $+12.4\text{‰}$ (Fig. 7B). However, $\delta^{15}\text{N}$ values for eclogitic diamonds are mostly ($\sim 70\%$) negative (Fig. 7F). Furthermore, about half of the eclogitic diamonds with low $\delta^{13}\text{C}$ values also show negative $\delta^{15}\text{N}$ values. While Figure 7 is a compilation of worldwide nitrogen isotope data, eclogitic and peridotitic diamonds from a single kimberlite often show striking similarities in range and distribution of $\delta^{15}\text{N}$ values. Distinct carbon sources for eclogitic and peridotitic diamonds are therefore not supported by nitrogen isotope systematics. On the basis of the average negative $\delta^{15}\text{N}$ values (Fig. 7F), the carbon comprising most eclogitic and

peridotitic diamonds is mantle-derived rather than subduction-related.

In light of the $\delta^{13}\text{C}$ and $\delta^{15}\text{N}$ data, a variation to Model 1, above, would involve mixing of mantle-derived carbon with subduction-related organic carbon (Navon 1999). Subducted organic carbon should produce diamond with low $\delta^{13}\text{C}$ values, whereas mantle carbon should grow diamond (separate, overgrowth, or via mixing) with higher $\delta^{13}\text{C}$ values, approaching -5‰ . Given the high nitrogen contents of metamorphic diamonds, an enrichment in nitrogen with decreasing $\delta^{13}\text{C}$ might be expected. However, both eclogitic and peridotitic diamonds show the opposite trend of decreasing N contents with decreasing $\delta^{13}\text{C}$ values (not shown). Also, metamorphic diamonds are not as depleted in ^{13}C as some eclogitic diamonds, and this model would predict some overlap. Thus, C and N isotopes data do not provide evidence of a connection between subduction-related carbon and E-type diamonds.

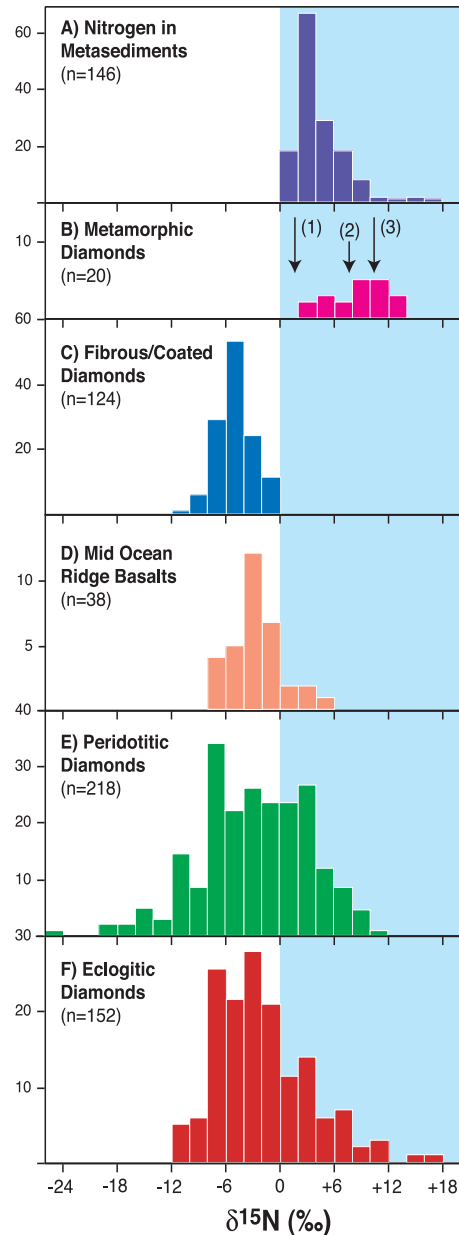


FIGURE 7 Comparative histograms of $\delta^{15}\text{N}$ values for (A) metasedimentary nitrogen; (B) metamorphic diamonds from Akluilák (Canada); the three arrows represent the mean values for metamorphic diamonds from three different areas in the Kokchetav massif (Kazakhstan) (see Ogasawara this issue); (C) fibrous/coated diamonds; (D) mid-ocean ridge basalts (E) peridotitic diamonds; and (F) eclogitic diamonds.

METASOMATIC DIAMOND FORMATION IN EARTH'S MANTLE

The evidence provided by S and O isotopes, on the one hand, and by C and N isotopes, on the other, can be reconciled if diamonds grew from external carbon and nitrogen introduced into eclogites and peridotites through a metasomatic process—that is, one in which a new mineral grows from or by reacting with a fluid permeating a mineral aggregate.

Evidence supporting a metasomatic process includes (1) 3D X-ray tomographic imaging of eclogite nodules (Schulze et al. 1996), showing that diamonds are confined to metasomatic veins; (2) trace-element analysis of inclusions in diamonds (Stachel et al. 2004); (3) fluid(s) trapped during

fibrous/coated diamond growth (Navon 1999); and (4) the presence of metasomatic inclusions within diamonds (Loest et al. 2003). These studies demonstrate that carbonate-bearing melt/fluid(s) are involved in diamond crystallization.

With metasomatic growth of diamond, both eclogitic and peridotitic types can be derived from the same carbon source, which was initially homogenous isotopically (i.e., no need to call for multiple, isotopically distinct sources) and mantle derived (with $\delta^{13}\text{C}$ values of about -5%). In the simplest scenario, isotopic fractionation associated with diamond crystallization is not significant because it cannot be the main process responsible for the distinct distributions shown in Figures 2b and 2c. The distinct distributions are produced before diamond formation, diamond being a *passive recorder* of the event(s). The carbon precursors are likely to have been carbonates, and as decarbonation reactions are known to be restricted to eclogitic mineral assemblages (Luth 1993), the escape of CO_2 enriched in ^{13}C

would leave a ^{13}C -depleted residue from which eclogitic diamonds can subsequently crystallize (Cartigny et al. 1998). In conclusion, the varied isotopic compositions of carbon in mantle-derived diamonds may reflect, in part, distinct carbon sources, but mineral-fluid reactions controlled by the mineral assemblages of the rocks in which the diamonds formed are probably the most important factor involved in producing the observed isotopic variations.

ACKNOWLEDGMENTS

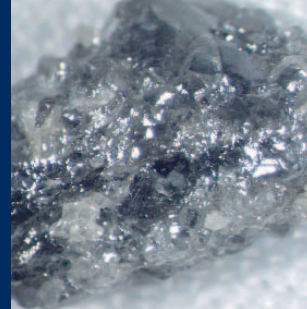
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Strange Diamonds: The Mysterious Origins of Carbonado and Framesite

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Polycrystalline aggregates of diamond called carbonado and framesite have excited the attention of scientists because their crystallization histories are thought to depart markedly from established modes of diamond genesis. In contrast to kimberlitic diamonds, the geochemical signatures of carbonados are systematically crustal. Since the apparent age of carbonados is Archean (~3.2 Ga), a number of exotic formation theories have been invoked, including metamorphism of the earliest subducted lithosphere, radioactive transformation of mantle hydrocarbon, and meteorite impact on concentrated biomass. Unlike carbonados, framesites are known to originate in the mantle. They appear to have crystallized very rapidly, shortly before the eruption of the kimberlites that brought them to Earth's surface, suggesting that old cratonic materials can be remobilized after long-term storage in the lithosphere.

KEYWORDS: carbonado, framesite, polycrystalline diamond

INTRODUCTION

Most people who like diamonds like them large. Nevertheless, a small cadre of geochemists and mineralogists has focused its efforts on diamondiferous grunge—the black multigranular masses of uncertain pedigree that fall below even the basest standards of the Gemological Institute of America grading scales. Generically called bort, these diamonds have earned some measure of respect not as gems but as the best abrasives for jobs that require superhardness and supertoughness (Feenstra 1985). Single-crystal diamonds cleave so easily that they wear rapidly during drilling applications, and inclusions can explode a single-diamond host when heated. In contrast, the high densities of grain boundaries in polycrystalline diamonds (PCD) impede fracture propagation, and the porosity in natural PCD allows for thermal expansion of included mineral grains without catastrophic failure of the entire compact.

The taxonomy for polycrystalline diamond tends to be based on qualitative external characteristics, as the names are of a cultural rather than scientific origin. Consequently, even the modern literature is inconsistent in its application of the terminology. In this review, “carbonado” refers specifically to multigranular diamond aggregates from the Central African Republic and Brazil with distinctive properties (summarized in TABLE 1 and FIG. 1). “Framesite” is used more broadly to describe clusters of randomly oriented

microcrystalline diamonds found in association with kimberlites all over the world. The unusual physical features observed in carbonados and framesites have provoked a wide array of hypotheses regarding their origin. This article will focus on the chemical and structural properties that unite and divide these two puzzling diamond varieties.

CARBONADO

Mineralogical Characteristics

Carbonado nodules typically are pea-sized or greater. Indeed, the largest known diamond of any

type is the Carbonado of Sergio (Brazil), weighing in at 3,167 carats. Named for the Portuguese word for “burned,” carbonados are black polycrystalline masses. As with framesite, carbonado nodules often exhibit a “microporphyritic” texture in which euhedral crystals measuring hundreds of microns across are cemented by a matrix of micron-sized grains (Fettge and Sturges 1932). In contrast to framesites, however, X-ray microtomography reveals pervasive macro-porosity with tunnel sizes in excess of 1 mm (Vicenzi et al. 2003).

Haggerty (1999) has described carbonados as “the most enigmatic of all diamonds,” and the number of scenarios proposed for their formation would seem to support this claim. Unlike framesites, carbonados have never been found in direct association with kimberlite pipes, raising the possibility that the Earth's mantle was not their ultimate source. Although carbonados have been reported from Venezuela (Kerr et al. 1948) and various Russian localities (e.g., Gorshkov et al. 1996), carbonados *sensu stricto* are found in Mid-Proterozoic (1–1.5 Ga) metaconglomerates overlying the São Francisco and Congo-Kasai cratons in Brazil and the Central African Republic, respectively. The São Francisco craton contains the oldest rocks in South America, at least ~3.2 Ga (Martin et al. 1997; Magee 2001), and the great age of carbonado is part of its fascination. Both bulk and in situ analyses of radiogenic lead isotope compositions of carbonado diamond and its inclusions indicate that crystallization occurred between 2.6 and 3.8 Ga ago (Ozima and Tatsumoto 1997; Sano et al. 2002).

Carbonados are distinguished from other polycrystalline diamonds by the inclusions that line pore spaces (Trueb and Buttermann 1969; Trueb and deWys 1969, 1971; Dismukes et al. 1988). The hydrated rare-earth phosphate florencite is the most abundant of these, but over 30 other

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TABLE 1

COMPARISON OF CARBONADO, FRAMESITE, AND ECLOGITIC SINGLE-CRYSTAL DIAMOND.

	Carbonado	Framesite	Single-Crystal Eclogitic Diamond
Color and Surface Properties	Black, dark gray, or brown with smooth exterior	Light gray or brown with irregular surface	Clear to yellow single crystals are most common
Grain Sizes	Euhedral grains (Typically up to 200 μm) set in microcrystalline matrix (<0.5–20 μm)	Shares bimodal texture with carbonado but euhedral grains are larger	Variable, but mm-sized and larger crystals are common
Porosity	High (10% void space)	Low (1% void space)	Zero
Common Inclusions	Florencite-goyazite-gorceixite, xenotime, kaolinite, quartz, orthoclase, zircon, Fe, Fe-Ni, SiC, Si, Sn	Pyrope and almandine-pyrope garnet, Cr-rich clinopyroxene, chromite	Pyrrhotite, omphacite, almandine-pyrope garnet
$\delta^{13}\text{C}$ Composition	-23 to -30‰ with a mode at -27‰	-1 to -24‰ with a mode at -19‰	+3 to -34‰ with modes at -5‰ and -12‰
$\delta^{15}\text{N}$ Composition	-17 to +8‰	-3 to +15‰	-12 to +5‰

minerals have been identified, including orthoclase, quartz, and kaolinite. These phases are distinctly crustal, and, conversely, the mantle-derived inclusions commonly found in kimberlitic diamond (e.g., pyrope-rich garnet, chromian clinopyroxene, pyrrhotite) have never been reported from carbonado. The TEM results of Gorshkov et al. (1996) and De et al. (1998) also have revealed inclusions of native metals and metal alloys, such as Fe, Fe-Ni, Ni-Pt, Si, Ti, Sn, Ag, Cu, and SiC. These metal phases are nanometers to hundreds of microns in size, and they can be either enveloped within the diamond itself or present as a coating of the pores. Gorshkov et al. (1999) describe similar metal assemblages in kimberlitic polycrystalline diamonds from the Udachnaya pipe in Yakutia.

Geochemical Indicators for Formation

The similarities in the inclusion assemblages of carbonados from the Central African Republic and Brazil provide strong evidence that these now geographically distant carbonados are genetically related. Equally compelling support for a common origin comes from the tight clustering of carbon isotope compositions of nodules from the two localities, with $\delta^{13}\text{C}$ values ranging from -21 to -32‰ (Vinogradov et al. 1966; Galimov et al. 1985; Ozima et al. 1991; Kamioka et al. 1996; Shelkov et al. 1997) (Fig. 1). In situ isotope analyses (De et al. 2001) have shown that within individual samples, $\delta^{13}\text{C}$ values are very uniform, with a slight bimodality between the larger euhedral crystals (-26‰) and the finer-grained matrix (-24‰). Further confirmation for a connection between Central African and Brazilian carbonados is provided by noble gas analyses (Ozima et al. 1991; Burgess et al. 1998), which show that carbonados from both provenances contain high concentrations of implanted, radiogenic noble gases arising from ^{238}U fission. They also exhibit high contents of tightly trapped atmospheric gases.

Evidence that would serve as a "smoking gun" for the origin of carbonado is frustratingly elusive, and the ambiguity surrounding the role of mantle versus crustal processes in the forging of carbonados is even more pronounced than in

the case of framesites, as described below. It is possible that carbonados are merely composite diamond clusters that formed in the same way as kimberlitic diamond nodules but with enrichment in light isotopes of C and He. If so, carbonados may represent the end member of a chemical continuum in which framesites serve as a bridge to eclogitic diamonds. In this scenario, the strong crustal signature in carbonados is related to the subduction of cold slabs beneath continental margins, such that organic matter is imported to the mantle with virtually no mixing of carbon reservoirs (Robinson 1978). This idea could perhaps explain light rare-earth element (LREE) patterns suggestive of a crustal origin (Shibata et al. 1993; Kamioka et al. 1996), the high concentrations of polycyclic aromatic hydrocarbons in carbonado pores (Kaminsky et al. 1991), and the presence of aggregated N defects (Nadolniny et al. 2003).

If carbonados represent mineralized organic carbon, their measured age of ~3.2 Ga, when added to the time required for plate subduction, suggests that these diamonds are vestiges of some of the oldest biological material known. Nevertheless, it should be noted that mantle xenoliths are often depleted in ^{13}C , and efforts to model the range of $\delta^{13}\text{C}$ values in these samples by simple mixing models of carbon from organic and mantle reservoirs have not succeeded (Deines 2002). Deines' study suggests that poorly understood kinetic fractionation effects may play a role in the generation of isotopically light diamonds.

The implications of the radiogenic gases in carbonados are especially controversial. Some authors have proposed that exposure of carbonados to radionuclides occurred post-eruption, so that the elevated levels of radiogenic gases are secondary (Kagi et al. 1994; Shelkov et al. 1998; Burgess et al. 1998). On the other hand, the recent observation of crustal nucleogenic Ne in framesites indicates that some parts of the mantle may contain significant quantities of crustal noble gases (Honda et al. 2004). It is possible that, in this fashion too, carbonados preserve evidence for early atmospheric chemistry and plate tectonic activity. Still another hypothesis is that the radiogenic gases reflect formation of carbonados by the transformation of a carbon-

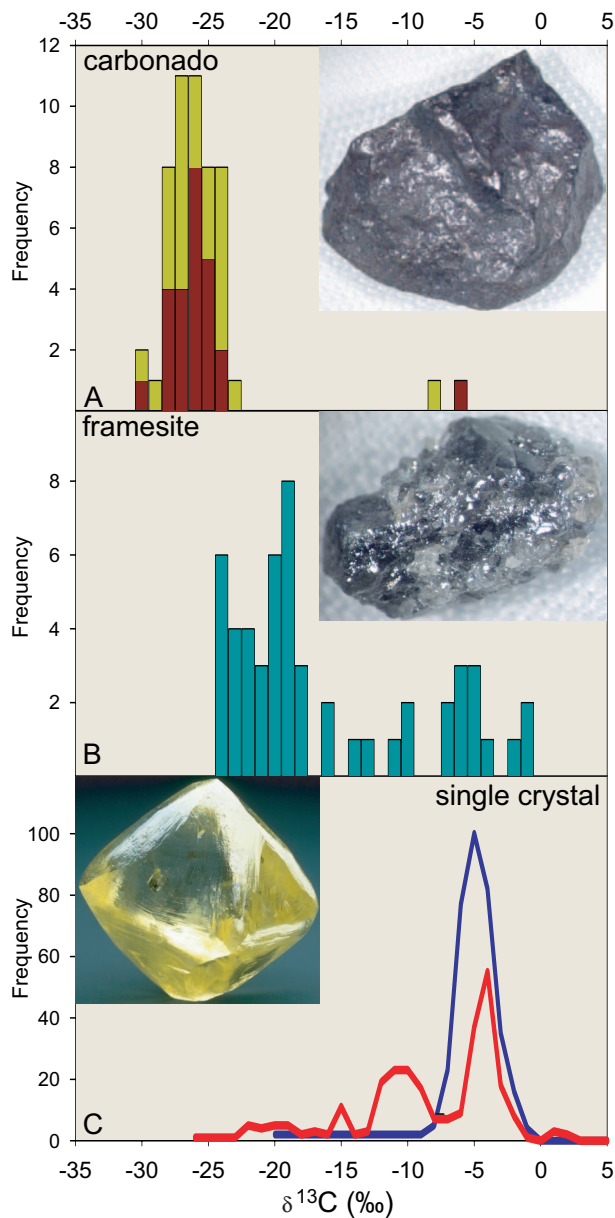


FIGURE 1 Compilation of published $\delta^{13}\text{C}$ values for (A) carbonado (avocado – Brazil; burgundy – Central African Republic); (B) framesite; and (C) monocrystalline diamonds (blue – harzburgitic; red – eclogitic). Insets: (A) carbonado specimen from Mambere River, Haute-Sangha Province, Central African Republic (15.9 mm across); (B) framesite specimen from Jwaneng, Botswana (9.0 mm across); (C) Oppenheimer diamond, Dutoitspan Mine, South Africa (38 mm across).

rich matrix to diamond through ^{238}U irradiation (Kaminsky 1987; Ozima et al. 1991; Ozima and Tatsumoto 1997). However, since natural examples of radiogenic diamonds (Daulton and Ozima 1996) do not exceed 500 nm in diameter, it seems that radiosynthesis might have provided, at most, the seeds for carbonado diamond growth.

Evidence for an Impact Origin

The nearly complete absence of a mantle fingerprint in carbonados has caused some researchers to seek a purely surficial crystallization process—a tricky proposition in light of the high pressures needed to stabilize the diamond structure. Smith and Dawson (1985) attacked this issue by invoking a meteorite impact within what was once a united landmass. The light $\delta^{13}\text{C}$ values for carbonado can then be attributed to shock metamorphism of organic matter,

and the tightly trapped atmospheric gases, crustal inclusions, high polycyclic aromatic hydrocarbon levels, and magnetic inclusions all are logical results (Girdler et al. 1992; Kletetschka et al. 2000). Moreover, pervasive defect lamellae indicative of plastic deformation have been observed in TEM studies of both Central African and Brazilian carbonados (De et al. 1998).

Despite their undeniable appeal, however, impact scenarios for carbonado formation are troublesome. Deformation lamellae have been documented in framesites (DeVries 1973) and reproduced experimentally at mantle temperatures and pressures (De et al. 2004); thus, they may not be analogs of planar deformation features in shocked quartz. Unlike the impact-generated variety of PCD known as yakutite (Kaminsky 1991; Titkov et al. 2004), carbonados have never been shown to contain the hexagonal C polymorph known as lonsdaleite or any other high-pressure phase. Shock wave calculations (DeCarli 1998) indicate that the maximum size for a diamond formed by impact is ~1 cm, and impact-generated diamonds typically are sub-millimeter in dimension (e.g., Hough et al. 1995; Pratesi et al. 2003; Ding and Veblen 2004). As their large size is one of the hallmarks of carbonados, the impact scenario is difficult to reconcile with the physical attributes of this PCD variety.

FRAMESITE

Mineralogical Characteristics

In contrast to carbonados, there is no doubt that framesites are derived from kimberlite pipes that sample Earth's deep interior. Named for P. Ross Frames, chairman of the De Beers and Premier companies in the 1920s, framesite is produced from the Premier and Venetia mines in South Africa and the Orapa and Jwaneng mines in Botswana, where it can represent several weight percent of the total diamond output. Framesites from Russian localities (e.g., the Mir pipe) are known as well (Sobolev et al. 1975). A rigorous study of the range of diamond crystal sizes in framesite is lacking, but nodules comprising black or brown, euhedral, mm-scale diamonds cemented by randomly oriented, micron-sized crystals are not uncommon.

Framesites from different pipes exhibit subtle variations in diamond textures and included assemblages in the polycrystalline mass, but several studies have revealed evidence for a mixed eclogitic and peridotitic paragenesis. Two varieties of pyrope-rich garnet inclusions typically occur. Orange garnets with low Cr and moderate Ca contents have chemistries characteristic of eclogites, and pink garnets with higher Cr and lower Ca contents are representative of harzburgite (Gurney and Boyd 1982; McCandless et al. 1989; Kirkley et al. 1991). Olivine and eclogitic clinopyroxene or omphacite are curiously absent, but garnet, orthopyroxene, and peridotitic clinopyroxene commonly intergrow with the diamond and sometimes envelop diamond crystals, suggesting that diamond and silicate crystallization were contemporaneous (Kurat and Dobosi 2000). Chromite also can be a major accessory phase in framesites, and Cr concentrations in clinopyroxenes associated with framesites from Orapa, Jwaneng, and Mir are extraordinarily high (Sobolev et al. 1975; Gurney and Boyd 1982; Kirkley et al. 1991). Where present, magnetite imparts a strong natural remanent magnetization (Collinson 1998), giving rise to a subvariety of framesite called stewartite.

Carbon isotope studies of framesites from the Venetia, Orapa, and Jwaneng pipes (Kirkley et al. 1991; Shelkov et al. 1997; Burgess et al. 1998; Jacob et al. 2000) reveal a broad distribution of $\delta^{13}\text{C}$ values ranging from -2‰ to -25‰,

with a major mode at -19‰ (Fig. 1). Moreover, noble gas analyses of framesite have yielded low $^3\text{He}/^4\text{He}$ ratios, indicating little contribution from primordial mantle-derived ^3He , and they also show high concentrations of crustal nucleogenic Ne (Burgess et al. 1998; Honda et al. 2004).

Theories of Formation

So how did framesites form? Virtually all authors attribute the fine grain size of framesites to rapid crystallization in localized areas of the mantle containing high concentrations of C and incompatible and volatile elements. Many scientists invoke subduction of ocean floor and subsequent mixing with upper mantle lithosphere as a mechanism for framesite crystallization (Kirkley et al. 1991; Burgess et al. 1998; Honda et al. 2004). This process explains the mixed eclogitic and peridotitic chemical signatures imprinted on many framesite samples, the unusual noble gas compositions measured for framesite diamonds, and possibly the broad range of $^{13}\text{C}/^{12}\text{C}$ ratios. Kirkley et al. (1991) propose that metamorphism of C from two crustal environments—one that was carbonate-rich and another that contained organics—could have generated populations of diamonds with distinct C isotope compositions.

Other researchers are less convinced of a crustal role. Kurat and Dobosi (2000) discount the importance of an eclogitic precursor and argue that framesite assemblages crystallized from upper mantle fluids containing a carbonatitic component, as suggested by trace-element profiles of garnets and of fluid inclusions in silicates. Jacob et al. (2000) also invoke a carbonatitic melt to explain trace-element, radiogenic, and stable isotope variations, but they argue that eclogitic material reacted with the melt. Moreover, these authors propose that framesites in the Venetia pipe crystal-

lized very shortly before the kimberlite erupted. If true, framesites provide surprising evidence that remobilization of material stored for long periods in the cratonic lithosphere can lead to the formation of relatively young diamonds, that is, close to the emplacement age of 533 Ma in the case of Venetia.

SUMMARY

Polycrystalline diamond varieties once were regarded as eccentric expressions of the processes that generate kimberlitic diamonds, but state-of-the-art characterization studies have rendered the origins of carbonados and framesites more ambiguous. To the extent that these different varieties of PCD formed by unrelated mechanisms, their proper classification becomes an interpretive rather than merely a taxonomical exercise. As this review illustrates, widely accepted genetic models for these diamond aggregates remain an unfulfilled challenge, particularly with regard to the roles played by mantle and crustal components. Nevertheless, enough about these diamond varieties has been discovered to be sure that they will offer some startling insights about our planet and its history.

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The eighty-fifth annual awards luncheon of the Mineralogical Society of America was held on November 9, 2004, during the 2004 Geological Society of America meeting in Denver, Colorado.



KEVIN ROSSO received the **Mineralogical Society of America Award** for outstanding research early in his research career. His research interests are the relationships between the atomic and electronic structure of mineral surfaces and their reactivity and physical properties. Citationist Michael F. Hochella Jr. (left) and MSA President Michael Carpenter (right).



The **Distinguished Public Service Award** was presented to ROBERT F. MARTIN, editor of *The Canadian Mineralogist* for 26 years. Robert Martin has done research in many areas, but was recognized this day for his work with *The Canadian Mineralogist*, one of the premier journals in the field. Citationist John M. Hughes (left), and MSA President Michael Carpenter (right).



FRANCIS R. "JOE" BOYD was awarded (posthumously) the **Roebling Medal**, the Society's highest honor, in recognition of lifetime scientific achievement. With Joseph England, he designed and developed a high-pressure, high-temperature apparatus, which has been central to the work of a generation of experimental petrologists. Boyd's initial focus was on high-pressure phase equilibria, and this work provided the basis for continued studies on the composition, structure, and history of the lithosphere and upper mantle. Elected to the National Academy of Science in 1974, Boyd also served as president of the Geochemical Society, the Geological Society of Washington, and the VGP section of the American Geophysical Union. Citationist Stephen Haggerty (left), Marguerite J. Kingston, widow of Francis R. (Joe) Boyd, and MSA President: Michael Carpenter.



Prof. YONG-FEI ZHENG, University of Science and Technology of China, Hefei, China won a **National Natural Science Award of China** for 2004. These awards recognize a series of prominent achievements in a certain field of natural science and are the highest awards for achievement in scientific research. Prof. Zheng's award is for his work on theoretical calculations and experimental measurements of oxygen isotope fractionation factors for minerals.

Julie Roberge on the Outreach Path

Julie Roberge is finishing her PhD at the University of Oregon, under the supervision of Paul Wallace and in close collaboration with Kathy Cashman. She is studying volatiles in magma and, in particular, analyzing basaltic glass from the Ontong Java plateau in order to establish the subsidence rate of the plateau. She is also studying volatiles in melt inclusions and the permeability of pumice (from which the crystals containing the melt inclusions come) from the Bishop tuff to characterize the fragmentation/degassing behavior of volcanoes. At Christmas time, while she was visiting her family in Québec, her boyfriend had contacted the local media



Julie Roberge ascending the Villarica volcano in Chile.

to tell them about her fascinating work. As a result, three regional newspapers published articles on this local girl studying far-away volcanoes and she made the first page in

one of them. The headline read "Volcanoes tattooed on her heart", and the article went on to talk about her unconditional love for volcanoes. She was also interviewed on several radio stations when Mount St. Helens started erupting again (she just happened to be doing field work nearby). Julie has been under the spell of volcanoes since she was 8 years old, but it was not until she got to university that she discovered that you could study them and actually make a living at it. She wants every child to know that fact, so whenever she gets a chance she does presentations in classrooms as well. She has set up her own web page and she gets e-mails from young people all over the world wanting to know more about volcanoes and how to become a volcanologist.

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Microdiamonds in Ultrahigh-Pressure Metamorphic Rocks

Yoshihide Ogasawara¹

Since the first report of microdiamonds of metamorphic origin in crustal rocks of the Kokchetav Massif, northern Kazakhstan, diamonds have been described from several other ultrahigh-pressure (UHP) metamorphic terranes. In situ diamond is the best indicator of ultrahigh-pressure conditions (>4 GPa), and testifies to subduction of continental crust to depths within the diamond stability field followed by relatively rapid exhumation. In contrast to other UHP terranes, the Kokchetav Massif contains rocks with unusually abundant diamonds, particularly in the Kumdy-Kol region. Kumdy-Kol diamonds exhibit diverse morphologies, dependent upon the host rock. Raman and cathodoluminescence spectra and carbon isotope compositions differ between core and rim, indicating two distinct growth stages.

KEYWORDS: microdiamond, ultrahigh-pressure metamorphism, continental collision, Kokchetav

INTRODUCTION

After the discovery of coesite in metamorphic rocks from the Dora Maira Massif, western Alps (Chopin 1984), and the Western Gneiss Region, Norway (Smith 1984), many researchers were stimulated to look for coesite and other minerals indicative of extremely high-pressure formation in metamorphic rocks. What is so interesting here? Coesite, a dense form of SiO₂, forms at ~3 GPa (900°C), equivalent to a depth of 90 km under a continent, while diamond requires ~4 GPa (1000°C), or roughly 140 km depth. These minerals would be expected in the deep Earth where sufficient silica or carbon is present, so there is nothing revolutionary in their discovery. However, up to that time it was not thought that tectonic processes could send slabs of crust down to extreme depths and, more amazingly, bring them up again quickly enough to preserve these high-pressure minerals. As discussed by Stachel et al. in this issue, most diamond found on Earth is carried to the surface by deep-rooted volcanism. The collision of fragments of Earth's crust in the dance of plate tectonics was known to return rocks such as eclogites to the surface with minerals indicating pressures of >2 GPa, but these minerals are typically overprinted by reactions that returned most minerals to lower-pressure assemblages. Preservation of high-pressure coesite and even higher pressure diamond challenged existing models of Earth processes and required a whole new paradigm as more discoveries of ultrahigh-pressure metamorphism (UHPM) were reported. The subject has taken off in the last 20 years, and many reviews are available (e.g., Rumble et al. 2003; Roselle and Engi 2002). In the present article, some of the discoveries and implications

will be reviewed, with attention to recent results from at least one occurrence pointing to multiple generations of diamond formation.

OCCURRENCES OF UHP METAMORPHIC DIAMOND

Although microdiamond was initially reported many years ago by Rozen et al. (1972) from the Kokchetav Massif, northern Kazakhstan, its metamorphic origin was accepted much later following a report by Sobolev and Shatsky (1990). Since then, additional occurrences have been discovered in the Dabie Mountains (Xu et al. 1992) and north Qaidam

(Yang et al. 2003), China; the Western Gneiss Region, Norway (Dobrzhinetskaya et al. 1995; Van Roermund et al. 2002); Erzgebirge, Germany (Massonne 1999; Stöckhert et al. 2001); Sulawesi, Indonesia (Parkinson and Katayama 1999); and perhaps the Rhodope Massif, Greece (Mposkos and Kostopoulos 2001). The Dabie and north Qaidam rocks have been dated at 230–209 Ma (Ames et al. 1996) and 510–485 (Yang et al. 2001), respectively. Peak P–T conditions of the Dabie metamorphism are considered to be around 5–6 GPa and ca. 850°C (Zhang and Liou 1998). More than 10 diamond grains have been reported as inclusions in zircon from north Qaidam (Yang et al. 2003).

Several grains of diamond were first described from residues separated from Western Gneiss Region gneisses by Dobrzhinetskaya et al. (1995) and confirmed in situ by Van Roermund et al. (2002). Peak P–T conditions for the Norwegian rocks were P >2.8 GPa and T >790°C (Carswell et al. 1999), and peak metamorphism occurred at 425–406 Ma (Griffin and Brueckner 1985). Metamorphic diamonds are far more abundant in the Erzgebirge than in other diamondiferous terranes, except for Kokchetav. Diamondiferous gneisses are restricted to a 1 km-long strip, and the diamonds are abundant as inclusions in garnet, kyanite, and zircon (Massonne 2001). Peak P–T conditions were >4.2 GPa and 900–1000°C (Massonne 2001) and occurred at 360–333 Ma (Schmadicke et al. 1995). A number of in situ diamond grains were identified by laser Raman spectroscopy within quartz pseudomorphs after coesite in garnet in jadeite quartzite of the Bantimala complex of Sulawesi, Indonesia. These rocks have yielded radiometric ages of 130–120 Ma and recrystallized at P >2.7 GPa at around 750°C (Parkinson et al. 1998).

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UHP rocks in these regions display some diversity in terms of tectonic setting. However, the commonalities are perhaps more significant—they are all restricted to collisional orogens and are predominantly of continental parentage. In general the distribution of diamond-grade rocks is restricted to considerably smaller areas than that of coesite-grade metamorphism, which is regional in extent in many UHPM terranes. Presumably, diamonds produced by subduction of carbon-bearing crust are not an unusual product of Earth processes, but their return to the planet's surface without an explosive kimberlite elevator requires special conditions. High-pressure metamorphic rocks are a characteristic feature of the “scars” of plate collisions, but UHP rocks appear to be limited to collisions of continental fragments, either full continent–continent collisions or ones involving microcontinental fragments.

Although still somewhat controversial, wedge extrusion appears to have gained widespread acceptance as a general exhumation model. It can explain the regional nature of UHP metamorphism (at least for coesite-grade metamorphism), whereas channel flow and diapiric transport provide models for exhumation of discrete, essentially “exotic” blocks. In channel flow, the subducted rocks are considered to have sufficiently low viscosity that they can be squeezed back up the subduction channel in a reverse flow (e.g., Lardeaux et al. 2001). Diapiric emplacement relies on buoyancy forces of either low-density continental material or encapsulating hydrated peridotite (serpentinite) (e.g., Burov et al. 2001) to lift the UHP blocks. Each model has its own set of criteria to test its validity, and the jockeying of the models continues.

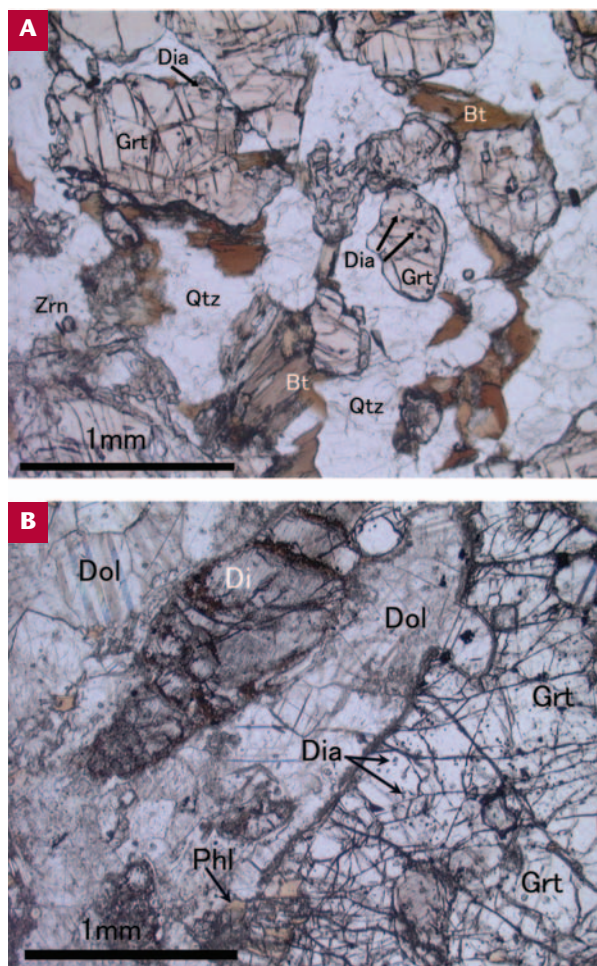


FIGURE 1 Photomicrographs (PPL) of (A) diamond-bearing garnet–biotite gneiss and (B) diamond-bearing dolomite marble at Kumdy-Kol. Qtz: quartz; Grt: garnet; Bt: biotite; Dia: diamond; Zrn: zircon; Di: diopside; Phl: phlogopite; Dol: dolomite.

Presumably, the considerable momentum of colliding continents and the pull of an attached oceanic lithosphere ‘anchor’ buries a continental edge to diamond-producing pressures. Then exhumation lifts the buried rocks some 140 km, sufficiently fast that the UHP signature is not erased by thermal relaxation associated with slow ascent. Exhumation by regional uplift and erosion alone is not rapid enough, so several models of tectonic emplacement have been suggested: wedge extrusion, channel flow, and diapiric transport. Break-off of the subducting slab during collision is argued to cause extrusion of a buoyant narrow wedge of buried UHP material by normal and thrust faulting (e.g., Ernst and Liou 1995; Hacker et al. 2000).

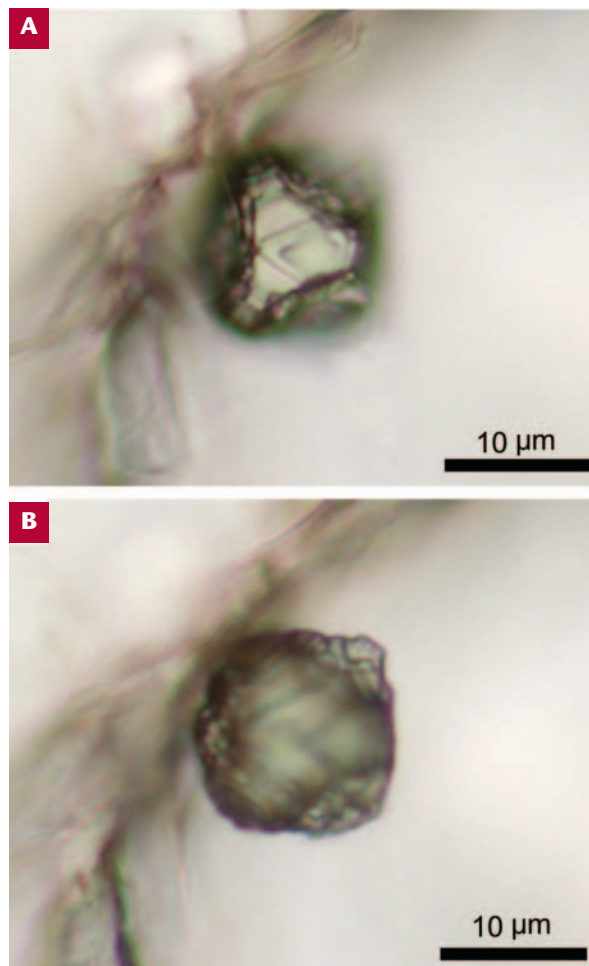


FIGURE 2 Photomicrographs (PPL) of a representative microdiamond in a garnet–biotite gneiss at different focus positions. A, B; stepped octahedral faces are visible in (A).

Among the recognized microdiamond occurrences, the Kokchetav Massif is perhaps best suited to provide sufficient data to determine the local processes and environment of formation of metamorphic diamonds because of their extremely high concentration and unequivocal in situ occurrence in UHPM rocks. For these reasons, I focus on the diamonds of Kumdy-Kol. Studies of diamonds in the dolomite marble (dominant carbonate is dolomite) there provide a keystone for understanding their “metamorphic” origin and help to resolve the debate as to whether UHPM diamond is produced by a solid-state transformation or by crystallization from a fluid or a melt.

MICRODIAMOND IN THE KOKCHETAV UHPM TERRANE

Diamond in the Kokchetav Massif is best known from the Kumdy-Kol area where it was once mined. It occurs in carbonate rock, pyroxene–garnet rock, tourmaline-rich rock, and most abundantly in garnet–biotite gneiss (FIG. 1A) and dolomite marble (FIG. 1B) (see Parkinson et al. 2002 for a review). Diamonds are included in garnet and less frequently in phlogopite (pseudomorphic after garnet), zircon, tourmaline, and diopside in the silicate and carbonate rocks. All these diamonds are very fine grained, <25 μm . Diamond with an octahedral form in garnet in garnet–biotite gneiss is shown in FIG. 2.

Diamond occurs in greatest abundance in dolomite marble. Small amounts have been found in layers of calcite marble, but, for an as yet unknown reason, Ti-clinohumite-bearing dolomitic marbles (dominant carbonates are Mg-calcite and dolomite) contain no diamonds. Diamond abundance in the dolomite marble has been estimated by Yoshioka et al. (2001) as up to 2700 carat ton^{-1} , and Ishida et al. (2003) counted 4458 grains of diamond in four thin sections (a volume of $\sim 20 \times 160 \text{ mm}$ by 30 μm in thickness) with grain sizes ranging from 5 to 25 μm . Some garnet grains contain unusually high concentrations of diamond, as shown in FIG. 3, but the distribution of diamonds in garnet is heterogeneous. Polycrystalline aggregates (5 to 30 μm) of graphite, probably after diamond, are included in garnet, diopside, phlogopite, and dolomite. Indeed, many microdiamonds are partially surrounded by graphite.

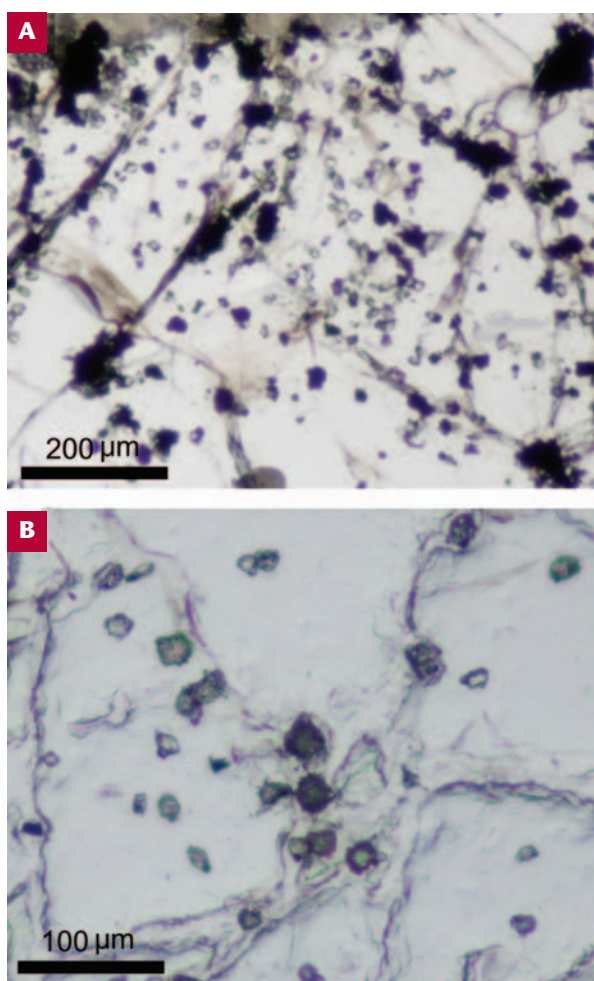


FIGURE 3 Photomicrographs (PPL) of the highest concentration domain of microdiamond in Kumdy-Kol dolomite marble.

Ishida et al. (2003) classified microdiamonds, according to their morphology and other characteristics, into three types: (1) S-type—“star-shaped” diamond consisting of a translucent core and transparent, subhedral to euhedral, very fine-grained, polycrystalline rims (FIG. 4); (2) R-type—translucent crystals with “rugged” surfaces; (3) T-type—transparent, very fine-grained crystals. S-type diamonds predominate (85%), the R-type is minor ($\sim 10\%$), and the T-type is rare (<5%). In a given rock, the spatial distribution of these types with respect to one another appears to be random. The authors proposed a two-stage growth mechanism for diamonds in the dolomite marble based on morphology and other characteristic features. Micro-Laue diffraction using a finely collimated synchrotron X-ray beam (1.6 to 50 μm in diameter) demonstrated that the rims of S-type diamonds have crystallographic orientations that are different from those of the cores, which are single crystals, and that R-type diamonds are single crystals.

Yoshioka and Ogasawara (in press) reported strong broad bands in the cathodoluminescence (CL) spectra at 514 to 537 nm from the rims of all S-type diamonds. This band is a green color that is not common among mantle-derived diamonds (FIG. 5). The cores also have the same broad band, but its intensity is very weak. Moreover, the main CL band of S-type diamonds is very similar to the 520 nm CL band of carbonado (Magee and Taylor 1999 and see Heaney et al. in this issue). These data may indicate different geochemical environments for the growth of cores and rims of S-type diamonds and support evidence for two-stage growth.

Imamura et al. (2004) conducted SIMS (ion-probe) carbon isotope analyses of S- and R-type diamonds in a Kokchetav dolomite marble. Rims of S-type diamonds have light isotopic compositions with $\delta^{13}\text{C}$ values ranging from -17.2 to -26.9‰ , whereas cores have isotopically heavier carbon, with $\delta^{13}\text{C}$ values ranging from -9.3 to -13.0‰ . The $\delta^{13}\text{C}$ values for two R-type grains fall between -8.3 and -15.3‰ and are similar to those for cores of S-type diamond. Thus, R-type grains may form at the same stage of growth and from the same carbon source as the cores of S-types. These data also suggest two stages of growth for S-type diamonds. The extremely light carbon isotopic compositions of rims of S-type diamond may be explained by a light organic source or fractionation (see Cartigny article in this issue).

CONDITIONS OF DIAMOND GROWTH IN KUMDY-KOL CARBONATE ROCKS

The two-stage growth model of Ishida et al. (2003) is strongly supported by the morphology of S-type diamonds, the micro-Laue diffraction data, CL interpretations, and carbon isotope compositions. The first stage corresponds to the growth of R-type diamond and the cores of S-types. The second stage represents the growth of rims on S-type and of T-type diamonds. The origin of the microdiamond cores is still unclear, but one possibility is prograde (i.e., increasing T and P) transformation of graphite. Katayama et al. (2000) interpreted composite graphite–diamond inclusions in zircon in this way. Whatever the origin, mineral textures indicate that first-stage diamond growth was coeval with garnet and diopside crystallization. Because both S-type and T-type diamonds often occur in the same garnet grain, the second stage of growth is either not homogeneous, even on a μm scale, or some factor, like fast growth rate, controls the second stage, which is microcrystalline. Moreover, second-stage growth for the rims of S-types and T-types involves a source of carbon different from that of the cores, such as a fluid or melt rather than graphite.

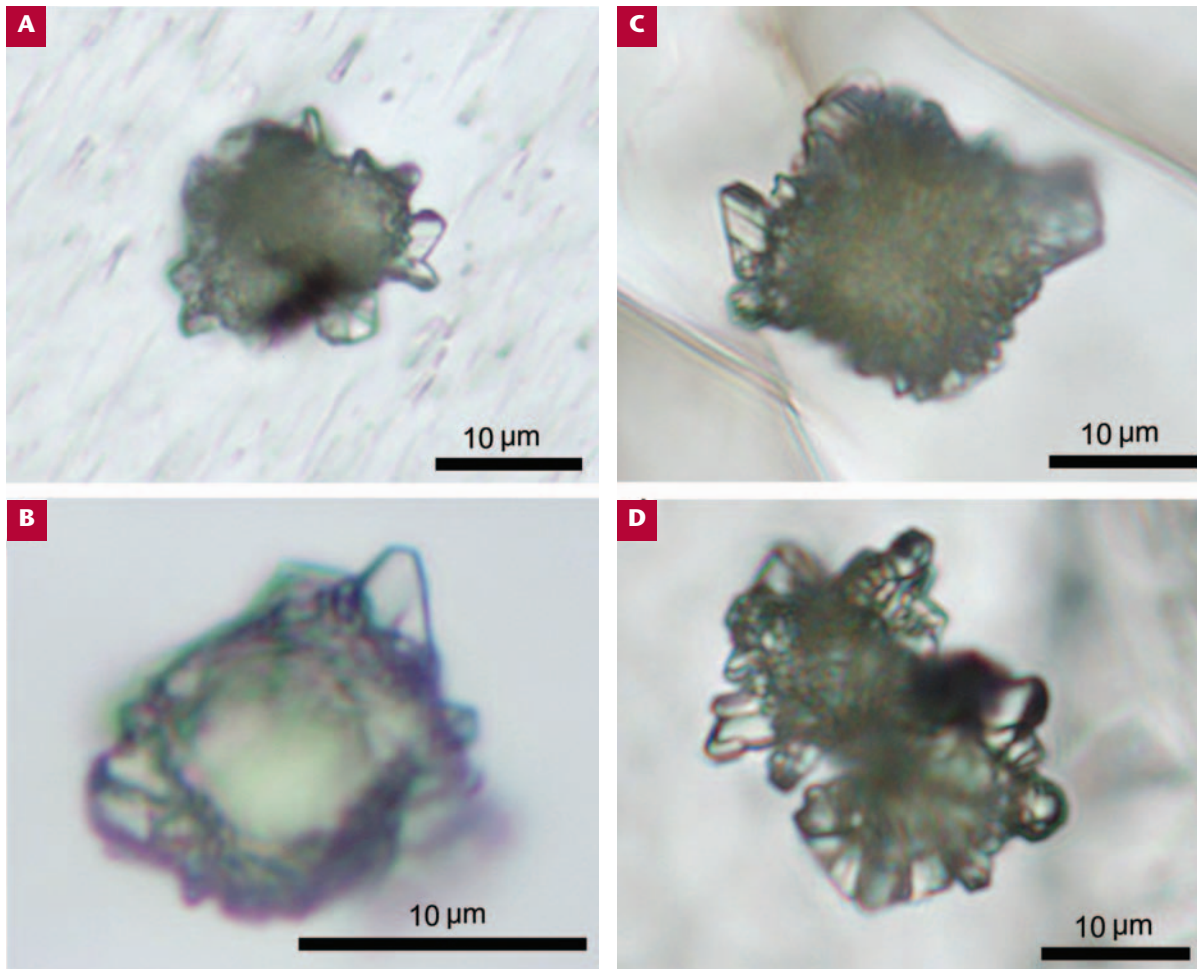


FIGURE 4 Photomicrographs (PPL) of representative S-type microdiamonds in dolomite marble. **A:** diamond inclusion in diopside. **B, C, D:** diamond inclusions in garnet.

Recent UHPM research has focused on determining whether microdiamonds formed from a fluid or a melt. Diamond has been synthesized stably from a $\text{CO}_2\text{-H}_2\text{O}$ fluid (Kumar et al. 2000) and from dolomite + carbon and dolomite + fluid + carbon systems (Sokol et al. 2001). Diamond has also been synthesized in the dolomite–Si (or SiC) system from a carbonatitic melt (Kozai et al. 2000). One of the possible media for second-stage growth of microdiamonds is an aqueous fluid. An important question is why dolomite marble contains diamond while some other types of marble do not. Ogasawara et al. (2000) argued that the CO_2 concentration (X_{CO_2}) in the metamorphic fluid could explain this distribution. Ogasawara and Aoki (in press) suggest that in diamond-bearing dolomite marble, $0.01 < X_{\text{CO}_2} < 0.1$, whereas in diamond-free dolomitic marble, $X_{\text{CO}_2} < 0.01$.

Numerous observations point to crystallization of microdiamond from a fluid, but a melt origin has been suggested as well. Dobrzhinetskaya et al. (2001) concluded that composite, nanometer-sized mineral inclusions (Cr_2O_3 , TiO_2 , MgCO_3) and presence of cavities in diamond from a Kokchetav felsic gneiss suggested that diamond had crystallized from a fluid; also, H_2O -bearing fluid inclusions in diamond from a garnet–pyroxene rock were confirmed by Fourier-transform infrared spectroscopy (De Corte et al. 1998). The study of fluid inclusions in diamond from dolomite marble indicates that microdiamonds crystallized in the presence of fluid and possibly from it (Dobrzhinetskaya et al. 2004). Diamond-bearing metal-sulfide inclusions in garnet in a garnet–clinopyroxene–quartz rock have been interpreted as evidence of diamond growth from a fluid (Hwang et al. 2003). Similar composite inclu-

sions (phlogopite, quartz, paragonite, phengite, apatite, and rutile) were also reported in UHP gneiss from Erzgebirge, Germany, and suggest a dense C–O–H fluid rich in K, Na, and SiO_2 under UHP conditions (Stöckhert et al. 2001). Conversely, Massonne (2003) proposed that diamond in silicate rocks of the Kokchetav and Erzgebirge crystallized from a silicate melt, and Herman and Korsakov (2003) and Korsakov and Herman (2004) proposed that diamond in Kokchetav dolomite marble crystallized from carbonate melt, based on textures and trace-element analyses. However, it is difficult to explain the extremely negative $\delta^{13}\text{C}$ values (Imamura et al. 2004) by diamond crystallization from carbonate melt, because strong isotopic fractionation is not expected between diamond and carbonate melt at such high temperatures.

Constraining P–T conditions for diamond formation in the dolomite marble is difficult. Two-stage growth, by itself, does not provide such information. If the carbon source was graphite for the first stage, diamond, in principle, may have started to crystallize near the minimum pressure for diamond stability, or slightly above. However, rim growth requires an additional source of carbon, such as fluid or melt. The release of H_2O by dehydration reactions from surrounding rocks may be one of the fluid sources, and growth of rim diamond could be near peak P–T conditions, which for the Kokchetav UHP marble are 6 to 9 GPa (Ogasawara et al. 2002) and 980 to 1250°C. (Ogasawara et al. 2000).

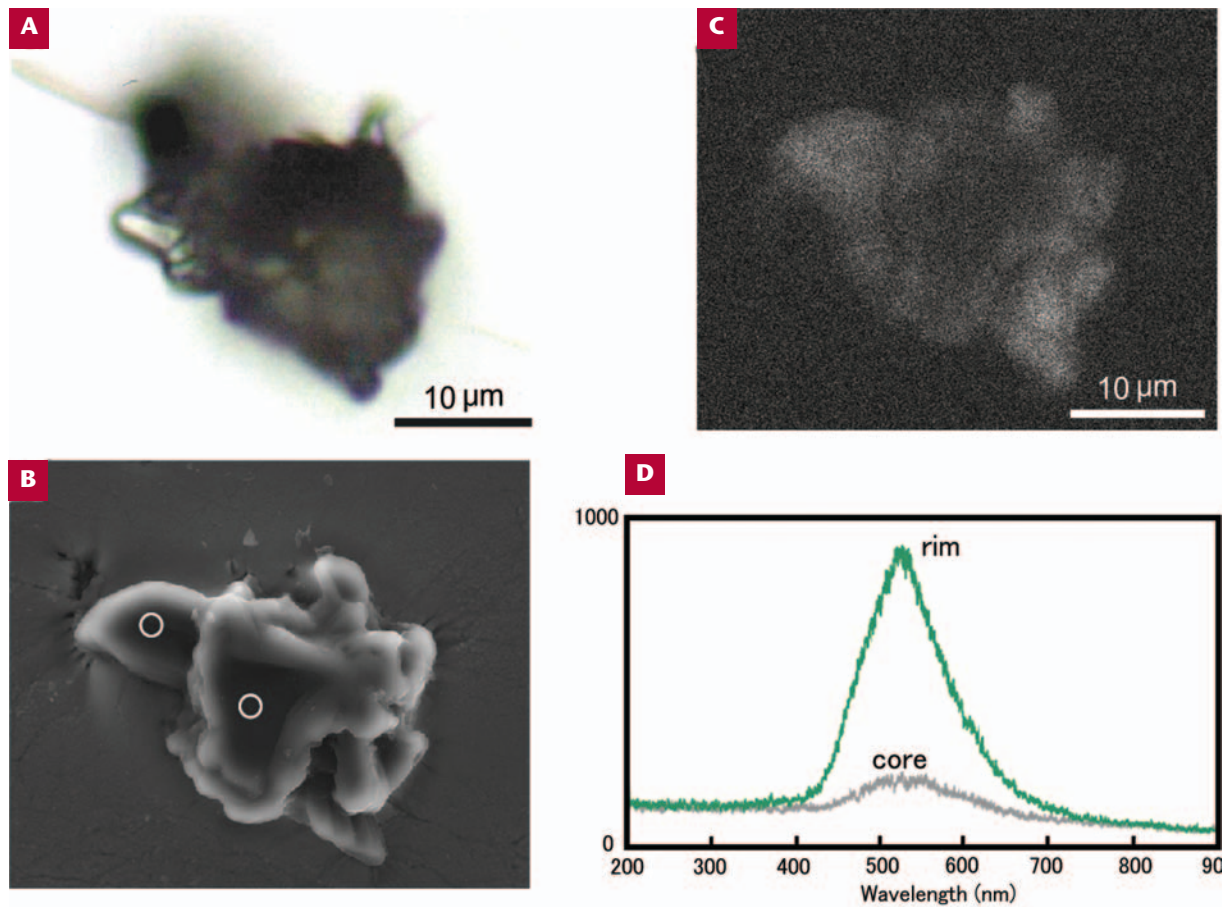


FIGURE 5 Images and cathodoluminescence (CL) spectra of an S-type microdiamond in dolomite marble (after Yoshioka and Ogasawara in press). **A:** Photomicrograph of analyzed grain. **B:** Secondary electron SEM image of analyzed grain. Small circles are locations from which CL spectra were obtained. **C:** CL image at the peak wavelength (523 nm) of the strongest CL band. **D:** CL spectra of core and rim.

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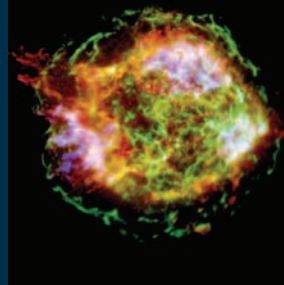


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Meteoritic Nanodiamonds: Messengers from the Stars



Gary R. Huss¹

This spectacular X-ray image of the supernova remnant Cassiopeia A is the most detailed image ever made of the remains of an exploded star. Colors represent different

X-ray wave lengths. The outer green ring, ten light years in diameter, marks the location of the shock wave generated by the supernova explosion. Inside this shock wave is the ejecta of the supernova, some of which condenses into tiny grains, perhaps including the nanodiamonds discussed in this article.

Scale: Image is 8 arcmin per side.

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Primitive chondritic meteorites contain up to ~1500 ppm of nanometer-sized diamonds. These nanodiamonds contain isotopically anomalous noble gases, nitrogen, hydrogen, and other elements. The isotopic anomalies indicate that meteoritic nanodiamonds probably formed outside our solar system, prior to the Sun's formation (they are thus presolar grains), and they carry within them a record of nucleosynthesis in the galaxy. Their characteristics also reflect the conditions encountered in interstellar space, in the solar nebula, and in the host meteorites.

KEYWORDS: nanodiamond, chondrite, presolar grains, isotopic anomalies, solar nebula

INTRODUCTION

Primitive chondritic meteorites date from the earliest times in solar system history and have survived largely unaltered until today. These meteorites preserve the first objects to form in the solar system, such as calcium–aluminum-rich inclusions, metal grains, and chondrules—the round, millimeter-sized, crystallized melt droplets for which chondrites are named and whose origin is poorly understood. They also preserve dust from the dense, cold, interstellar molecular cloud that collapsed to form the solar system. This presolar dust was the raw material from which the solar system formed. Although scientists had hints in the form of anomalous isotopic compositions in meteoritic components that presolar material was present in chondrites, it was not until 1987 that the first presolar grains were recognized. Diamond was recognized first (Lewis et al. 1987), followed by silicon carbide and graphite. Because presolar diamonds are only a few nanometers in diameter, the term “nanodiamonds” was coined. To date, more than ten different minerals from primitive meteorites have been identified as presolar (e.g., Nittler 2003). Most of these condensed from the ejecta of dying stars that existed long before the solar system formed. Presolar minerals permit us to investigate the stellar nucleosynthetic processes that produced the chemical elements, to study processes in interstellar space, and to probe the events that occurred during the earliest epochs of solar system history.

Nanodiamonds were recognized as presolar because of the isotopically anomalous noble gases that they contain. In general, an element will have the same isotopic composition (within tight limits) anywhere on Earth and in objects formed in the solar system. However, starting in the early 1960s, scientists noticed that xenon in some meteorites had a very strange isotopic composition. It was more than a decade before a group at the University of Chicago determined that the strange xenon was located in a carbonaceous

residue that makes up only a small portion of the host meteorite (Lewis et al. 1975). It took another ten years to determine that the carrier of the strange xenon was nanodiamond (Lewis et al. 1987).

Nanodiamonds were the first presolar component to be recognized, but in many ways they are the least well understood. This is primarily because of their size. Each ~2–3 nm diamond grain contains only a few thousand carbon atoms. No instrument currently available can determine the isotopic composition of a grain this small, and even if such an instrument were available, only carbon is present with enough atoms to give a meaningful composition. The isotopic and trace-element information that we do have comes from samples containing billions of individual nanodiamonds. Unlike μm -sized SiC and Al_2O_3 grains, which provide detailed information about the star around which each grain formed, nanodiamonds provide only a general picture of their source(s).

CHARACTERISTICS OF METEORITIC NANODIAMONDS

Transmission electron microscopy is necessary to determine the characteristics of individual nanodiamonds (e.g., Daulton et al. 1996). The crystal structure of most nanodiamonds is cubic, i.e., true diamond structure, but a few grains show hexagonal symmetry, indicating the carbon polymorph lonsdaleite. Most grains exhibit multiple twins indicative of rapid growth. Meteoritic nanodiamonds have a log-normal size distribution with a median effective diameter of ~2.7–3.0 nm.

The isotopically strange xenon that led to the discovery of nanodiamonds is enriched in both Heavy and Light isotopes compared to “normal” solar system xenon (FIG. 1). It occurs in the diamonds as a trapped gas component, called HL, which also contains isotopically distinct helium, neon, argon, and krypton (Huss and Lewis 1994a). Nanodiamonds also contain two other noble gas components, called P3 and P6 for historical reasons, with isotopic compositions much closer to those of solar system gases. Heating or oxidizing nanodiamond samples in steps can effectively separate these three components. The P3 component is released at low temperatures (FIG. 2A) and has much less

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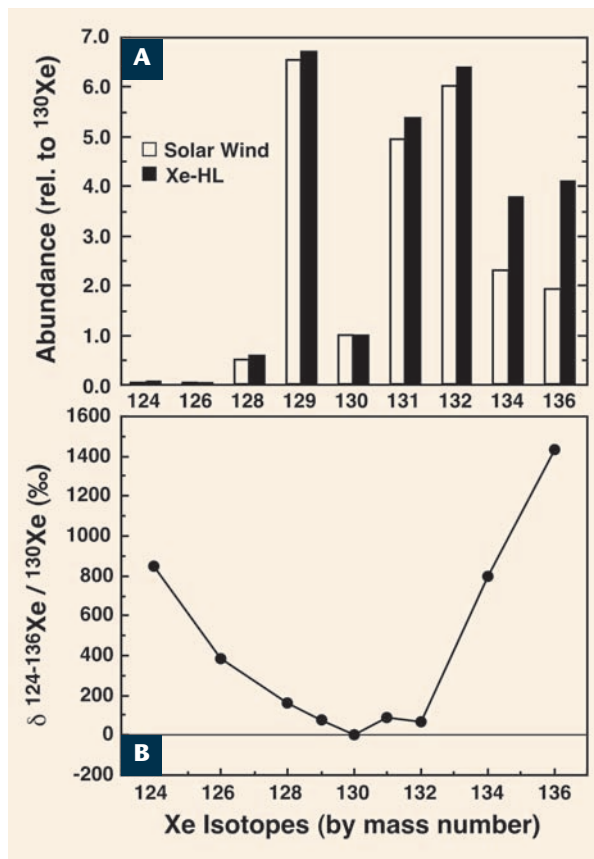


FIGURE 1 Isotopically anomalous xenon in meteoritic nanodiamonds. **A.** Histogram of the abundances of xenon isotopes in Xe-HL and in solar wind. **B.** Xenon isotopes in Xe-HL normalized to the composition of solar wind (the flat line at 0) and plotted as deviations from solar wind composition in parts per thousand (permil = ‰). Note the large excesses of the light and heavy isotopes that give Xe-HL its name.

helium and neon and more argon, krypton, and xenon than the HL component. The P6 component is volumetrically much smaller and is released at higher temperatures than HL (Huss and Lewis 1994a). Although P3 and P6 have isotope ratios similar to solar system xenon, their isotopic compositions are distinct and cannot be produced from solar system xenon by any known process.

The noble gas content of meteoritic nanodiamonds is extremely high, so high that helium and neon from nanodiamonds dominate the helium and neon in the host meteorites, and argon, krypton, and xenon make up several percent of the total budget. This is true even though nanodiamonds comprise only ~0.15% of the fine-grained “matrix” material in primitive chondrites. Yet in spite of the high gas content, only about one diamond in a million contains a xenon atom and only about one in ten contains helium. (For example, nanodiamonds contain about 1.5 ppb of xenon, about 10,000 times more gas than most terrestrial rocks). Thus, there is no such thing as an isotopic composition for the xenon in a single diamond; measured compositions are for the gas extracted from billions of diamonds.

The mean carbon isotopic composition of these billions of nanodiamonds ($\delta^{13}\text{C} = -31\text{‰}$ to -38‰ ; Russell et al. 1996) is within the range of compositions measured in solar system materials, but it is quite different from those of most terrestrial diamonds, which concentrate between -25‰ and $+5\text{‰}$. Chondritic nanodiamonds are rich in nitrogen, the isotopic composition of which is highly enriched in ^{14}N ($\delta^{15}\text{N} = -348\text{‰}$; Russell et al. 1996), and their surface atoms are bonded to hydrogen that is enriched in deuterium

by $\geq 280\text{‰}$ (Virag et al. 1989). The trace elements tellurium and palladium show small excesses of the heaviest isotopes, analogous to, but somewhat smaller than, the anomalies in Kr-H and Xe-HL (Mass et al. 2001).

Origin of Meteoritic Nanodiamonds

The origin of meteoritic nanodiamonds is still very much an open issue. A longstanding interpretation of Xe-HL is that the excess light and heavy isotopes were produced in a supernova and were implanted into the diamonds before the solar system formed (e.g., Heymann and Dziczkaniec 1979). On the other hand, because the carbon isotopic composition of nanodiamonds is within the compositional range of solar system materials and because only about one diamond in a million contains a xenon atom, some scientists have suggested that most nanodiamonds formed in the solar system. This view received support from a transmission electron microscope study of interplanetary dust particles (IDPs) (Dai et al. 2002). These authors did not observe nanodiamonds in IDPs thought to have originated from comets, but they did observe them in IDPs thought to be asteroid particles. Because comets probably formed far from the sun from material that was not heavily processed in the solar system, the near absence of diamonds in cometary IDPs suggests that the bulk of the diamonds originated inside, not outside, the solar system.

Although a local origin for meteoritic nanodiamonds is currently popular, I argue that the bulk of the evidence indicates that nanodiamonds formed outside the solar system. The compositions of Xe-HL, Kr-H, tellurium, and palladium show that at least some of the diamonds came from a source where heavy isotopes were preferentially synthesized, probably a supernova. Xe-HL is associated with four other isotopically distinct noble gases, and when all five gases are considered, one out of ~10 diamonds contains a noble gas atom that can reasonably be associated with a supernova source (but see below). The P3 component in nanodiamonds is isotopically distinct from both the major heavy noble gas component in chondrites and from solar wind for all five noble gases (Huss and Lewis 1994a). The P3 gases were probably trapped after nanodiamonds formed, and their distinctive isotopic compositions indicate that they originated outside the solar system. Also, as will be discussed below, the relative abundances of nanodiamonds and other types of presolar grains in chondrites can best be understood in terms of solar system thermal processing of a single mixture; there is no evidence that diamonds are decoupled from other types of presolar grains. The major challenge to this view is the near absence of nanodiamonds in supposed cometary IDPs. However, there is currently no estimate of the abundance of another type of presolar grain in these IDPs to show that other grain types are present at the expected abundances. Without such data, the possibility that we simply do not understand how and from what comets formed cannot be ruled out.

How do nanodiamonds form? We are normally taught that high pressures are required to make diamond, but meteoritic nanodiamonds apparently formed in the low pressures of space. One early idea was that nanodiamonds were produced by high-pressure shock metamorphism of graphite through grain–grain collisions during the passage of interstellar shocks (Tielens et al. 1987). This process is not expected to be efficient, so the diamonds should be accompanied by a large amount of graphite, which has not yet been observed. (The word “shock” has two meanings in this context. An interstellar shock is a discontinuity in gas velocity, pressure, density, etc. Gas atoms typically do not cross the discontinuity, but dust grains can penetrate the shock and collide with other dust grains at high velocity.

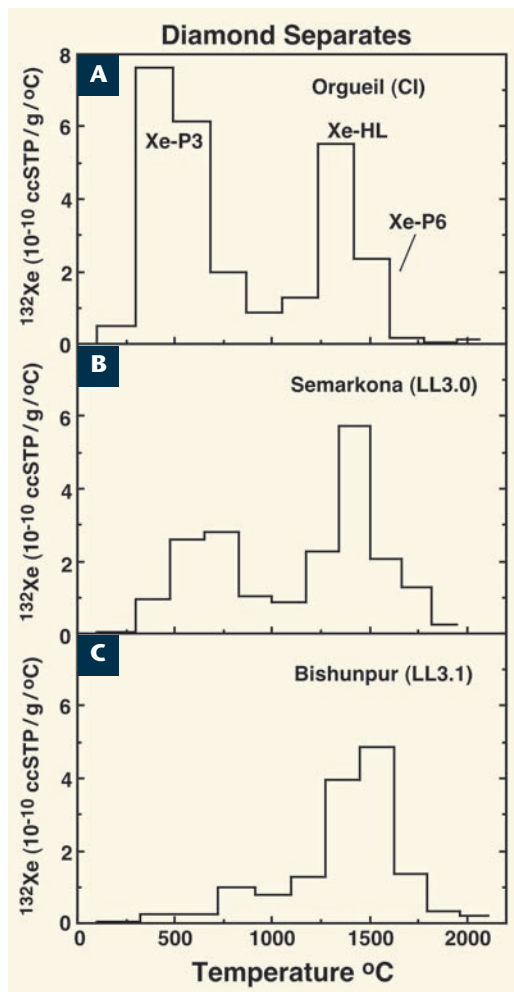


FIGURE 2 Histograms showing xenon released from nanodiamonds from three primitive meteorites as a function of temperature during stepped heating in the laboratory. The ordinate shows the volume of ^{132}Xe released from one gram of nanodiamonds at each temperature step in units of 10^{-10} cubic centimeters at standard T and P. The gas volume for each step has been normalized to the width of the step in $^{\circ}\text{C}$ so that the area under the curve accurately represents the gas volume. The meteorites: Orgueil is a CI chondrite thought to best represent the composition of the early solar system. Semarkona and Bishunpur are LL chondrites, which have matrix compositions very similar to CI except they have lost siderophile elements. These meteorites have experienced very little thermal metamorphism with temperatures increasing from Orgueil to Semarkona to Bishunpur.

Xenon in Orgueil diamonds (**A**) is released in two distinct peaks. Xenon in the first peak (the P3 component) has an isotopic composition similar to that of solar system xenon. This low-temperature gas is apparently trapped in the surface layer of the diamonds where many of the bonds are C-H, C-O, C-O-O-H, C-N, etc. These bonds break and recombine at relatively low temperature releasing the noble gases. The second peak is dominated by isotopically anomalous Xe-HL. A third component, Xe-P6, is released on the high-temperature tail of the Xe-HL release. Both of these components are sited within the diamond structure and are released when the diamond reacts with the Pt or Ta foil in which the sample is wrapped or with surrounding minerals. Note that the size of the Xe-P3 peak is lower in Semarkona diamond (**B**) and lower yet in Bishunpur diamond (**C**). This reflects heating of the LL chondrites that released some of the low-temperature gases on the meteorite parent body (Huss and Lewis 1994b). The petrologic types of the LL chondrites (3.0, 3.1) are derived from measurements of thermoluminescence sensitivity (e.g., Sears et al. 1991), which give the degree of heating each meteorite experienced.

High-velocity collisions generate pressure waves within solid grains, which are also called shock waves. These shock waves can cause pressure excursions into the diamond stability field and convert graphite to diamond.) In recent years, diamonds have been produced industrially at low pressures by a process called chemical vapor deposition

(CVD; see Hemley et al. p. 105). The conditions for optimum diamond growth are remarkably similar to those in stellar ejecta (e.g., Anders and Zinner 1993 and references therein). Industrial CVD synthesis makes use of kinetic factors to stabilize diamond production. However, there may be a thermodynamic reason to expect diamond to form preferentially over other carbon allotropes at very small sizes. Badziag et al. (1990) showed that when the surface bonds are terminated with hydrogen, diamonds smaller than ~ 3 nm in diameter are energetically favored over polycyclic aromatic hydrocarbons (the precursors to graphite). Thus, diamond may well be the stable form of carbon in the nm size range. Other ideas have also been suggested. Graphite grains might be induced to transform to diamond by intense UV irradiation or by intense particle irradiation. However, transmission electron microscope work on meteoritic nanodiamonds and terrestrial analogues strongly indicates that nanodiamonds formed by a vapor-deposition process (Daulton et al. 1996).

The isotopic anomalies in meteoritic nanodiamonds are hard to explain by a single stellar source. This is not surprising, since the measured isotopic compositions represent billions of grains that may have formed in hundreds of different sites. For example, Xe-H and Xe-L are produced in different zones of a supernova (e.g., Heymann and Dziczkaniec 1979), so one might expect that the two components should be separable in the laboratory. Several workers have claimed marginal evidence of separations of Xe-H and Xe-L, but in most cases the effects turned out to be due to additional noble gas components or other experimental artifacts (e.g., Huss and Lewis 1994a). Meshik et al (2001) used a laser and selective optical absorption to extract gases from different populations of nanodiamonds and again found marginal evidence of a separation, but they were unable to demonstrate clearly that Xe-H and Xe-L are separable in the laboratory.

The measured Xe-HL and Kr-H compositions are also significantly less extreme than compositions from nucleosynthetic models (Heymann and Dziczkaniec 1979; Clayton 1989). This implies that an isotopically "normal" component is intimately intermixed with the isotopically anomalous gas. To calculate the supposedly pure end-member isotopic composition from the stellar source, the "normal" component is typically removed by assuming that all of the ^{130}Xe , which is not produced by the processes that generate Xe-H or Xe-L, is in the "normal" component, usually assumed to have the composition of solar wind. Several ideas for the production of Xe-H in a supernova setting have been suggested. An early idea invokes the classical r-process, in which large numbers of neutrons released from deep in the exploding star are captured by seed nuclei on a timescale that is short with respect to their lifetime against β -decay, to produce large excesses of heavy xenon isotopes (Heymann and Dziczkaniec 1979). Clayton (1989) suggested that when a massive star collapses to become a type II supernova, the neutrino burst generated in the core would release enough neutrons from the helium shell of the pre-supernova star to produce large excesses of neutron-rich isotopes. Ott (1996) suggested that classical r-process nucleosynthesis accompanied by separation of xenon from iodine and tellurium precursors within a few hours after termination of the process could produce Xe-H. Each model has its problems, and none has been generally accepted.

A recent experimental study in which noble gas ions were implanted into nanodiamonds produced a remarkable result. A single component was implanted, but when the sample was measured by stepped heating, the gases were released in two peaks that were almost identical to the bimodal release shown in Fig. 2a (Koscheev et al. 2001).

This suggests that the isotopically “normal” component intimately mixed with the HL component might be P3, and if so, then calculations of the pure Xe-HL composition have been done incorrectly in the past. A calculation subtracting P3 gases produces a Xe-HL composition not too different from previous ones but suggests that Kr-H is accompanied by Kr-L. Direct evidence for Kr-L has not been seen before. This calculation also suggests that the exotic component was implanted and then largely outgassed before the P3 component was implanted (Huss et al. 2000).

NANODIAMONDS AS PROBES OF SOLAR SYSTEM PROCESSES

The noble gases in nanodiamonds and the abundances of nanodiamonds and other presolar materials among chondrites are sensitive probes of thermal processing, both in the solar nebula and in the meteorite parent bodies (Huss and Lewis 1994b, 1995; Huss et al. 2003). The P3 component is released at low temperatures, and the release temperature seems to be largely independent of the surroundings in which the diamonds are located. Because of this, the P3 abundances from diamond separates provide a relatively precise measure of the temperature to which the meteorites were heated during their history (cf. Fig. 2). This P3-based “metamorphic” scale can be calibrated to give a quantitative estimate of the maximum temperature experienced by the diamonds and associated material, and this calibration seems to be consistent across the chondrite classes. The abundances of diamonds in chondrite matrices can be reliably determined by measuring the amount of Xe-HL in meteorite residues (Huss and Lewis 1995; Huss et al. 2003). Among presolar materials whose abundances in the host meteorite are easily determined (diamond, SiC, and graphite), nanodiamond is among the most resistant to thermal processing. Within a meteorite class, the relative and absolute abundances of presolar grains can establish the relative amount of heating each meteorite experienced

(Huss and Lewis, 1995). Among the essentially unmetamorphosed members of the various meteorite classes, the relative abundances of presolar materials and the amount of P3 gas in diamonds seem to reflect the nebular thermal processing that produced the chemical classes of chondrites (Huss et al. 2003). Thus, nanodiamonds are potentially powerful probes of both nebular and parent-body processes in the early solar system.

FUTURE RESEARCH

Future research on meteoritic nanodiamonds should address the following questions:

1. How many different kinds of diamonds are present in bulk nanodiamond samples and how can they be recognized?
2. Are the diamonds dominantly presolar or were they mostly produced in the solar system?
3. How did the diamonds form?
4. What nucleosynthetic source or sources are reflected in the isotopically anomalous noble gases and trace elements in the diamonds?
5. Can these sources be identified and characterized effectively from the diamond samples?

These are essentially the same questions that scientists have been working on since the diamonds were discovered. But because of the small size of individual diamonds, we do not currently have the tools to address them effectively. Instrumentation is improving rapidly, however, and detection limits are getting better. So I am confident that eventually the tools will be developed that will permit us to answer these basic questions about meteoritic nanodiamonds.

ACKNOWLEDGMENTS

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High-Pressure–High-Temperature Treatment of Gem Diamonds



Three diamonds (4.11–5.34 carats) decolorized by the HPHT-annealing process developed by General Electric. PHOTO BY ELIZABETH SCHRADER, © GEMOLOGICAL INSTITUTE OF AMERICA (GIA).

James E. Shigley¹

Annnealing of gem-quality diamonds at very high pressures (above 5 GPa) and temperatures (above ~1800°C) can produce significant changes in their color. Treatment under these high-pressure–high-temperature (HPHT) conditions affects certain optically active defects and their absorptions in the visible spectrum. In the jewelry industry, laboratory-treated diamonds are valued much less than those of natural color. Polished diamonds are carefully examined at gemological laboratories to determine the “origin of color” as part of an overall assessment of their quality. Currently, the recognition of HPHT-treated diamonds involves the determination of various visual properties (such as color and features seen under magnification), as well as characterization by several spectroscopic techniques. HPHT-treated diamonds were introduced into the jewelry trade in the late 1990s, and despite progress in their recognition, their identification remains a challenge. While some detection methodologies have been established, the large number of diamonds requiring testing with sophisticated analytical instrumentation poses a logistical problem for gemological laboratories.

KEYWORDS: diamond, gemstone, color, treatment, HPHT, annealing, identification

INTRODUCTION

Diamonds are the most important gemstones, and their sales are the foundation of the international jewelry industry. Gem diamonds hold a special fascination, as evidenced by the popularity of, and media interest in, exhibitions and events featuring them (e.g., King and Shigley 2003). In 2003, retail diamond jewelry sales in the United States amounted to over US\$29 billion. Continued confidence in the jewelry marketplace depends both on an accurate determination of whether a diamond (or any gemstone) is natural, synthetic, or laboratory-treated and on a full disclosure of this information at the time of sale.

Commercial treatments to improve the color of gem diamonds have existed since the 1930s (see Nassau 1994, pp. 141–151). These processes mostly involve exposure to high-energy radiation, sometimes followed by heating to temperatures up to several hundred degrees Celsius or more. Over time, diamond color (as well as clarity) treatments have become both more sophisticated and widespread, and new treatment processes have been developed. In some cases, a gemologist, using just a binocular microscope and a simple spectroscope, can recognize color-treated diamonds. However, detecting them often requires more sophisticated instruments such as UV–visible or photoluminescence spectrometers. For some treated diamonds, this

determination still cannot be made with certainty; this is especially true when the treatment processes (e.g., irradiation) mimic natural processes that affect diamonds in the Earth. The fact that some natural-color gem diamonds sell at prices in excess of US\$100,000 or more *per carat* emphasizes the importance of a correct “origin of color” determination.

This article deals with the most difficult current identification challenge—the recognition of diamonds that have had their color either removed or changed by annealing at high pressures and temperatures (referred to as HPHT treatment).

DIAMOND TYPES AND COLORATION

Diamonds can be divided into categories, called types, based on

differences in certain physical properties, particularly optical absorption. Initially, diamonds with strong absorptions of both IR and UV radiation were designated as Type I, whereas those without were labeled Type II (Robertson et al. 1934). These “types” are related to the presence of impurities (see TABLE 1). The boundaries between categories are somewhat arbitrary, and mixed types are possible within a single diamond.

The structural arrangements of these impurities within the diamond lattice are perhaps more interesting than their abundances. Nitrogen (and to a lesser extent boron and hydrogen), along with point and extended defects, cause absorptions in the visible spectrum, which give rise to coloration (see Table 1).

Certain colors in diamond are due not to trace-element impurities, but to absorptions resulting from various optically active defects. In brown and pink diamonds, the “color centers” (which produce a broad region of absorption centered at about 550 nm) are thought to be caused by dislocations and point defects that result from deformation of the diamonds during their extended storage in the Earth. Exposure of diamonds to radiation, either in nature or the laboratory, creates defects that cause green and some blue colors (due to the GR center at 741 nm and its associated sidebands, see Table 1; for further information, see Fritsch 1998; Collins 2001).

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TABLE 1

DIAMOND TYPES AND DEFECTS OR SUBSTITUTIONS

	Type I	Type II
Natural Abundance*	~98% Ia ~0.1% Ib	~2% IIa Extremely rare: IIb
Nitrogen content (ppm)	Ia: ~10–3000 Ib: ~25–50	IIa: < 10 IIb: none (< 0.1)
Nitrogen distribution	Ia: as small aggregates (see below) Ib: individual substituted atoms	
Other constituents		IIb: boron

* For diamonds larger than 0.1 ct (0.02 g). Type II is more common in microdiamonds than is indicated above.

Color Centers and Nitrogen Aggregates[†]:

A aggregate: 2 nitrogen atoms in adjacent lattice sites—no color

B aggregate: 4 nitrogen atoms and a vacancy in adjacent lattice sites—no color

C center: single nitrogen atom—strong yellow

GR center: a vacancy (i.e., a carbon atom missing from a site)—green to blue

N-V center: single nitrogen atom and a vacancy in adjacent sites—pink to red or purple

N3 center: 3 nitrogen atoms and a vacancy in adjacent sites—pale yellow

N-V-N (H3, H2) center: a vacancy trapped at an A aggregate—green

H4 center: a vacancy trapped at a B aggregate—yellow, orange, or brown

[†] Nomenclature mostly comes from labeling of spectroscopic peaks that are used to identify defects and substitutions in diamond. Diamond colors typically result from absorption at the zero-phonon line and associated sidebands at shorter wavelengths (see Fritsch 1998; Collins 2001). Additional colors result from boron or hydrogen impurities, or from other color centers of uncertain structure.

HPHT-TREATMENT OF DIAMONDS

Experimental studies in the 1970s showed that the degree of aggregation of nitrogen atoms could be increased or decreased by heating Type I diamonds to very high temperatures at high pressures (see Evans and Rainey 1975; Brozel et al. 1978). This was accompanied by either a weakening or an intensification of the yellow color. Because of the difficulty in achieving these conditions, this procedure was not commercially viable as a treatment of gem diamonds.

In March 1999, the jewelry industry was taken by surprise when the prominent U.S. jewelry firm, Lazare Kaplan International, announced a new process developed by the General Electric (GE) Company for transforming certain Type IIa diamonds from brown to colorless (see p. 101). Initially sold under the name “GE POL” (for Pegasus Overseas Ltd., a foreign GE subsidiary), these color-treated diamonds are currently marketed under the trade name “Bellataire” (e.g., <http://www.ge.com/uk/bellataire/>). No details of the process were provided by GE at the time (patents have since been published; see Vagarali et al. 2004). However, it was subsequently established that the technique involved annealing diamonds for brief periods of time at very high temperatures and pressures (1800 to ~2700°C, and at 5 to 9 GPa to prevent transformation to graphite). Under such conditions, lattice-scale defects in the structure that produce brown coloration are annealed out, thereby rendering the diamonds colorless.

This process is carried out with the same equipment typically used for diamond synthesis, including the “belt”, tetrahedral, cubic, and octahedral presses, as well as the

Russian-designed “BARS” units (= *besspressoverye apparaty tipa razreznaya sfera*, or “split sphere no press apparatus”). One or more rough or polished diamonds are loaded into a capsule, which is then placed in the apparatus. The exact P and T used depend on the type of diamonds being treated, the color change desired, and the equipment configuration, with annealing times being as short as a few minutes. At the end of a treatment run, the diamonds may have a black, graphitized outer surface, which can be removed by heating to several hundred degrees Celsius for a short time in a laboratory oven. Following treatment, all diamonds exhibit surface damage in the form of etching and pitting, so after processing, a cut diamond requires repolishing. Polished diamonds of all sizes (0.01 to more than 30 ct) have been treated by the HPHT process.

Annealing of Type IIa brown diamonds under HPHT conditions removes structural defects by means of plastic flow (Schmetzer 1999; Collins et al. 2000). This decreases the broad absorption in the visible spectrum that causes the brown coloration (Fisher and Spits 2000; also see FIGS. 1 AND 2). It is also possible to change certain very rare brown-pink and gray-blue Type II diamonds by elimi-

inating the brown component of their coloration and thereby enhancing the underlying pink or blue color, respectively (Hall and Moses 2000, 2001). Wang et al. (2003) recently described an intensely colored green-yellow Type IIa diamond that had been treated by this method.

Initially this treatment focused on removal of brown color from Type IIa diamonds, but experiments on changing the color of Type I diamonds soon followed (De Weerd and Van Royen 2000; Reinitz et al. 2000; De Weerd and Collins 2003). Brownish-yellow Type Ia diamonds can be transformed to yellow, orange-yellow, or green-yellow as annealing

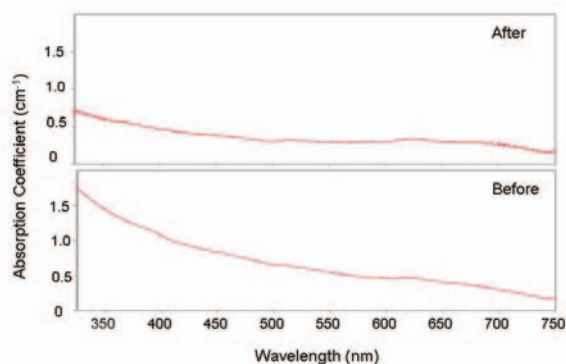


FIGURE 1 The visible spectrum of a Type IIa brown diamond (lower spectrum) exhibits absorption extending from the blue (400 nm) to the red (700 nm). HPHT annealing resulted in a removal of much of this absorption (upper spectrum), so that the diamond now appears nearly colorless.

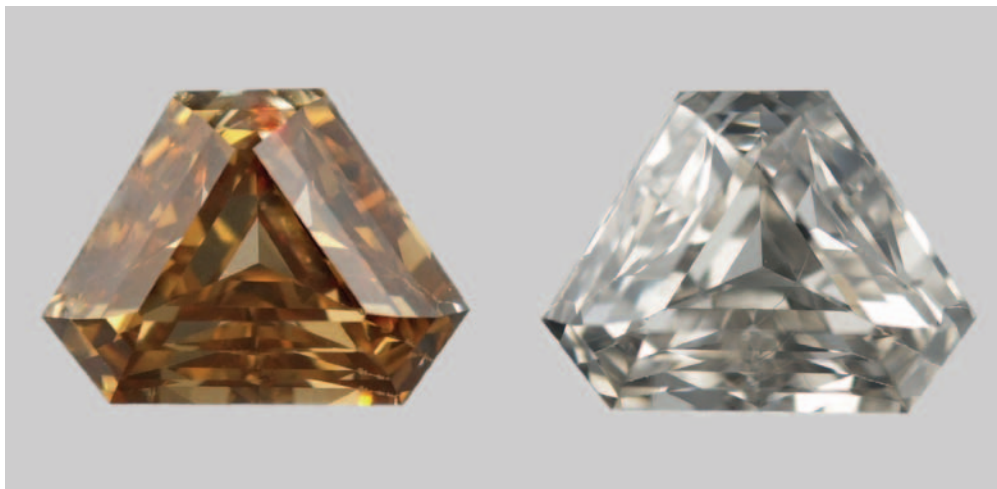


FIGURE 2 A 6.60-carat, faceted Type IIa diamond transformed from brown to colorless by HPHT annealing. PHOTOS BY ELIZABETH SCHRADER, © GIA.

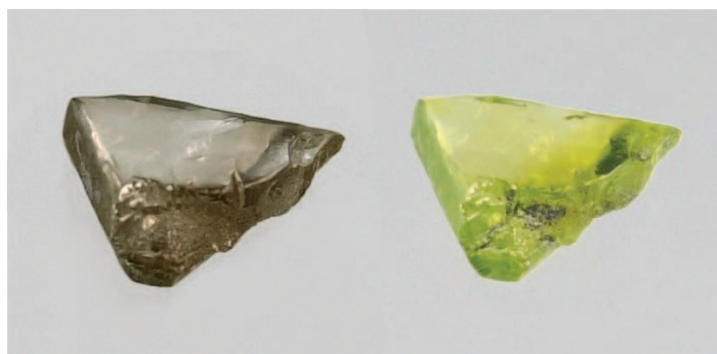


FIGURE 3 HPHT annealing of this 1.08-carat, Type Ia crystal changed the color of the diamond from brown to yellow-green. PHOTOS BY ELIZABETH SCHRADER, © GIA.

permits vacancies to migrate and combine with aggregated nitrogen to form nitrogen-vacancy-nitrogen (N-V-N) centers that give rise to strong green coloration (due to the H3 optical center; Collins et al. 2000; see FIG. 3). At higher T, some A nitrogen centers are also broken up, forming C centers. This is accompanied by H3 changing to H2 centers and the formation of the nitrogen-vacancy (N-V) centers (see Collins 2001; Zaitsev 2001). Only recently have Type Ia diamonds been reported whose light yellow color is the result of HPHT treatment.

When the challenge for gemological laboratories focused on detecting decolorized Type IIa diamonds, the problem was limited because of their rarity. Now, with the treatment of Type I diamonds added, the identification problem is much greater because the latter are far more abundant and more variable in gemological properties.

DETECTING HPHT-ANNEALED DIAMONDS

HPHT treatment presented significant challenges for the jewelry industry in terms of identification and disclosure. Even though only a relatively small number were initially involved, HPHT-treated diamonds often exhibited few if any visual clues for a jeweler or gemologist to detect this process. As an aid to recognition, General Electric inscribed an identification mark easily visible at 10 \times magnification on the polished “girdle” surface of each of their treated diamonds (those sold by other companies may or may not have similar laser inscriptions). However, these marks can be removed by repolishing the inscribed surface.

HPHT-treated diamonds can exhibit visual features that are lacking in untreated diamonds, for example, the above-mentioned surface damage. They can also display graphitized fracture surfaces and inclusions (see Chalain et al. 1999; Moses et al. 1999). Colorless Type IIa diamonds display greater transparency to short-wave (265 nm) UV radiation than the more abundant Type Ia diamonds, and this offers a preliminary way to separate the former for further testing (Moses et al. 1999; Chalain et al. 2000).

Since visual features are not always present in polished diamonds, detection of this treatment requires the use of spectroscopic techniques (Collins 2001). For example, in HPHT-treated Type II diamonds, Chalain et al. (1999, 2000) interpreted the 637 nm absorption peak (due to the neutral N-V center) as a potential distinctive feature (also see Fritsch et al. 2001). Fisher and Spits (2000) described the broad 270 nm band (due to C nitrogen centers) seen in the spectra of HPHT-treated diamonds with increasing yellow coloration. Using 514-nm Ar-laser excitation, they also reported that the photoluminescence (PL) peaks at 575 and 637 nm (due to neutral and negative charge states at N-V centers, respectively) have an intensity ratio (637>575) in treated diamonds that differs from that in untreated Type IIa diamonds (575>637). Other non-destructive analytical tools, including X-ray topography and cathodoluminescence, have been tried, but further work is needed on a larger population of untreated and HPHT-treated diamonds to support their use for detection purposes (e.g., Smith et al. 2000).

In yellow Type Ia diamonds, HPHT treatment produces new absorption features while again reducing the brown coloration (Van Royen and Pal'yanov 2002). For example, strong green H3 luminescence, along with the contribution of the sideband of the H2 center, causes the treated diamonds to be yellow-green to green (Collins et al. 2000; Collins 2001; see Fig. 4). Just as in Type IIa diamonds, isolated

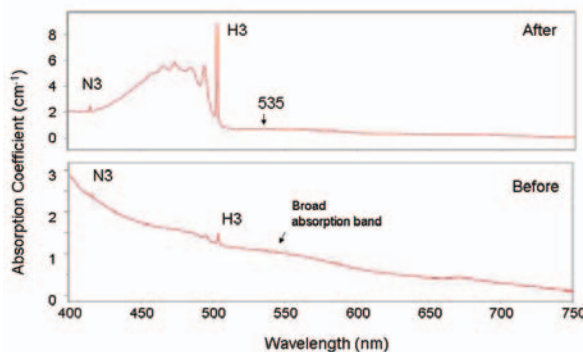


FIGURE 4 Before HPHT annealing, the visible spectrum of this Type Ia brown diamond displayed sharp absorption bands at 415 and 503 nm (due to the N3 and H3 optical centers, respectively), as well as a broad region of absorption centered at about 520 nm (lower spectrum). Following treatment, the latter broad band has been removed, and the H3 absorption band (along with its sidebands between 450 and 500 nm) is increased in intensity. These spectral changes produce the transformation of brown to yellow-green coloration in Type Ia diamonds as in Fig. 3.

nitrogen (C centers) are formed in Type Ia diamonds by annealing, as can be seen in mid-infrared spectra (Reinitz et al. 2000; De Weerd and Van Royen 2000). Current gemological research is focused on confirming the use of spectral features in both diamond types and on establishing additional means of treated-diamond identification.

Several potential detection techniques have been developed to quickly check diamonds to see if they have been HPHT treated. A patent issued to General Electric describes a method using the presence or absence of one or more PL lines for this purpose (Anthony et al. 2002). Researchers at the De Beers Diamond Trading Company (DTC) Research Centre have developed a prototype screening instrument that again is based on the detection of spectral features (Welbourn and Williams 2002). At gemological laboratories, separation of natural-color from HPHT-treated diamonds is based on as many features as possible. Development of identification criteria rests on assembling a database of information on large numbers of known untreated and known treated diamonds. Creation of such a database represents a significant research activity in the major diamond-testing gemological laboratories.

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CONCLUSION

Gemologists face continued challenges in recognizing natural, treated, and synthetic gem materials. HPHT-treated diamonds pose a special difficulty since some colors produced correspond to those of high-priced untreated natural diamonds, and yet they are valued very differently. Their detection often requires the use of sophisticated scientific equipment. Treatment experiments undertaken by the Gemological Institute of America and other researchers have been able to reproduce the kinds of color changes in diamonds that can be brought about by HPHT annealing. Systematic documentation of the gemological properties of a vast number of treated and untreated diamonds has yielded new identification criteria. Nonetheless, the distinction of HPHT-annealed diamonds represents a difficult challenge for gem-testing laboratories that receive numerous gems on a daily basis. Despite much progress, the detection of HPHT-treated diamonds will remain a concern for the jewelry industry as the use of this process becomes more widespread.

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Growing Diamond Crystals by Chemical Vapor Deposition



Russell J. Hemley, Yu-Chun Chen, and Chih-Shiue Yan¹

The synthesis of large single-crystal diamonds by chemical vapor deposition (CVD) at high growth rate has opened a new era for applications of the material. Large and thick single crystals can now be produced at very high growth rates, and the mechanical properties, chemistry, and optical and electronic properties of the material can be tuned over a wide range. The single crystals can have extremely high fracture toughness and exceptionally high hardness following high-pressure/high-temperature annealing. CVD single-crystal diamonds will make possible a new generation of high-pressure-temperature experimentation to study Earth and planetary materials and should enable a variety of other new scientific and technological applications.

KEYWORDS: Diamond, chemical vapor deposition, carbon, high pressure, diamond anvil cell

INTRODUCTION

By every measure, diamond is a unique material. The supreme hardness, singular strength, high thermal conductivity, low thermal expansion, chemical inertness, excellent optical, infrared, and X-ray transparency, and semiconductor properties of the material continue to attract scientific and technological interest worldwide. However, the lack of large, high-quality single crystals of diamond prevents its use in many applications. Although the impurity content, strain, and overall quality of diamonds produced by high-pressure/high-temperature techniques (HPHT; e.g., >4.5 GPa, ~1200°C) have improved in recent years (Barnard 2000; Hazen 1993), these diamonds cannot be produced as perfect single crystals in the range of several tens of carats. Instead, they are limited commercially to up to ~3 carats (or 0.6 g, roughly 7 mm across). In addition, diamond crystals need to be produced in different shapes for many applications (e.g., as large plates). Indeed, our imagination regarding the applications of single-crystal diamond in many ways has been circumscribed by the limited size of available high-quality HPHT diamond crystals, created either by nature or in the laboratory.

One of the most important developments in diamond synthesis is Chemical Vapor Deposition (CVD). The first attempt at creating diamond using this process was reported by Eversole in 1949 (see Liu and Dandy 1995). This discovery launched a significant period of exploration of various CVD techniques for synthesizing diamond films and coatings in the 1980s (Kamo et al. 1983; Spitsyn et al. 1981). In 1982, a group at the National Institute for Research in

Inorganic Materials (NIRIM) reported growth rates for diamond films of up to $10 \mu\text{m h}^{-1}$ (Matsumoto et al. 1982). The production of single-crystal particles, polycrystalline films, and epitaxially grown films using the CVD method started in the late 1980s (Kamo 1990). Most of the thick (greater than $10 \mu\text{m}$) polycrystalline diamond films produced then were not transparent. In 1992, General Electric (GE) demonstrated the technology for producing thick and transparent polycrystalline CVD diamond films (Anthony and Fleischer 1992). During this period, CVD diamond was grown at low growth rates up to a few $\mu\text{m h}^{-1}$ at substrate

temperatures below 1000°C in hydrogen gas mixtures with a low concentration of methane (typically 0.1–2%).

Under the auspices of the NSF Center for High Pressure Research, our group at the Carnegie Institution launched a program with the University of Alabama–Birmingham (UAB) in the mid-1990s to produce large homoepitaxial single-crystal diamonds. This work resulted in the development of the high-temperature (>1000°C) and relatively high-pressure (150 torr) processes that led to the growth of single-crystal diamond at very high growth rates (Yan 1999). During the current decade, developments in this technique have overcome some of the constraints of HPHT methods. The technique can be used to coat diamonds on various materials, control the doping with other elements, and grow diamonds of larger sizes. Single-crystal diamonds can now be produced at very high growth rates of 50–150 $\mu\text{m h}^{-1}$ (Yan et al. 2002), and the fabrication of these crystals can be tuned to exhibit remarkable mechanical properties (Yan et al. 2004).

CHEMICAL VAPOR DEPOSITION

Chemical vapor deposition (CVD) involves a series of gas-phase and surface chemical reactions and the deposition of reaction products, i.e., diamond, on a solid substrate surface. For diamond deposition, a carbon-containing precursor is required for diamond nucleation and growth. Many gas-phase carbon sources can be used, and methane is the most common. In 1981, it was found that adding atomic hydrogen to the CVD process stabilized the thermodynamically metastable diamond surfaces and promoted diamond growth, preferentially etching non-diamond carbon deposits and giving growth rates of the order of one $\mu\text{m h}^{-1}$ (Spitsyn et al. 1981). Unlike HPHT synthesis, which is typically carried out at pressures in excess of 5 GPa, diamond

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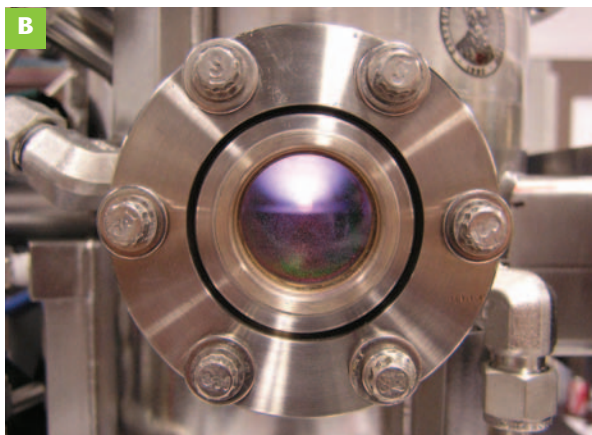
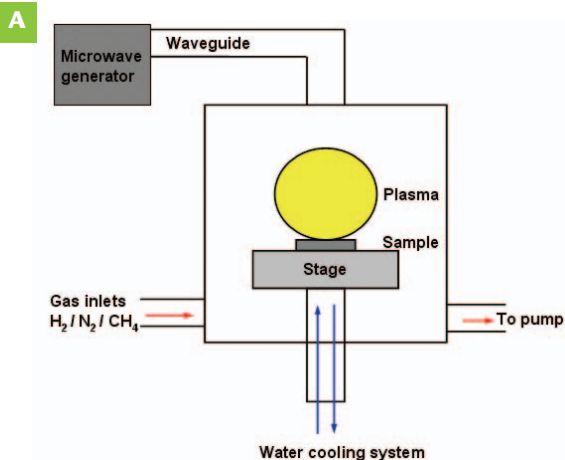


FIGURE 1 **A.** Schematic diagram of a microwave plasma CVD chamber; **B.** Photograph of a diamond growing in the CVD chamber (Model: SEKI AX5400). The substrates can be Si, Mo, or other materials for heteroepitaxial growth, as well as natural or synthetic diamond plates for homoepitaxy.

CVD is usually done at a fraction of one atmosphere. The deposition is controlled by strongly coupled parameters, all of which have an impact on the final product. In general, the substrate temperature, the concentration of plasma species, and the substrate materials determine the crystallinity of the growing material.

CVD techniques are generally applied using various methods to activate the gases to generate radicals responsible for the deposition. Electrical discharge CVD, especially microwave plasma CVD, is now the most widely used technique for diamond deposition (Fig. 1). Microwaves dissociate the molecules in the gas to generate a plasma containing carbon atoms for deposition onto the substrate surface. The substrate is heated by the absorption of microwaves, the bombardment by energetic plasma species, and exothermic recombination of radicals such as atomic hydrogen on the diamond growing surface.

SINGLE-CRYSTAL CVD DIAMOND

Single-crystal, homoepitaxial growth of diamond is being carried out by a growing number of research groups (Martineau et al. 2004). Homoepitaxial growth of single-crystal diamonds uses diamond as the substrate material. Several research groups have produced thin homoepitaxial layers, usually less than 0.1 mm thick. In the 1990s, fabrication of thicker layers was reported (Badzian and Badzian 1993; Janssen et al. 1990; Linares and Doering 1999; Plano



FIGURE 2 Modified, brilliant-cut, single-crystal diamond grown by CVD. The crystal is 2.45 mm high and was grown in one day. The top 0.5 mm (table) of the crystal is a yellow Type Ib HPHT substrate; thus the yellow tint is due to internal reflection (the CVD diamond is transparent and colorless) (Yan et al. 2004).

et al. 1994; Schermer et al. 1994). Most recently, the Carnegie group reported high-quality single crystals with thicknesses of 4.5 mm (Yan et al. 2004).

For bulk single-crystal diamond deposition, single-crystal diamond substrates are used, since the quality of the diamond films is strongly affected by the quality of the substrates. Single-crystal CVD diamond deposition on single-crystal HPHT synthetic substrates was accomplished in the early 1990s by plasma torch CVD (Snail et al. 1991) at growth rates of 100–200 $\mu\text{m h}^{-1}$, but there are significant difficulties with precise temperature and growth control with this technique. Growth by hot filament (Vitton et al. 1993) and microwave plasma (Tzeng et al. 1993; Vitton et al. 1993) yields stable growth conditions, but for years the growth rates were low (0.1–10 $\mu\text{m h}^{-1}$), and most plates produced were only 0.1–1 mm thick. Single-crystal CVD diamonds have been used by Element Six and Sumitomo in electronics applications (Isberg et al. 2002; Okushi 2001) and by Apollo Diamond as gems (Wang et al. 2003). Boron, whose presence in diamond transforms it from an electrical insulator into a *p*-type semiconductor, can be introduced during the growth process, and development of boron-doped CVD diamond for electronic applications is in progress (Kondo et al. 2002). Large-scale industrial production of single-crystal CVD diamonds has not yet occurred because of the high costs when the growth process is slow (such as 0.1–10 $\mu\text{m h}^{-1}$), the limited size of the substrates (maximum area around 10 × 10 mm), and the poisoning of surfaces by twins and polycrystalline structures (Angus et al. 1992; Tamor and Everson 1994). Many of these problems and limitations have recently been overcome.

Working originally with the UAB team, the Carnegie Institution group has focused on the growth of large, single-crystal CVD diamond for use as anvils in high-pressure research. Producing large and durable diamonds at high growth rates with high strength, absence of twinning, and optical transparency are the main goals and challenges. This work led to optimal conditions for enhancing growth rates and producing smooth, twin-free {100} diamond surfaces (Yan 1999). With high gas pressures of 150 torr, methane concentrations up to 20% in the CH_4/H_2 gas mixture, and the addition of a small amount of nitrogen gas, diamond growth rates of up to 150 $\mu\text{m h}^{-1}$ were achieved (Yan et al. 2002), much faster than the typical CVD diamond growth rate of 1 $\mu\text{m h}^{-1}$. The growth-rate enhancement with the addition of nitrogen is consistent with



FIGURE 3 **A.** Photograph of a typical, three-dimensional, as-grown CVD crystal sitting atop a type 1b substrate. The CVD layer is 1.2 mm thick and was grown in 12 hours. The yellow color is due to the substrate. **B.** Left: 5 × 5 × 0.5 mm diamond plate grown in about 5 hours by CVD. Right: plate produced by De Beers. **C.** Color changes after HPHT annealing: (i) brown, as-grown CVD layer deposited on yellow type 1b HPHT seed; (ii) annealed at 1900°C and 6.5 GPa for 1 hour—CVD layer turned blue; (iii) annealed at 2200°C and 7.0 GPa for 10 hours—CVD layer turned colorless while the substrate became light yellow (from Charles et al. 2004).

observations for polycrystalline diamond films (Muller-Sebert et al. 1996). This microwave plasma CVD method can routinely produce one 3 mm-thick, twin-free, gem-quality diamond in approximately one day (FIG. 2). Interestingly, single crystals produced in this way exhibit very high toughness (Yan et al. 2004).

In addition to controlling the variety of impurities that can be introduced for electronic applications, challenges for single-crystal CVD diamond growth include producing large-area plates (>10 × 10 mm) and large-volume crystals (>10 × 10 × 10 mm, >20 carats), as well as improving crystal quality (i.e., reducing strain). Microwave plasma CVD permits growth on a single surface of the diamond substrate. Potential solutions for producing larger area CVD diamonds include use of a mosaic or tile arrangement of several {100}-surfaced diamond seeds (Kobashi et al. 2003), 3-dimensional growth on multiple {100} faces, and enlargement of each surface (FIG. 3A).

Diamond produced by the high-growth process is classified as Type IIa (nitrogen <20 ppm) and can be made transparent (FIG 3B). On the other hand, yellow material grown under certain conditions can be subjected to high P-T annealing to produce transparent material. In fact, brown

single-crystal CVD diamond annealed at 2000°C and 5–7 GPa results in color changes (FIG. 3c) (Charles et al. 2004; Yan et al. 2004) (see also Shigley, this issue). In addition, the hardness of the material can be significantly enhanced, beyond that of conventional natural and as-grown synthetic diamonds (Yan et al. 2004). The high fracture toughness of the material prior to annealing and the enhancement of the hardness correlate with changes in the mosaic character of the crystals and transformation of residual carbon defects present in the as-grown crystals.

APPLICATIONS OF LARGE SINGLE-CRYSTAL CVD DIAMOND

A principal goal of the Carnegie effort has been to produce large, single-crystal diamonds for new classes of high-pressure devices (FIG. 4). These would be used to pressurize significantly larger samples at very high pressures and reach much higher pressures and temperatures in the laboratory (e.g., 500 GPa, or 5 megabars). For this, we need very large (e.g., many tens of carats), ultrastrong, single-crystal diamond material that is simply not available in nature and cannot be produced by current HPHT methods (Hemley and Mao 2002). Such diamonds will allow a broad range of

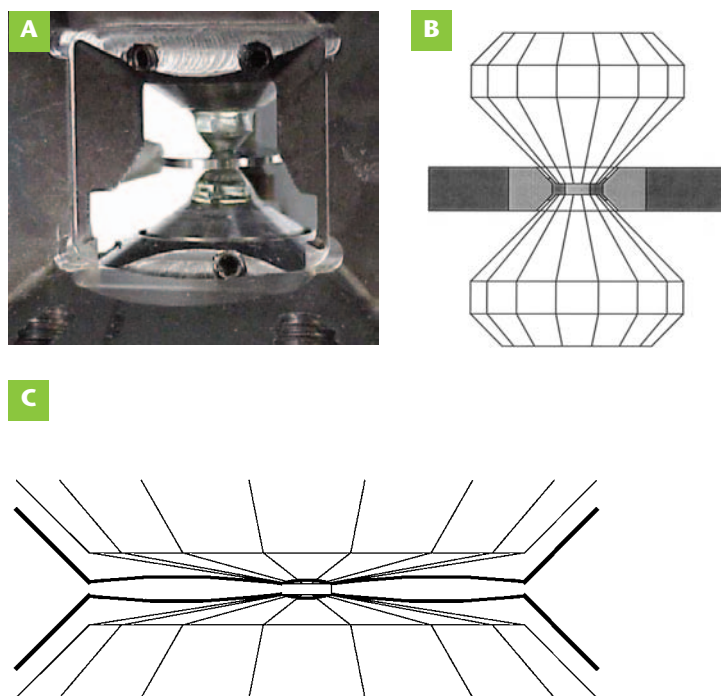


FIGURE 4 **A.** Example of a current 'panoramic' cell, shown here with 'conventional' 0.3 carat diamonds. This type of device can be scaled up in size for anvils in the tens of carat range (centimeter dimensions) and is also currently used with other high-strength gems such as moissanite (single crystal SiC) (Xu et al. 2004). In addition to using large diamond crystals with significantly larger culets, a 'belt' can be placed around the anvils (**B**) to provide additional support at higher loads and to increase sample thickness. The anvil tips can be shaped by micromachining techniques to further enhance sample volume. An example is shown in (**C**), which is the shape to which diamonds deform at very high loads (Hemley et al. 1997); it is also the pre-formed shape of 'toroidal anvils' used in lower pressure devices (see Hemley 1998). The sample volume is enhanced without sacrificing the versatility of conventional diamond anvil cells. This will make possible new kinds of experiments at very high pressures, such as NMR, inelastic neutron scattering, and in situ petrology studies.

experiments that cannot yet be performed under the P-T conditions that prevail not only within our planet but also within the larger planets in this and other solar systems. Already, the first experiments have been conducted at close to 200 GPa with CVD-grown diamond anvils (Mao et al. 2003).

There are many other applications of large, single-crystal CVD diamonds that derive from the unique hardness, toughness, electrical properties, and thermal conductivity of diamond. The excellent hardness and toughness of the single-crystal CVD diamond grown at high growth rate is potentially important for high-precision cutting tools. With diamond's uniquely high thermal conductivity and low coefficient of thermal expansion, fabrication of monolithic heat spreaders or microchannel structures from single-crystal CVD diamond would perform well beyond that of thin diamond films in high-power thermal management applications. The availability of large, transparent single-

crystal diamonds will greatly extend their use as far-infrared or high-power microwave windows. In each of these applications, chemical and thermal shock resistance is an important feature. Other applications include large electron field emission sources, micro-electromechanical systems, surface acoustic wave devices, and large semiconductor devices. In conclusion, with the rapid progress in the development of CVD diamond, and especially with advances in single-crystal diamond growth during the last 2–3 years, the full potential of diamond for a broad range of applications is being realized.

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Energy, Waste and the Environment: a Geochemical Perspective

All scenarios for the 21st century, however they may differ in detail, agree on one thing: the world energy consumption should steadily increase during the next decades, as a result of both the growth of the global population and the economic development of countries like China, India, and Brazil, which will have to satisfy an increasing domestic demand for consumer goods. It is predicted that the energy needs should be about 18 GTep in 2050 and 23 GTep in 2100, compared to 9.3 GTep in 2000 (GTep: gigatonnes equivalent petroleum). This massive increase in energy production will require the solution of complex technological and economic problems, as no energy source can meet the demand alone. In addition, these developments will generate huge amounts of gaseous, liquid, and solid wastes, which will have to be properly managed if we are to control and ultimately reduce the environmental consequences. The impact of energy-related wastes, whatever the source (petroleum, nuclear, renewable sources such as wind, sun, tides and biomass), cannot be neglected anymore, as the fluxes of matter released into the environment are now large enough to directly affect (bio)geochemical cycles and basic self-regulated processes at the Earth's surface. For instance, there is now a wide consensus within the scientific community that the continuous injection of huge amounts of carbon dioxide into the atmosphere since the beginning of the industrial revolution, essentially due to the consumption of fossil fuels, is responsible for global warming through the "green house effect". This will be a major issue for this century, and it will have to be dealt with in ways that will take into consideration all the political, ethical, economic, industrial, scientific, and technological aspects.

Energy, waste, and the environment are thus strongly linked terms that provide the title to this remarkable book, edited by Prof. R. Gieré and P. Stille, with contributions from a panel of world-class experts, and published by the Geological Society Publishing House. The book has an original perspective, as it focuses on geochemical approaches to the treatment, confinement, and dispersion of wastes generated by energy production and consumption. Its greatest merit is that it demonstrates that international research at the highest level is being carried out on energy-related wastes and, therefore, that the scientific community is dealing with the issue

as seriously as possible. Indeed, this field has become, in less than three decades, a major area of interaction between science and society, in which diverse considerations and interests are intimately entangled. Through thirty-six contributed chapters, the reader is led to a deep understanding of the main environmental issues and the techniques developed to determine the fate of these wastes when released or disposed of in nature. In particular, emphasis is put on the use of the so-called "natural analogues" to build strategies for the confinement of toxic and radioactive components in natural systems over extremely long periods of time, a procedure that cannot be properly simulated in the laboratory. Natural analogues are diverse materials and geochemical processes, occurring in a range of geological (or even archaeological) sites, that can be investigated by scientists. Analogues contribute to the development of waste immobilization techniques, the design of disposal concepts, the confirmation of key mechanisms identified in laboratory experiments, and the testing of the robustness and credibility of models. Such a combined approach guarantees, with reasonable confidence, the stability and safe isolation of wastes in the environment. In particular, thermodynamic modeling and kinetic concepts are critical geochemical tools in this respect. All these aspects are described in the book.

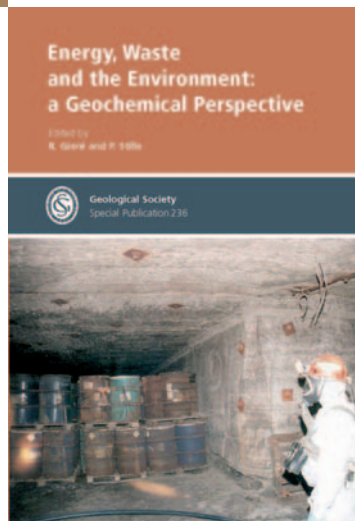
The five sections of *Energy, Waste and the Environment: a Geochemical Perspective* contain numerous and thought-provoking ideas, a few of which I shall highlight. The first section deals with issues related to the nuclear fuel cycle. It is argued that advanced fuel cycles and waste management technologies must be developed if this source of energy is to contribute significantly to decreasing the carbon dioxide concentration in the atmosphere. Due to the very long time spans over which safety must be

guaranteed for the underground disposal of nuclear wastes, the role of natural analogues is emphasized. The fossil fuel cycle is discussed in the second part of the book. The reduction of carbon dioxide emissions is envisaged through injection and trapping in deep geological formations. In addition, the mineralogical and geochemical characterization of mining and combustion wastes appears essential to assess the environmental impact of the extensive use of coal. Among alternative sources, the exploitation of geothermal heat, supposedly an environment-friendly technology, is described in part four of the book as generating huge amounts of waste fluids. The deep underground reinjection of these fluids is explored as a possible way to minimize their environmental impact. The fifth part of the book deals with the waste-to-energy cycle. The interesting idea of considering "wastes" as a possible

source of valuable chemical components and energy (an idea already defended in the fifties but since forgotten) is discussed. Finally, water-waste interactions, which are the main ways in which toxic and radioactive elements can be released and dispersed in the environment, are carefully examined in part six.

In conclusion, this timely book demonstrates that geochemistry is a key science to help us solve the difficult environmental issues raised by the world's economic development.

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WANTED

The Hudson Institute of Mineralogy, a not-for-profit organization chartered by the Board of Regents of the State University of New York is seeking used analytical equipment, thin sections and mineral specimens for its descriptive mineralogical laboratory and educational programs. We are dedicated to classical mineralogical research, preservation of mineral specimens, and educational outreach to primary and secondary school teachers and students. If your institution is upgrading its analytical equipment, we want your used, working devices. Further, if you are disposing of minerals, thin sections or similar geological artifacts, let us put them to good use; aesthetics are unimportant, labels are! Please contact:

The Hudson Institute of Mineralogy
PO Box 2012 • Peekskill, NY 10566-2012
www.hudsonmineralogy.org

R. Gieré and P. Stille (editors) 2004. *Energy, Waste and the Environment: a Geochemical Perspective*. Geological Society of London, Special Publication 236, 688 pp, ISBN 1-86239-167-x, 135 £



European Association for Geochemistry



FROM THE PRESIDENT

The European Association for Geochemistry (EAG) is delighted to be joining this great new publishing venture, which I hope heralds a renaissance for learned societies in the fields of geochemistry and mineralogy. I am very pleased to have this opportunity to congratulate the whole *Elements* editorial team on an outstanding first issue that has established a benchmark of quality for the future. This is going to be a publication that gets opened and read when it arrives! We may be late to the party, but the EAG is in the process of expanding its range of activities, and we hope to be able to make valuable contributions to *Elements* in the future.

Bruce Yardley, EAG President

EAG NEWS AND ANNOUNCEMENTS

A Few Words about EAG

Founded in 1985 to promote geochemical research and study in Europe, EAG is now recognized as the premiere geochemical organization in Europe encouraging interaction between geochemists and those of associated fields, and promoting research and teaching in the public and private sectors. Visit our website at www.eag.eu.com

Development of European Web Network Database

Towards the integration of geochemistry in Europe, the EAG is currently building a web directory of active European geochemists and geochemistry groups. We encourage you to list your personal and/or group website in this database. To include yourself and/or your research group in this database, simply send an e-mail to m.e.hodson@reading.ac.uk Include website address, your name or group name, country, and a SHORT descriptive title. Examples might include:

www.aschmidt.xyz,
Anne Schmidt, Germany, stable Fe isotopes, or

www.johnsmith.xyz,
John Smith, England, molecular dynamics modeling, or

www.unipa.l'enviro.xyz,
Environmental Geochemistry Centre, France, weathering processes and the water cycle.

UPCOMING EAG-SPONSORED MEETINGS/SESSIONS

European Geosciences Union General Assembly 2005, Vienna, Austria, April 24–29

The EAG is co-sponsoring three sessions at the 2005 EGU General Assembly (<http://www.copernicus.org/EGU/ga/egu05>)

SESSION GM4: Climatic and tectonic controls on the Earth's weathering system

Convenor: F. von Blanckenburg;
co-convenors: K. Burton and S. Gíslason

Weathering and erosion are amongst the primary processes responsible for the evolution of the landscape and affect the cycles of many elements at the Earth's surface; both are influenced by active tectonics or climate change. This session aims to bring together the range of approaches used to study the chemical, physical, and biological processes involved in weathering and erosion, both today and in the past. Contributions will deal with field, experimental, and modeling studies, including work on catchment areas and deltas, soils, hydrology, vegetation, lithology, and topography.

SESSION VGP24: Application of novel geochemical techniques to problems of cosmochemistry and early Earth evolution

Convenor: C. Münker;
co-convenors: S. Weyer and T. Elliott

The understanding of processes active during the first billion years of the solar system and the Earth strongly relies on geochemical criteria because any direct rock record is either absent or very scarce. In the past decade, new techniques such as MC-ICP-MS, high precision TIMS or microanalytical developments have spurred investigations of early solar system materials and old terrestrial rocks. Major breakthroughs include the application of new extinct nuclide series, non traditional stable isotopes, and the search for nucleosynthetic and elemental anomalies in small particles. The aim of this session is to provide an overview of the current state of knowledge with an emphasis on new geochemical techniques and concepts.

SESSION VGP12: Geochemical ins and outs of subduction zones

Convenor: C. Chauvel;
co-convenor: W. Sun

This session aims at evaluating the geochemical budget of subduction zones. Approaches to this budget can be related to the composition of oceanic crust that will be subducted, to the composition and variability of the sedimentary piles, and to the quantification of the subducted material. Geochemical studies centered on the composition of volcanic arcs and of the materials found in back-arc and fore-arc basins are also central keys for the general budget. Confrontation of these different approaches should help our community to decipher the complex processes occurring in one of the key environments of our planet and consequently to better understand its long-term evolution.

The 15th Annual Goldschmidt Conference: A Voyage of Discovery, Moscow, Idaho, USA, May 20–25

The Goldschmidt Conference is the premier annual meeting in geochemistry and mineralogy. The 2005 meeting will cover the full range of geochemistry from cosmochemistry to the origin of life. It will be special because 2005 is the 50th anniversary of the Geochemical Society. Come celebrate this anniversary in the foothills of the Rocky Mountains! The conference also takes place during the bicentennial of the Lewis and Clark expedition—the Corps of Discovery.

Seventh International Symposium on the Geochemistry of the Earth's Surface (GES-7), Aix-en-Provence, France, August 23–27

The principal focus of past meetings has been on processes operating at the surface of the Earth rather than on deep crustal geochemical processes. The GES-7 meeting continues that overall theme with some greater emphasis on the multiscale environmental biogeochemistry of the Earth's surface and subsurface (www.cerege.fr/GES7). The technical sessions will consist of invited

EUROPEAN GEOCHEMICAL NEWS BRIEFS

oral contributions and posters that complement the themes of the oral presentations. All contributions must be accompanied by a four-page abstract. The abstracts will be reviewed and published in a special issue of *Journal of Geochemical Exploration*, a sister publication of *Chemical Geology*. Abstract submission deadline is April 1, 2005.

The themes of the symposia are:

1. Environmental impact of waste management
2. Water cycle and resources: geochemical tracers and contaminants
3. Biogeochemical processes in soils and ecosystems: from molecular to landscape scale
4. Weathering: processes, rates and ages
5. Coastal biogeochemistry: from land to continental slope
6. Global element cycles and climate change through Earth history

Update on the European Research Council

The creation of a new European Research Council (ERC) is reported to be gaining support in Brussels. All but two of the European Union members officially supported the creation of the ERC during a November 2004 meeting and have requested the European Commission to draft a formal proposal. The ERC is to be a new funding agency that would support basic research in all areas of science based solely on scientific quality; this agency would be similar to the National Science Foundation in the United States. The ERC would be created as part of the Seventh Framework Program and would start in 2007. The estimated ERC budget for the seventh framework (2007–2010) is rumored to be approximately 2 billion Euros.

Opening of the new Earth Sciences Institute, Toulouse, France

In June 2004, the Laboratoire des Mécanismes et Transferts en Géologie (LMTG) abandoned its old laboratories in the center of



Toulouse to move into a new state-of-the-art research and teaching facility near the main campus in Rangueil. The laboratory is composed of 72 researchers and academic staff, 40 administrative and technical staff, 36 students, and 6 postdoctoral fellows. The LMTG is devoted to studying the interactions between water and the solid Earth, from the mantle to the biosphere. The particular strength of the LMTG is that it can master the whole range of scientific concepts as well as most of the analytical and experimental methods needed to make a significant contribution to this challenging scientific problem. Members of the permanent staff of the LMTG include its director, Bernard Dupré, Jacques Schott, and Eric Oelkers (website: www.lmtg.obs-mip.fr).

New Earth Sciences Institute, opened in the summer of 2004, Toulouse, France.

Cosmochemistry. The Head of School is Professor Richard Pattrick. The Director of Research is Professor David Vaughan.

European Weathering Systems Science (WSS) Initiative

European scientists, with support from the Worldwide Universities Network, convened a round table discussion in London on October 14, 2004, creating a scientific framework for a joint European–US research program in Weathering Systems Science (WSS). This London meeting established a commitment between European and US researchers to pursue a jointly directed program between the EC and NSF to build an international WSS Consortium contributing to the delivery of EU research on the sustainable management of soils (EU Soil Directive, now being drafted) and sustainable management of water (EU Water Directive, now being implemented). At present the European and international communities are addressing many of the outlined weathering and soil issues, but in a fragmented manner. The European WSS Initiative proposes to advance, in a holistic way, our knowledge of the life cycle of the entire soil system by using an integrated multidisciplinary approach. Contact K.V. Ragnarsdottir at vala.ragnarsdottir@bris.ac.uk

Creation of new School of Earth, Atmospheric and Environmental Sciences in Manchester

The recent merging of the University of Manchester with UMIST in October 2004 has led to the formation of a new School of Earth, Atmospheric and Environmental Sciences (website: www.seaes.manchester.ac.uk). Largely comprising staff from the former Department of Earth Sciences at the University of Manchester and the Atmospheric Chemistry and Physics Group in the Physics Department at UMIST, the new school has research strengths in atmospheric physics and chemistry, physics and chemistry of minerals and fluids, geochemistry including environmental geochemistry, petroleum geology and basin studies, isotope geochemistry, geomicrobiology, structural geology, and experimental rock deformation. Facilities include those of the Williamson Research Centre for Molecular Environmental Science and of the Centre for Isotope Geochemistry and

Please send any potential items for inclusion in future EUROPEAN GEOCHEMICAL NEWS BRIEFS to either Eric Oelkers (oelkers@lmtg.obs-mip.fr) or Mark Hodson (m.e.hodson@reading.ac.uk).

SEVENTH INTERNATIONAL SYMPOSIUM ON THE GEOCHEMISTRY OF THE EARTH'S SURFACE (GES-7)

AIX-EN-PROVENCE, FRANCE



AUGUST 23-27, 2005

web-site: <http://www.cerge.fr/GES7/ges7second.htm>

The GES organization is a working group of the International Association of Geochemistry and Cosmochemistry (IAGCC). Past meetings of the working group have been held in Granada, Spain (1986), Aix-en-Provence, France (1990), University Park, Pennsylvania, USA (1993), Ilkley, England (1996), Reykjavik, Iceland (1999) and Honolulu, Hawaii (2002).

The principal focus of the past meetings dealt with processes operating at the surface of the Earth. The GES-7 meeting continues that overall theme with some greater emphasis on the multiscale environmental biogeochemistry of the Earth's surface. The major venues of presentation at the technical sessions are invited oral contributions and posters that complement the themes of the oral presentations.

Aix-en-Provence: a living history book

Aix-en-Provence is located in the Southeast of France, near the Mediterranean Sea. Aix-en-Provence is a town of sun, water and fountains, a town of art and culture with a rich patrimony. From the celtic-roman Oppidum of Entremont to the new Sestius-Vinobaou Quarter, with the City of Counts and the many mansions of the Mazarin Quarter, Aix-en-Provence is a living history book. <http://www.aixenprovence tourism.com>



Important dates

1st December 2004: Call for Abstract
13th January 2005: Opening of early registration
1st April 2005: Abstract deadline
May 2005: Deadline for early registration
August 23-27, 2005: GES-7 in Aix-en-Provence, France

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International Association of GeoChemistry



FROM THE PRESIDENT

We are pleased to join *Elements*, not only because of the timely advent of this publication, but also because of the need to build links between the major geochemical and mineralogical societies of the world.

Many of you will have known the IAGC, now the International Association of GeoChemistry, by its former name, the International Association of Geochemistry and Cosmochemistry. This subtle change reflects the "new look" of the Association, which has involved a migration away from the more fundamental fields of geochemistry towards applied research. This is reflected, not only by IAGC's association with the journal *Applied Geochemistry*, but also by the working groups and special symposia organised by the Association, for example in geochemistry and disease, the Water-Rock Interaction meetings, and geochemistry training in developing countries. We hope to use the magazine to build links with other societies and expand the knowledge of geochemistry worldwide.

John Ludden, President IAGC

ACTIVITIES OF THE IAGC

This year has seen some big events and changes for the IAGC. First, the Annual Council Meeting was held in conjunction with the International Geological Congress (IGC) in Florence, Italy, on August 20. The meeting was well attended by both council members and chairmen of IAGC working groups. Two meetings were held, in fact. The first included a vote by the outgoing council and executive members, who had served for up to the last eight years, to appoint new officers. In the subsequent meeting, the new statutes were approved and, more significantly, the name of the IAGC was changed from the International Association of Geochemistry and Cosmochemistry to the International Association of GeoChemistry. This change reflects the shift in

emphasis of IAGC members over the years, away from theoretical geochemistry and cosmochemical research, to applied geochemistry, especially in the biogeochemical, medical, and environmental fields. This is borne out by the fact that the IAGC's journal, *Applied Geochemistry* has become an important and increasingly read journal in the geological world.

One of the main aims of the IAGC is to sponsor symposia and international meetings on various aspects of geochemistry, primarily through its working groups but also through a conference grants program. For instance, the IAGC sponsored a thematic session entitled "Frontiers in Analytical Geochemistry" at the International Geological Congress, in Florence, Italy, last year, and a

THE INTERNATIONAL INGERSON LECTURE

The International Ingerson Lecture originated from a bequest by Earl Ingerson to the International Association of Geochemistry and Cosmochemistry in 1985 to provide an award for distinguished geochemists. The award, which includes a framed certificate and a \$500 honorarium, is given every two to four years. To distinguish this award from the Ingerson Lecture Award presented by the Geochemical Society (from a similar bequest by Earl Ingerson), the IAGC in 2002 designated the award as the *International Ingerson Lecture*. The recipient is invited to present the lecture at a suitable international geochemical meeting, such as the Goldschmidt Conference, where the award is presented.

The *International Ingerson Lecture* for 2004 was delivered in Florence, Italy at the 32nd International Geological Congress



Stephen Moorbath (right) receiving award from IAGC President John Ludden

by Prof. Stephen Moorbath of Oxford University and was entitled "Oldest rocks, earliest life, heaviest impacts, and the Hadean-Archaean transition". The full text of Professor Moorbath's presentation will be published shortly in *Applied Geochemistry*. Previous recipients of the award have included A.E. Ringwood, A.A. Levinson, K.-H. Wedepohl, A. Masuda, D.M. Shaw, U.G. Cordani, and B.F. Jones.



collection of papers on this will appear in the near future as a special issue of *Applied Geochemistry*. In 2005, IAGC will also sponsor a special session on archaeological geochemistry at the April EGU meeting in Vienna, and will join in the sponsorship of the 15th Goldschmidt Conference in Moscow, Idaho in May (see article next page). IAGC will also be a general sponsor of the International Symposium on Applied Isotope Geochemistry in Prague on September 11-16 (AIG-6).

At present IAGC has seven working groups: Water-Rock Interaction, Global Geochemical Baselines, Geochemistry of the Earth's Surface, Applied Isotope Geochemistry, Thermodynamics of Natural Processes, Geochemical Training in Developing Countries, and Geochemistry of Health and Disease. The activities of each of these will be featured in upcoming issues of *Elements*.

The IAGC has recently revised its website, which now contains information on the Association, its history, details of sponsored meetings, the biannual Newsletter, how to join, and the activities of the working groups. The site address is <http://www.iagc.ca>.

APPLIED GEOCHEMISTRY, THE JOURNAL OF THE IAGC

Applied Geochemistry is the official journal of the International Association of GeoChemistry. The journal was launched in 1986 under the editorship of Brian Hitchon. The early volumes of the journal consisted of around 700 pages in six issues. The journal has expanded dramatically since those early days with 2000 pages being published in the twelve issues of volume 19 in 2004.

Applied Geochemistry is an international journal devoted to publication of original research papers, rapid research communications, and selected review papers in geochemistry that have some practical application to an aspect of human endeavour, such as the preservation of the environment, environmental monitoring, agriculture, health, waste disposal and the search for resources. Topics covered include:

1. Environmental geochemistry (including natural and anthropogenic aspects, and protection and remediation strategies)
2. Hydrogeochemistry, surface and groundwater
3. Medical geochemistry
4. Agricultural geochemistry
5. The search for energy resources (oil, gas, coal, uranium, and geothermal energy)
6. The search for mineral deposits (metalliferous and non-metalliferous)
7. Upgrading of energy and mineral resources where there is a direct geochemical application
8. Waste disposal including the specific topic of nuclear waste disposal.



Papers on applications of inorganic, organic, and isotope geochemistry are therefore welcome provided they meet the main criterion. The executive editor is Ron Fuge (Institute of Geography & Earth Studies, University of Wales, Aberystwyth, Ceredigion, Wales SY23 3DB, UK. Fax: +44 (0) 1970 622659, e-mail: rrf@aber.ac.uk). IAGC members benefit from discounted subscription cost for *Applied Geochemistry*.

Some of the papers scheduled to be published in the early part of 2005 are listed below.

- J. Jönsson, P. Persson, S. Sjöberg, and L. Lövgren: Schwertmannite precipitated from acid mine drainage: phase transformations, sulphate release and surface properties.
- J. E. Gray, D. L. Fey, C. W. Holmes, and B. K. Lasorsa: Historical deposition and fluxes of mercury in Narraguinnep Reservoir, southwestern Colorado, USA.
- D. N. Castendyk, J. L. Mauk, and J. G. Webster: A mineral quantification method for wall rocks at open pit mines, and application to the Martha Au-Ag mine, Waihi, New Zealand.
- B. L. Brown, A. D. Slaughter, and M. E. Schreiber: Controls on roxarsone transport in agricultural watersheds.
- G. Jaks, P. Bhattacharya, and V. Chaudhary: Controls on the genesis of high-fluoride waters in India.
- M. A. Glaus, B. Baeyens, M. Lauber, T. Rabung, and L. R. Van Loon: Influence of water-extractable organic matter from Opalinus Clay on the sorption and speciation of Ni(II), Eu(II) and Th(IV).
- R. L. Seiler, K. G. Stollenwerk, and J. R. Gabarino: Factors controlling tungsten concentrations in ground water, Carson Desert, Nevada.
- Z. Cheng and K. A. Foland: Lead isotopes in tap water: implications for Pb sources within a municipal water supply system.

THE GOLDSCHMIDT CONFERENCE 2005

For the first time, IAGC is collaborating with the Geochemical Society, the European Association for Geochemistry, and the Mineralogical Society of America to sponsor the 15th annual Goldschmidt Conference. This premier international geochemistry conference (www.uidaho.edu/gold2005) will be held in Moscow, Idaho (USA) from 20 to 25 May, 2005. IAGC will organise the three symposia described below. Interested geochemists are encouraged to participate in this special conference and, if appropriate, one of the three IAGC-sponsored sessions.

The geochemistry of mercury – session SS-74

Conveners: John Gray (jgray@usgs.gov), U.S. Geological Survey, and Mark Hines (Mark_Hines@uml.edu), University of Massachusetts

There is currently abundant research involved in the evaluation of natural and anthropogenic mercury contamination of the air, land, water, and wildlife worldwide. Presentations in this session will discuss the global mercury cycle, mercury distribution and speciation at contaminated sites, and mercury cycling in terrestrial and aquatic systems.

The halogens and their isotopes in marine and terrestrial aqueous systems – session SS-75

Conveners: Glen Snyder (gsnyder@rice.edu), Rice University and Jean Moran (moran10@llnl.gov), LLNL

The generally conservative nature of halides in groundwater and marine systems has led to their

application as tracers in marine and hydrological systems. Over the past 25 years, the development of accelerator mass spectrometry (AMS) techniques for determination of I-129 and Cl-36, along with the development of stable isotope techniques for chlorine, has opened up new avenues for examining halogen migration and residence times. The goal of this session is to provide a forum to address any aspect of the halogens and their relation to aqueous systems, including the interactions between ocean, soil, freshwater, and atmospheric reservoirs.

Watershed-scale geochemistry – session SS-81

Conveners: Berry Lyons (lyons.142@osu.edu), Ohio State University, and David Long (long@msu.edu), Michigan State University

The focus of this session is geochemistry at the watershed scale. Of specific interest are the geological, mineralogical, and geochemical nature of sources and sinks and their impact on local and global geochemical cycles; the factors determining mineral alterations at the Earth's surface; geochemical kinetics of mineral-water interactions during rock weathering; the hydrological, hydrochemical, and biogeochemical processes that occur along fluid pathways and influence the migration of elements through the landscape; and the geochemistry of human impacts on watersheds.

GORDON RESEARCH CONFERENCE ON INORGANIC GEOCHEMISTRY AND ORE DEPOSITS**Metals in ore-forming systems: Sources, transport, and deposition**

PROCTOR ACADEMY, ANDOVER, NEW HAMPSHIRE, JULY 31 – AUGUST 5, 2005

The Gordon Research Conference on Inorganic Geochemistry addresses the geochemistry of metal-rich systems. The organizers are seeking expressions of interest from those who wish to participate. Subsidies for students and junior level participants are anticipated, particularly for those presenting posters. We also seek the participation of women and members of minority groups.

A preliminary program and conference details are available at www.grc.uri.edu/programs/2005/inorggeo.htm. The organizers are Jean Cline, Steve Garwin (steve.garwin@geoinformex.com), and Chris Heinrich (heinrich@erdw.ethz.ch). Those who wish to participate should contact Britt Meyer by e-mail at meyer@erdw.ethz.ch. Those who wish to present a poster are invited to send a brief abstract together with expression of interest. To apply for funding, contact Jean Cline (cline@ccmail.nevada.edu).



The Clay Minerals Society

In Memory of Robert Coltart Reynolds Jr.

October 4, 1927–December 12, 2004



Bob Reynolds in 1983-1984. PHOTO FROM DARTMOUTH COLLEGE'S ARCHIVES.

Born to Ludmilla and Robert C. Reynolds Sr. on October 4, 1927, in Scranton, PA, Robert C. Reynolds Jr. was a 1945 graduate of Dalton (PA) High School. After serving in the Army Air Force, he graduated from Keystone Junior College and Lafayette College. He then earned his doctorate from Washington University in St. Louis in 1955. After working for Pan-Am Petroleum for five years, he went to Dartmouth College in 1960 where he rose to the Frederick Hall Professor of Mineralogy Chair. Prof. Reynolds, a Distinguished Member of The Clay Minerals

Society and a Brindley Lecturer, was president of the Society in 1991–1992. He received the Roebling Medal from the Mineralogical Society of America, its highest award and recognition. The Clay Minerals Society has created a Robert C. Reynolds Jr. Research Award and supports the awarding of the Reynolds Cup at a biannual contest to quantitatively analyze samples of mixtures of clay-size minerals. He leaves behind, in addition to the inspiration he has given to generations of students, a long list of seminal papers. Perhaps the most influential of these is his 1967 paper in volume 52 of *American Mineralogist*, "Interstratified clay systems: calculation of the total one-dimensional diffraction function", which is the basis of his computer program, NEWMOD[®]. In 1994 he added WILDFIRE[®], a program for calculating the three-dimensional X-ray diffraction tracing of illite polytypes and degrees of disorder in illite and illite-smectite mixed-layered minerals. It is not an exaggeration to say that these programs have revolutionized the way in which clay minerals and other layered minerals are studied.

Professor Reynolds's journey through life ended on Sunday, December 12, 2004. In the course of that journey, he accomplished much and touched the lives of many. Robert (Bob) C. Reynolds Jr. grew up in tiny Dalton, just 12 miles from Scranton. How tiny you ask? There were 16 in his 1945 high school graduating class, 14 of whom had been in the first grade with him. While at Lafayette College, he married Roseann Fabio from Scranton. They had met and become sweethearts while in high school. They had three children, Fayette, Jolene, and Bob III. Fate brought Bob and John Hower together at Washington University, where they met standing in line to register for classes. They became lifelong friends in the fullest sense of the word. At Dartmouth College, Bob became an institution. He was too broad a man for any one of us to have known him completely. He is remembered by each person he touched, but each in a different way. The composite of these memories, some of which are expressed below, conveys the sense of this influential man.

“

Bob was known as an outstanding teacher amongst the geology students at Dartmouth. I remember Bob's teaching style as a mix of clear explanations, organized lecture style, practical lab exercises, hands-on review sessions, experiments and field trips, and use of humorous and illustrative analogies (e.g., in an undergraduate mineralogy class, deconstructing the complexity of XRD patterns by drawing an elephant on the board and asking us what it was, then pointing out that these XRD patterns he was showing us were no more than mere representations of mineralogical structures, much like his elephant was just a representation of a living creature). Outside of the classroom, Bob's humbleness sometimes made it hard for him to understand that he understood his field at a level that left him with few peers. This did not translate to his classes, which were so well taught, but rather to the informal conversations that groups of students and faculty have together. I remember leaving his office with other grad student colleagues and professors and just marveling, both at Bob's wondrous mind, and also his cluelessness about how smart he really was.

Jim Aronson, Page Chamberlain, Mike Poage, and I went to see Bob and Roseann a couple of years ago. After a while Roseann left the room. Bob peered around the corner, said, 'Is she gone?' then pulled out a cigarette and lighter. He was on O₂ and had a hissing supply tank over in the corner of the room. As he flicked the lighter, all four of us flinched, our faces showing fear of explosion. Bob chuckled and said 'Don't worry, I've done the calculations, there's not enough free oxygen in the air to cause an explosion.' We all laughed, in part because it was so fun to laugh with Bob, perhaps in part due to nervous release, but it summed up so much about Bob—his hell-be-damned attitude and penchant for living on the edge, his boyish approach to certain things (as if Roseann leaving the room for five minutes would keep her from knowing that he had just smoked), and his analytical approach to life.

Peter Ryan

When we were students at Dartmouth, we all called him the Big Guy, and thoroughly meant it in scientific stature, love and zest of life, total inspiration, and not just girth.

Dougal McCarty

Bob and Denny (Eberl) taught me how to climb when I first got to Dartmouth, and I climbed quite a bit with Bob in those days. When I was finishing my Master's with Bob at Dartmouth, he just sent me to John (Hower) to do a PhD; I never asked what I should do next or about continuing grad studies; Bob just SENT me to John. It was like he was giving me to his friend. He was so god-damned strong and energetic as a young man; I guess that's how he survived so long with all the alcohol and cigarette smoke he pumped into himself. I'm still coming to terms with his dying.

Gray Thompson

The most distinctive aspect of Bob Reynolds for me is that I have never run into anybody who had an unkind thing to say about him. How can someone who has been such a leader, who has had to make tough decisions, accomplish this? I don't have the answer. Perhaps it was his exercise of tolerance for the views of everyone, not just the elite; perhaps it was that such a great scientist could be so modest; perhaps it was his finely tuned sense of fairness; perhaps it was his great sense of humor. Whatever it was, I hope we as a clay society can find a way to honor him for being such a great scientist and a great person.

Herman Roberson

I know Professor Reynolds as a brilliant scientist, and without any exaggeration one may state that he is the best-known expert in the world on X-ray diffraction analysis of finely dispersed layer compounds and, first of all, of clay minerals.

Victor Anatolievitch Drits

Bob always had to do things for himself. He didn't just use someone's equation. He had to derive the whole thing to be sure he understood it and that it was correct. He was very "hands on" in the lab and in everything. When he needed to know the time of day, he'd build a clock! Fred Mumpton once told me that Reynolds' papers were just about the only ones submitted that needed no editing. They were always perfect. Hower said Reynolds was the smartest person he knew.

David Pevear

Some things you might not have known about Bob Reynolds: The day he was awarded the title Distinguished Member of CMS, he came to the room almost disabled with astonishment. I think his humility prevented him from anticipating that others saw him in that category. Or, that he really appreciated classical music. His favorite piece was Mahler's Ninth Symphony. Or, that there was a Mozart piece that he associated with working with John Hower in Venezuela and, when he heard it, it brought tears to his eyes. Or, that he was a student of World Wars I and II. Or, that he built his own rifle from scratch. Or, that he changed the shock absorbers on his motorcycles every 5000 miles whether they were apparently worn or not. Or, that he delighted in the challenge of identifying mushrooms and then testing that identification by eating them. He was full of stories about the awful things the wrong mushrooms would do to you. Or, that if *you* were interested in something, *he* was interested in it.

I loved him; we all loved him.

Dewey Moore

STUDENT RESEARCH GRANTS AWARDED

The CMS congratulates the following eight students upon receiving research grant awards for 2004:

Michael K. DeSantis, University of Cincinnati, "Regional Correlation of the Tioga K-bentonites Cluster Using Apatite Trace Element Fingerprinting"

Cinzia Fissore, Michigan Tech, "Effect of Temperature and Clay Minerals on Long-term Soil Carbon Stabilization"

Michelle Leigh Foster, The University of Montana, "K-Bentonites in the Belt Supergroup, Montana"



Debra Jennings



Deb Jaisi

Deb P. Jaisi, Miami University, "Investigation of Microbially Mediated Clay Mineral Reaction"

Debra S. Jennings, University of Kansas, "A Paleoenvironmental Analysis of Morrison Formation Deposits, Big Horn Basin, Wyoming: A Multivariate Approach"



Pankaj Kulshrestha

Pankaj Kulshrestha, SUNY-Buffalo, "Investigating the Molecular Interactions of Oxytetracycline in Clay and Organic Matter"

Scott Mitchell, Brigham Young University, "An Improved MUSIC Model for Gibbsite"

Gayle Anthony Ordway, Portland State University, "Origin of Vermiculite in Well-drained Soils of the Southern Oregon Coast"

STUDENT RESEARCH GRANT APPLICATIONS

DUE MARCH 21, 2005

Grant applications for partial financial support of master's and doctoral student research in clay science and technology are due at the Society Office by March 21. Applications will be judged based on the technical quality of the research proposal, the qualifications of the applicant, and financial needs of the research project. The grants in amounts of up to \$2500 each will be awarded by September 2005. There is no restriction with regard to nationality, and a student does not need to be a member to apply. Application forms and instructions are available at www.clays.org or from the Society Office (cms@clays.org). Electronic submission is preferred.

STUDENT TRAVEL GRANT APPLICATIONS

DUE MARCH 21, 2005

Grants in amounts of up to \$500 per grant for students traveling within the country or region of the CMS Annual Meeting and in amounts of up to \$1000 per grant for students travelling overseas to the meeting are due at the Society Office by March 21. There is no restriction as to nationality. Students must submit an abstract for either an oral or poster presentation to the CMS Annual Meeting (www.middlebury.edu/cms). Application forms and instructions are available at www.clays.org or from the Society Office (cms@clays.org). Electronic submission is preferred. Applicants will be notified within about six weeks, in time to make travel arrangements for the meeting.



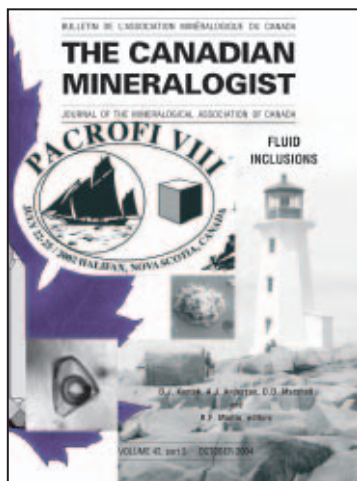
Mineralogical Association of Canada

FLUID AND MELT INCLUSIONS Alive and Well Thank You!

Daniel J. Kontak

The October issue of *The Canadian Mineralogist* includes a collection of papers stemming from the biennial meeting of the Pan-American Conference on Research on Fluid Inclusions (PACROFI) held in Halifax, Nova Scotia, in July 2002. These biennial meetings have provided a stimulating forum, for both advanced researchers and budding enthusiasts, on fluid and melt inclusion research over the past two decades. The collected abstracts (available at kontakdj@gov.ns.ca) and recently published papers cover such diverse topics as experimental techniques, novel analytical methods, P-T-t modeling of liquid petroleum inclusions, the assessment of ore deposit environments, culturing ancient microorganisms in primary fluid inclusions of halite, the documentation of Lower Paleozoic sea water chemistry, etc. Collectively the abstracts and papers reflect an area of active, vibrant, and exciting research. Below is a summary of the published papers.

The issue commences with applications of analytical techniques and theoretical modeling to extract meaningful data from inclusions. Linnean et al. use Fourier infrared spectroscopy on inclusions with varied mixtures of H₂O and CO₂ to deduce an empirical equation relating absorbency to the H₂O:CO₂ ratio. Bakker addresses the issue of determining salinity and ion ratios in inclusions by combining cryogenic Raman spectrometry and microthermometry in mixed H₂O-NaCl-MgCl₂ inclusions. An alternative method for determining solute chemistry is presented by Kontak, who describes the imaging and analysis (EMPA) of artificially generated evaporate mounds from inclusions. In contrast, a more rigorous analytical technique to define inclusion chemistry is presented by Gagnon et al., who integrate thermometric measurements with laser ablation ICP-MS in a real case example. In a novel paper, Elwood Madden et al. report on simulation of shock-induced re-equilibration of fluid inclusions



to prepare the way for examining inclusions in extraterrestrial objects and impact sites. Finally, Burnley and Davis use finite-element modeling to examine volume changes in fluid inclusions due to changing P-T conditions.

However, it is the application of fluid inclusion studies to the natural environment that is the prime focus of inclusion work,

and several papers illuminate this with clarity. Two papers on vein gold deposits (Mernagh et al. and Baker and Seccombe) combine fluid inclusion thermometric data with Raman analysis to characterize the fluid chemistry and ore formation. Similarly, Carruzzo et al. and Yang et al. integrate fluid inclusion and stable isotope data to examine the nature of fluids associated with mineralization in granitic rocks of Maritime Canada. Interestingly, despite similar settings, the fluid characteristics are notably different, with the deep penetration (10–12 km) of meteoric water demonstrated for one area. In another magmatic-related environment, Shin et al. described As-Bi-mineralized veins from South Korea and integrate fluid inclusion and stable isotope studies. The features of higher level, epithermal settings are addressed in two papers. Moore et al. discuss an active geothermal system in Indonesia, and in particular, the consequences of descending acid-sulfate waters. In contrast, Kouzmanov et al. describe the genesis of a high-sulfidation assemblage from a Bulgarian mineral deposit and apply infrared microscopy to the study of the textures and fluid inclusions of opaque phases.

The concluding papers illustrate well the forensic nature of inclusion studies. Marshall et al. characterize fluid conditions that favoured emerald formation in new localities in northern Canada. Next, Schandl combines fluid inclusion and mineralogical studies to constrain precious- and base-metal mineralization at a new site in the strongly mineralized Sudbury Basin. Buijs et al. describe an unusual and unique setting of fluid inclusions, in which microborings are preserved as fluid inclusions. Finally, the magmatic evolution within a mineralized porphyry setting is deciphered by Student and Bodnar by applying melt inclusion studies.

This issue of *The Canadian Mineralogist* presents an excellent synopsis of exciting work in a field that continues to be limited only by one's imagination. Sit back, scroll through the pages, and see authors turn the remarkable into the possible.

<http://pubs.nrc-cnrc.gc.ca/mineral/MN42-05.html>

MAC NEWS

Executive Meeting

MAC's Executive met in Montreal on October 23 and 24. Our discussions focused mainly on the incoming 50th anniversary celebrations. President Kontak also led a discussion on how we can improve collaboration with other Canadian Earth science societies and how we can broaden our appeal to the Canadian geochemical community.

Montreal 2006

A dynamic local organizing committee is in place to prepare a memorable GAC-MAC annual meeting, from May 15 to 17, 2006, in Montreal. The Technical Program Committee, chaired by Andrew Hynes, is putting the finishing touches on a program that will explore many of the themes of the International Year of Planet Earth. Montreal is a favourite tourist destination, easy to get to, and should be especially nice in spring.



50th Anniversary Celebrations

Several events are planned for Halifax 2005, May 15–18, 2005, to celebrate MAC's 50th birthday. A two-day symposium, convened by Frank Hawthorne, will feature invited contributions from leaders in the mineral sciences in Canada and beyond. The invited papers will be published in a special issue of *The Canadian Mineralogist*. A plenary talk entitled "Minerals are not just chemical compounds" will be given by Ian Parsons, President of the International Mineralogical Association. A public lecture at a local museum by André Lalonde on minerals in everyday life and a special exhibition of minerals from the Pinch collection of the Canadian Museum of Nature will be part of the outreach program. And of course, we will have a birthday party with cake and a visual presentation of the highlights of MAC's history. Join us!

The Canadian Light Source is On

The Canadian Light Source had its official opening on Thursday, October 21, and it made Canadian television history. Indeed, CBC's *The National* with host Peter Mansbridge was broadcast to the country from atop the CLS storage ring, before a delighted crowd of CLS staff, guests from the University of Saskatchewan,

and their families. It was the first time that a national news program had ever been broadcasted from a Canadian science facility. Mr. Mansbridge was joined by science columnist Bob McDonald and CLS staff scientist Dr. Colleen Christensen. The CLS was built in Saskatoon, Saskatchewan, at a cost of \$173 million and will be used by researchers from 18 different universities across Canada.

\$10 000 Scholarship

Deadline to apply:
May 1, 2005

The Mineralogical Association of Canada Foundation annual scholarship for graduate students involved in an MSc or PhD thesis program in the fields of:

MINERALOGY • CRYSTALLOGRAPHY • GEOCHEMISTRY •
MINERAL DEPOSITS • PETROLOGY

For more information, contact: **Roger H. Mitchell**, Department of Geology, Lakehead University, Thunder Bay ON P7B 5E1 E-mail: rmitchel@lakeheadu.ca

Terms of reference and application forms at
www.mineralogicalassociation.ca

Short course on

EXPLORATION FOR PLATINUM-GROUP ELEMENT DEPOSITS

August 6–7, 2005

ORGANIZERS: **Dr. James E. Mungall**
(Department of Geology, University of Toronto) and

Dr. Markku Iljina (Geological Survey of Finland, Rovaniemi)

SPONSORS: **IGCP Project 479** "Sustainable use of the PGE in the 21st century: Risks and opportunities", the Mineralogical Association of Canada, and the Geological Survey of Finland.

Interest in mineral deposits of the platinum-group elements (PGE) is at an all-time high. Demand is growing rapidly for these metals, which are prized as catalysts for automotive fuel cells or pollution abatement systems. The shrinking global reserves of the PGE, primarily hosted by only two countries, Russia and South Africa, are prompting a search for new deposits. This two-day short course will be held at the Ramada Hotel in the city centre of Oulu, Finland. The fee is 160 (double occupancy) or 200 (single occupancy) and includes hotel accommodation for one night, breakfasts, lunches, and dinner. The minimum number of participants is 10.


This course and its accompanying short-course volume are intended to fill a gap between the knowledge and experience of practising exploration geologists and the academic research community. The aim is to give non-specialist geologists a series of tools with which they can identify prospective areas, recognize significant indicators of mineralization, and synthesize geological, geochemical, and geophysical data to make new discoveries of PGE mineralization.

The course will begin with reviews of the geochemical controls on the distribution of PGE in igneous, hydrothermal, and surficial environments. The next section will comprise descriptive ore deposit models of the principal PGE producers and marginally economic but large-tonnage deposits. Controversial genetic models will be presented in a non-partisan way.


The sections on exploration methods will be presented by practitioners with extensive experience in mineral exploration. The emphasis will be on recognition of the signatures of mineralized bodies using geological, geochemical or geophysical probes.

For more information and the tentative workshop program:

<http://platinumsymposium oulu.fi/pdfs/Workshop3Program.pdf>



MERCURY



SOURCES, MEASUREMENTS, CYCLES, AND EFFECTS

Mineralogical Association of Canada Short Course
Co-sponsor: Environmental Earth Sciences Division, Geological Association of Canada
May 14-15, 2005, prior to the GAC-MAC-CSPG-CSSS
Joint Annual Meeting, Halifax, Nova Scotia, Canada

Conveners: Michael B. Parsons and Jeanne B. Percival, Natural Resources Canada

OVERVIEW


Mercury and mercury compounds are of significant human and environmental health concern because of their toxicity and ability to accumulate in fish and wildlife. Levels of mercury in the environment have risen considerably since the onset of industrialization, and even remote locations such as the Canadian Arctic have been adversely affected by the long-range atmospheric transport of mercury. This short course will discuss the current state-of-knowledge regarding:

- (1) natural and anthropogenic sources of mercury; (2) sampling protocols and analytical methods;
- (3) transport and transformation of mercury in the environment; and
- (4) effects on ecosystems and human health.

Most of the course material will be presented at a level suitable for senior undergraduate and graduate students and should appeal to all scientists interested in environmental issues. A two-day Special Session on Mercury in the Environment will complement the short course.

TOPICS

History of Hg and its environmental impact (M. Parsons & J.B. Percival, GSC); Geogenic sources of Hg (J. Rytuba, U.S. Geological Survey); Anthropogenic sources and global inventory of Hg emissions (J. Pacyna & E. Pacyna, Norwegian Inst. for Air Research); Field sampling and analytical protocols for total Hg (G. Hall, GSC); Inorganic Hg speciation methods (J. Lu & D.C. Grigore, Ryerson Univ. / GSC); Speciation of Hg using synchrotron radiation (C. Kim, Chapman Univ.); Measurement of gaseous Hg flux in the terrestrial environment (P. Rasmussen et al., Health Canada); Biogeochemical Hg cycles (D. Krabbenhoft et al., U.S. Geological Survey); Atmospheric distribution and long-range transport of Hg (C. Banic et al., Environment Canada); Hg in the marine environment (G. Gill & R. Mason, Texas A&M Univ. / Univ. of Maryland); Differentiating natural and anthropogenic Hg in animals (P. Outridge, GSC); Hg in biota and its effects (N. Burgess, Environment Canada); Hg exposure and human health effects (M. Barlow & S. Gupta, Health Canada); Hg management in Canada: domestic and global dimensions (G. Howland, T. Bender, & L. Hayes, Environment Canada).



Registration fees (PRIOR TO APRIL 15, 2005): CDN \$400 (regular) and CDN \$250 (students).
For more information e-mail Michael Parsons (Michael.Parsons@NRCan.gc.ca), or visit the conference website:
www.halifax2005.ca



Mineralogical Society of Great Britain and Ireland

Environmental Mineralogy BATH WINTER MEETING GIVES IT THE SPOTLIGHT

The Mineralogical Society's Winter Meeting was held at the Bath Spa University, Bath from 6 to 7 January 2005. The theme of the meeting was "Environmental Mineralogy, Geochemistry, and Human Health". The meeting was split into seven sessions: Biomineralisation, Toxicity of Micro- and Nano-Particles, Contaminated Environments, Environmental Geochemistry, Arsenic in Groundwater, Radwaste Management, and Platinum Metals in the Urban Environment. It was convened by Éva Valsami-Jones, Ed Stephens, Karen Hudson-Edwards, Kevin Taylor, Kym Jarvis, Kathryn Linge, Dave Polya, Roy Wogelius, Dave Sherman, Simon Redfern, and John Bowles. Sponsorship was provided by the Mineralogical Society, CCLRC Daresbury Laboratory, the Society for Environmental Geochemistry and Health, the Applied Mineralogy Group, the Geochemistry Group, and the Environmental Mineralogy Group.

The meeting attracted some 140 participants from around the world, including the USA, South Africa, and several European countries. The 80 contributed presentations were given in two parallel oral sessions and a series of poster presentations. The theme of the meeting allowed for a range of multidisciplinary topics to be presented, showing that mineralogy and geochemistry in the 21st century can be fundamental to many other disciplines, such as medicine, biology, material science, and archaeology. The highlight of the event was the

Hallimond Lecture, which was delivered this year by Professor Catherine Skinner (Yale University, USA). In her talk entitled "Biominerals—broadening opportunities", Professor Skinner gave a fascinating overview of the intimate relationship between living forms and the biominerals that support them.



Catherine Skinner and David Price

After the first day's presentations, the delegates celebrated in style with pre-dinner drinks in the atmospheric Roman Bath followed by a banquet in the beautiful Victorian Pump Room. Following the live piano entertainment, the President of the Society, Professor David Price, awarded the following Society medals:

Schlumberger Medal for 2004 to Prof. David A.C. Manning (University of Newcastle) for his outstanding contribution to the application of mineralogy in a wide range of environmental issues.

Max Hey Medals for 2004 jointly to Dr. Mark Hodson (Reading University) **and Dr. Lidunka Voadlo** (University College, London). These medals are awarded for excellence in research carried out by young researchers. Mark Hodson has done exceptional work on the understanding of geochemistry and biogeochemistry of mineral reactions in soils. Lidunka Voadlo has carried out pioneering research in the field of computational mineral physics combining experimental studies of materials at high temperatures and pressures with computer simulations and using the results to understand the chemistry and behaviour of the Earth's core.

Eva Valsami-Jones

OPEN UNIVERSITY HOSTS VMSG ANNUAL MEETING 2005

The Volcanic and Magmatic Studies Group held its annual meeting, together with the Geochemistry Group, at the Open University in Milton Keynes on 5–7 January 2005. The meeting was very successful, with over 100 participants and a wide variety of talks and posters. Thematic sessions included 'Boles: alteration, erosion and sedimentation in the volcanic environment'; 'Rates and timing of magmatism and volcanism'; 'Magmatism in Volcanic Arcs'; and 'Volcanic Edifice instability'. Keynote speakers were Dave Jolley (Sheffield University), Steve Blake (Open University), Julian Pearce (Cardiff University), and Ben van Wyk de Vries (Université Blaise Pascal, Clermont-Ferrand). The prizes for best student talks were awarded to Graham Andrews (University of Leicester) and

Eoghan Holohan (Trinity College, Dublin); prizes for the best student posters went to Eleanor Donoghue (Trinity College, Dublin) and Marie-Noelle Guilbaud (Open University).

Katharine Goodenough

BERNARD LEAKE HONOURED BY THE SOCIETY

On 11 November Professor Bernard Leake was guest of honour at the Society's President's Luncheon held at the Strathmore Hotel, South Kensington, London.



Bernard Leake during his acceptance speech at the luncheon.

At that event the President, Professor David Price, presented Bernard Leake with a certificate of Honorary Life Fellowship in the Society, given for exceptional service to the Society and the highest honour the Society bestows. In his citation, David Price thanked Bernard Leake for his long and continuing support to the Society as an associate editor of *Mineralogical Magazine*, as an abstractor, and as a managing trustee and astute financial advisor over the last 40 years. These services to the Society were set alongside his lifelong contribution as a petrologist and leading expert on the amphibole group of minerals. He successfully steered an IMA committee towards a now established classification of these minerals.



The President's table at the Pump Room banquet. From left to right: Brian Skinner, Mark Hodson (Max Hey Medallist), David Manning (Schlumberger Medallist), Lidunka Voadlo (Max Hey Medallist), David Price (President of the Society), and Catherine Skinner (Hallimond Lecturer)

MINABS ONLINE — A NEW ELECTRONIC DATABASE FOR THE MINERAL SCIENCES

Launched in January 2004

MINABS Online, launched in January 2004, has already established a cadre of enthusiastic users with over 10,000 searches carried out in the first nine months of operation.

This electronic abstracting journal is the successor to the printed journal *Mineralogical Abstracts* which it now replaces. Like *Mineralogical Abstracts* it is a specialized abstracting publication that targets journals and other publications in the fields of mineralogy, crystallography, environmental mineralogy, geochemistry, petrology, and related branches of Earth science. The coverage of abstracts is aimed at a wide range of Earth scientists in theoretical and applied fields, as well as undergraduate and postgraduate students. These include specialists in cosmology, physical geography, clay science, minerals resources, environmental studies, nuclear waste disposal, and volcanology, as well as mineralogy, petrology and geochemistry.

Initial feedback from users indicates that they find *MINABS Online* easy to use and a worthy successor to *Mineralogical Abstracts*.

Searching Capability

Searches can be carried out by words in titles or abstracts, year, abstract number, journal, or combinations of these, with categories and subcategories. A useful feature is that abstracts can be selected for downloading as editable text delivered direct to the user by e-mail. Quick prints of individual abstracts can also be obtained by the print screen command (Ctrl P). There is also a popular browse facility that allows users to see the latest additions to the database or review older records according to date and/or subject category.



Dr J.G. MacDonald, MBE, Principal Editor

Abstract and Database Content

The database includes abstracts published in *Mineralogical Abstracts* from 1982 to the present, and about 500 abstracts are currently being added to the database every month from over 180 journals published in Canada, China, Europe, India, Russia, South America, Japan, Saudi Arabia, Taiwan, Turkey, Ukraine, and the USA (altogether in excess of 115,000 abstracts). The archive of data includes an even wider geographical coverage and includes abstracts from journals that have ceased publication or only occasionally publish papers within the target areas of *MINABS Online*. Recent titles added are from India (*Journal of Applied Geochemistry*, Indian Society of Applied Geochemists, Hyderabad) and the Ukraine (*Mineralogical Journal*, Ukrainian Academy of Sciences, Kiev). The editors are seeking to expand the coverage of the literature outside Western Europe and North America.

Many of the abstracts are from papers written in the language of the country of origin but with English translations of citations and abstracts. Most of the abstracts, although usually based on author abstracts, are edited or rewritten to achieve conciseness and to reflect an accurate assessment of the content of papers with the target readership in mind. Where papers contain significant amounts of geochemical data this is identified.

Abstracts are written by a wide range of professionals in the fields of study covered. Abstracts from journals that contain papers written in languages other than English are often written by abstractors in the countries of origin but are thoroughly checked by the editors before publication.

CrossRef

A very useful feature of the service is that links are provided via *CrossRef* to the full papers in journals that have electronic editions. This feature will be of increasing value

to users as libraries sign up to bundles of electronic geoscience journals such as the GeoScienceWorld package being launched this year. The full texts of many papers will therefore be available and downloadable by the user.

The Organisation behind MINABS Online

MINABS Online is a truly international enterprise, and the database is published by the Mineralogical Society of Great Britain and Ireland, a registered charity in the United Kingdom. This abstracting service is approved by the International Mineralogical Association and is run on a not-for-profit basis to provide support for research and scholarship. Subscriptions from developed nations help to support the Society's plan to make the database available at token cost to scientists in less-developed countries. A small core of paid staff is supported by a large band of volunteer abstractors dedicated to the maintenance of the highest possible standards.

A Uniquely Valuable Database

When preparing our abstracts we consult the conclusions and body of the original paper and as a result often add details that were not included in the author abstracts. This is done with our target users in mind, so it makes our product different from other abstracting journals and metadata sources. It provides added value to researchers, especially those who do not have easy access to the original publication. Our coverage includes titles not covered by other abstracting services, and it is editorial policy to expand coverage in Asia and other areas outside Western Europe and North America. The e-journal aims to provide a service that complements and adds further quality to the other facilities available to researchers and students throughout the world. Visit *MINABS Online* at www.minabs.com and sign up for a free two-week trial.

NEW FROM THE SOCIETY: TRAINING WORKSHOPS

The Mineralogical Society, in response to demand for hands-on training on state-of-the-art techniques in the mineral sciences, has launched a series of workshops, which will take place at various research institutes around the UK. The first of these took place at the Natural History Museum, London from 23 to 25 February 2005 on the subject of electron probe microanalysis. It is hoped that these courses will be of value to postgraduates as part of their 'skills training' for their degree course and to others as part of their continuing professional development (CPD). Full-

time Natural Environment Research Council (NERC) PhD students may be able to apply for a bursary from their departments to attend these courses. More details on the courses can be found at: <http://www.minersoc.org/pages/education/edu.html>. Future courses are planned for June (see advertisement p. 96) and November 2005. The June course will be a repeat of the February course at the NHM, and in November the Society is planning a course at Bristol University on the characterisation of interfaces of (mineral) materials.

MEMBERS' NEWS FOR ELEMENTS

Adrian Lloyd-Lawrence

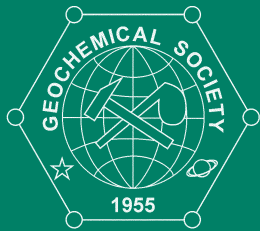
As News Editor for the Society reporting to *Elements*, I welcome news from members about their achievements, awards, and honours. Space is limited but when possible we will try to include your items; photos/digital images are also welcome. Please send your items to Adrian@minersoc.org

Call for Nominations for Council 2006

Nominations are being sought for two vacancies for Ordinary Members of Council for 2006 on the retirements of Prof. Chris.

Hawkesworth and Dr. Stephen Daly. Nominations are also sought for the next President of the Society to succeed Prof. David Price in January 2006. Nomination forms can be found on the website.

Nominations must be endorsed by four Ordinary Members of the Society, and nominees must be Ordinary Members or Fellows of the Society. Nominations should be sent to the Society Office at 41 Queen's Gate, London SW7 5HR, to arrive by Wednesday 22 June 2005 for consideration by Council at their meeting on 30 June 2005.



Geochemical Society

GOLDSCHMIDT UPDATE

Scott Wood
Goldschmidt Conference Organizer

The 15th Annual V.M. Goldschmidt Conference in Moscow, Idaho, USA on May 20–25, 2005 is shaping up to be an excellent meeting. As of this writing, approximately 1,400 abstracts have been submitted, a new record for Goldschmidt in North America! Also 16 exhibitors have reserved booths so far. Accommodation and travel bookings are beginning to fill fast. And remember, March 20, 2005 is the deadline for discounted early registration!

As of this time, the following plenary lectures are planned:

GS Presidential Address: James I. Drever, "Silicate weathering: where have we come in 50 years?"

Goldschmidt Medalist Address: E. Bruce Watson, "Crystallization temperatures of Hadean zircons: Plate tectonics at 4.35 Ga?"

Dana Medalist Address: William Carlson, "Rates and mechanisms of metamorphic processes from natural occurrences"

Clarke Medalist Address: James van Orman, "Diffusion in mantle and core materials"

Patterson Medalist Address: Ken Bruland, "The role of iron as a micronutrient influencing phytoplankton in coastal upwelling regimes"

The conference will start with an ice-breaker party in the evening of May 20. Oral and poster sessions will take place May 21, 22, 24, and 25. The plenary session will take place on the morning of May 23, followed by the Hells Gate barbeque and jet boat tour. Finally, don't miss the gala dinner-dance in celebration of the 50th anniversary of the Geochemical Society. This will be held on May 24 and is included in the conference registration fee for students and professionals.

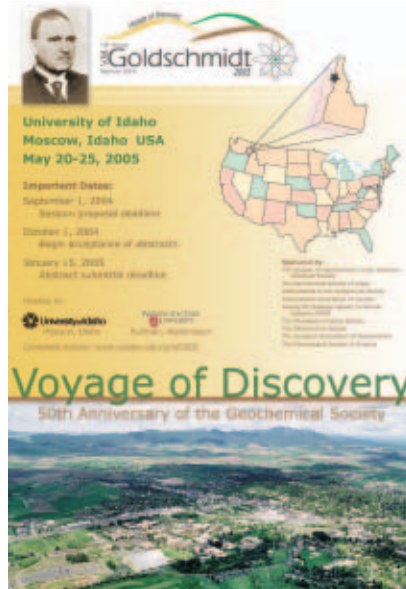
For further information, see the conference website at: www.uidaho.edu/gold2005

CALL FOR NOMINATIONS: ALFRED TREIBS MEDAL

Nominations must be received
by **June 1, 2005**

The **Alfred Treibs Medal** is awarded by the Organic Geochemistry Division of the Geochemical Society for career achievements, over a period of years, in organic geochemistry. Such achievements consist of pioneering and innovative investigations that have made highly significant contributions to the understanding of the origin and fate of organic materials in the geosphere and/or in extraterrestrial environments.

Submission requirements and procedures are available on the GS website at: <http://gs.wustl.edu/archives/nominations.html#TREIBS>



NOTES FROM ST. LOUIS

Seth Davis
GS Business Manager

■ With the creation of *Elements*, the quarterly *Geochemical News* will continue under the editorial expertise of Dr. Carla Koretsky and Dr. Johnson Hass as an online-only newsletter. Current and past issues are available at: <http://gs.wustl.edu/archives>. Highlights from the January 2005 issue include an article about geochemistry research (past and present) in eastern European countries as well as a continuation of the series on geochemistry research at U.S. National Laboratories with a look at the Oak Ridge National Lab.

■ The 2005 V.M. Goldschmidt Medal will be presented to E. Bruce Watson. The 2005 F.W. Clarke Medal will be presented to James A. van Orman. The 2005 C.C. Patterson Medal will be presented to Kenneth Bruland. The 2005 GS/EAG Geochemistry Fellows are: Nicholas Arndt, Stein Jacobsen, Stuart Wakeham, and Lynn Walter. All of these awards will be presented at the 15th annual Goldschmidt Conference in Moscow, Idaho.

■ Members may already submit nominations to the 2006 Award Committees. More information regarding submission requirements and procedures is available on our website at <http://gs.wustl.edu/nominations.html>

■ The GS Business Office is helping organize the Yucca Mountain preconference field trip. This will be a two-day field trip, with the first day devoted to regional geology and hydrology, and the second day being a visit to the proposed Yucca Mountain Civilian High Level Nuclear Waste Disposal Site. Registration is limited to 50 participants. More information on this and other field trips is available under Socials & Field Trips on the Goldschmidt website: www.uidaho.edu/gold2005

■ We are continuing the Special Publication Tribute Series with the release of Volume 9, *Geochemical Investigations in Earth and Space Science: A Tribute to Isaac R. Kaplan*. An order form is available in *Geochemical News* or on our website at: <http://gs.wustl.edu/publications/#SPS>.

■ And finally, I welcome any questions or comments you may have about the Geochemical Society. I may be reached via e-mail at gsoffice@gs.wustl.edu.



Short Course

THERMOCHRONOLOGY

October 14–15, 2005

Snowbird Resort, Snowbird, Utah, 84092, USA

Conveners

PETER W. REINERS, Department of Geology & Geophysics, Yale University

TODD A. EHLERS, Department of Geological Sciences, University of Michigan.

Analytical and modeling advances, combined with rapidly expanding interest in shallow-crustal and Earth- and planetary-surface processes, have led to significant advances in the techniques, applications, and interpretations of thermochronometry. Recent thermochronologic studies have provided unprecedented insights into a wide range of geological problems such as the timing and rates of development of topographic relief, the architecture and dynamics of orogenic wedges, and feedbacks between erosion, uplift, and climate at a variety of scales. New techniques and innovative applications of thermochronometry are also rapidly emerging in a wide variety of subdisciplines, including precise dating of weathering episodes, shock metamorphism, wildfires, and extended time-temperature histories from single crystals. As the range of geologic problems accessible to thermochronometry has expanded, so has the need for robust theoretical understanding of the crystal-scale kinetics (e.g., diffusion, annealing) that control thermochronometric ages, as well as the crustal- or orogen-scale tectonic and geomorphic processes that influence their spatial-temporal patterns across the landscape.

This short course will assess the current state of the art in thermochronometry and evaluate progress in analytical and interpretation techniques, future potential, example applications, and outstanding issues in the field that have recently emerged or need attention for robust progress. We will focus attention on several areas, including techniques for measuring data, innovations in interpretive techniques at both crystal and regional scales, and exemplary case studies that integrate multiple low-temperature thermochronometers or other techniques. This course will also serve not only to provide state-of-the-art assessments for practitioners of thermochronometry, but also as an introduction for Earth scientists seeking to use thermochronologic constraints in their research.

There will be a software demonstration session the evening of the first day, to introduce participants to forward and inverse models for interpretation of thermochronologic data, including diffusion/annealing, and tectonotopographic/thermal phenomena on orogen and crustal scales. The short course will be followed by thermochronology special sessions at the Geological Society of America meeting in Salt Lake City.

Topics, speakers, and registration information for the short course are on the MSA website (www.minsocam.org) or available from the MSA Business Office, 1015 18th St NW Ste 601, Washington, DC, 20036-5212, USA. Tel: 202-775-4344, Fax: 202-775-0018, e-mail: business@minsocam.org. All-inclusive registration fee covers short course sessions, hotel room for two nights (double occupancy), meals including refreshments at breaks, and the *Reviews in Mineralogy and Geochemistry* volume.

The course is sponsored in part by the U.S. Department of Energy, Yale University, University of Michigan, and Apatite to Zircon Inc.

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Mineralogical Society of America

FROM THE PRESIDENT

Diamond as Metaphor

A sparkling new year welcomes this, the second issue of *Elements*. How appropriate to emphasize diamond—a substance that epitomizes the scientific significance, the industrial utility, and the exceptional beauty of minerals. Once the exclusive baubles of royalty, diamonds now adorn hundreds of millions of gem-hungry consumers worldwide, while synthetic abrasive diamond is manufactured by the ton. As this issue attests, the mineralogy–petrology–geochemistry community embraces all of these varied aspects of diamond, and more.

Diamond's unique qualities have inspired many metaphors, some more apt than others. The gem trade hawks diamonds as symbols of intrinsic rarity, unrivaled permanence, and exquisite beauty. Such appealing romantic traits tempt the general populace, but every mineralogist recognizes the inherent flaws in these three metaphors. Diamonds are, in fact, relatively common compared to the vast majority of the 4,000-plus known mineral species. Other precious gemstones, including emeralds, rubies, and sapphires, are far scarcer than diamonds. Diamond's reputed permanence is another questionable metaphor, for diamond burns easily to colorless, odorless carbon dioxide gas in a hot flame, as the great French chemist Antoine-Laurent Lavoisier demonstrated more than two centuries ago. And what of beauty? Without laborious expert cutting and tedious polishing, most diamonds would appear to be dull, nondescript pebbles, something the average person would kick aside without a second thought. Only seductive advertising and hype, coupled with strict market control (and not a little hoarding), maintain the steady demand and hefty prices for these treasured stones.

To me diamond more appropriately represents something quite different—discovery and progress through the unmatched power of science to reveal the workings of our natural world. Two centuries ago, the origin of diamond remained a great mystery. Geological discoveries of in situ diamonds in South Africa provided essential clues pointing to the deep, hot genesis and violent surface delivery of diamonds, while crystallographic research revealed the key structural differences between the two carbon polymorphs.

Decades of effort culminated 50 years ago in General Electric's first reproducible synthesis of diamond. Until then, no one knew how to make a diamond. Today, thanks to the cumulative discoveries of scientists and engineers, anyone with a big basement and a few hundred-thousand dollars can do it. The hundred tons of diamond manufactured annually attest to the reality of scientific progress.

Diamond metaphors must thus extend beyond the romantic and utilitarian—diamonds now symbolize knowledge. In recent years diamonds have taken on a new, powerful role as a tool for public education, especially thanks to the extraordinary efforts of

George Harlow. George masterminded the blockbuster diamond exhibit at the American Museum of Natural History. He authored *The Nature of Diamonds*, one of the finest mineral books of our time, and he serves as guest editor of this issue. His vision has brought the art and science of minerals to millions of people.

George Harlow's service to mineralogy extends far beyond his contributions to the diamond story. As Secretary of MSA he has embraced what is probably the Society's most demanding elected office. And, in addition to this unsung labor, George Harlow is, year in and year out, one of the most generous financial contributors to MSA's operating funds. His commitment to our shared goals is inspiring.

Societies, like diamonds, do not achieve their true brilliance and worth without skilled, dedicated individuals and countless unseen hours of labor. As you read this issue of *Elements*, I hope that you, too, are inspired by the joy of our science, and that you feel a renewed sense of commitment to your society.

Robert M. Hazen, President

ELECTIONS 2005

The slate of candidates for the MSA Council elections is as follows:

PRESIDENT: **John W. Valley**

VICE PRESIDENT
(one to be selected):
**Harry Y. (Hap) McSween Jr.,
Barbara L. Dutrow**

SECRETARY: **George E. Harlow**

COUNCILLORS
(two to be selected):
**Jay D. Bass, Roberta L.
Rudnick, Edward Stolper,
and Simon A.T. Redfern**

John M. Hughes continues in office as Treasurer. Continuing councillors are **Mickey E. Gunter, David London, Ross John Angel, and Robert T. Downs.**

Election materials will be available to MSA members in April in time for the voting deadline of August 1, 2005.

Nominations Sought

Nominations must be received by June 15, 2005

The **Roebbling Medal** is MSA's highest award and is given for eminence as represented by outstanding published original research in mineralogy.

The **Dana Medal** recognizes continued outstanding scientific contributions through original research in the mineralogical sciences by an individual in the midst of his or her career.

The **Mineralogical Society of America Award** is given for outstanding published contribution(s) prior to 35th birthday or within 7 years of the PhD.

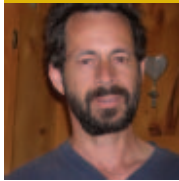
The **Distinguished Public Service Medal** is awarded for distinguished contributions to public policy and awareness about mineralogical topics.

Society **Fellowship** is the recognition of a member's significant scientific contributions. Nomination is undertaken by one member with two members acting as co-sponsors. Form required; contact committee chair or MSA home page.

Mineralogical Society of America

Submission requirements and procedures are on MSA's home page: <http://www.minsocam.org>

AMERICAN MINERALOGIST ADDS A THIRD EDITOR



Due to the growth in submissions, especially in Letters-style manuscripts, and with

approval of the MSA council, we welcome a third editor to our team: **Dr. Bryan C. Chakoumakos** of Oak Ridge National Laboratory. He will handle all the new Letters submissions and join the editors in other editorial duties.

Dr. Chakoumakos welcomes papers from all areas of Earth science. He is a Senior Staff Scientist in the Center for Neutron Scattering at Oak Ridge National Laboratory. His research at ORNL over the past 17 years has focused on the relationships between the crystal structure and physical properties of a wide range of high technology and Earth materials. He did a postdoctoral fellowship at the University of New Mexico with Rodney C. Ewing studying radiation damage effects in complex oxides and minerals. He

received his PhD from Virginia Tech where he studied mineralogy and crystallography under the guidance of Gerry Gibbs. His undergraduate training is in geology from the University of New Mexico. His professional career as a scientist grew out of a childhood fascination with minerals and crystals.

Letters papers, like all submissions, are submitted via our web-based system at <http://minsocam.allentrack.net>. Letters are to be no more than 15 double-spaced pages long, and each table or figure counts as a page. This works out to Letters papers being four typeset pages in length, a goal that has been missed in recent times, but one we are all eager to achieve again. Letters are also intended to be timely papers of significance in Earth sciences. A statement should be included when submitting the paper stating the paper's timeliness and significance (either cut-and-paste into the box in the web-based system or include in a cover letter).

INVITATION TO REQUEST A 2005-2006 MSA DISTINGUISHED LECTURER

Since its inception the Distinguished Lecture Program of the Mineralogical Society of America has proven to be a great success. The varied and interesting lectures presented by MSA Distinguished Lecturers have been appreciated by students and faculty at many colleges and universities worldwide. The Council of the Mineralogical Society is again offering the program for the 2005-2006 academic year with the arrangement that the MSA will pay travel expenses of the lecturers, and the host institutions will be responsible for local expenses, including accommodation and meals. The program will include three lecturers, one of whom resides in Europe, and MSA encourages universities to request lecturers. Depending on the response, one or more lecture tours will be arranged outside North America.

Names of the 2005-2006 Distinguished Lecturers and their lecture titles are not yet available, but they will be posted soon on the MSA website. If your institution is interested in requesting the visit of a MSA Distinguished Lecturer, check the website for lecturers and titles and e-mail your request to the Lecture Program Administrator: Dr. Cameron Davidson, Carleton College, Dept of Geology, 1 N College St, Northfield, MN 55057-0001, USA, e-mail: cdavidso@carleton.edu Tel: (507) 646-7144, Fax: (507) 646-4400. The Lecture Program is designed to run from September, 2005, through April, 2006. Lecturer requests received by **May 12, 2005** will be given priority. Late applications will be considered on a space-available basis. In making your request please include (1) airport proximity from, and travel time to, your institution; (2) the name of a contact person at your institution for the months of May and June (when Lecturer schedules will be assembled); (3) contact e-mail addresses and phone numbers; and (4) flexibility on Lecturer preference. (5) Schools outside the U.S. should indicate starting and ending dates of academic terms.

Please note that because of travel and schedule constraints it is normally not possible to satisfy requests for tightly constrained dates such as seminar days.

OUTSTANDING UNDERGRADUATES RECOGNIZED

The Society welcomes the following exceptional students to the program's honor roll and wishes to thank the sponsors for enabling the Mineralogical Society of America to 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, a Reviews in Mineralogy or Monograph volume chosen by the sponsor, student, or both.

The MSA website lists past AMU awardees and instructions on how MSA members can nominate their students for the award.

Bryan Anderson
Louisiana State University
Sponsored by Dr. Barbara L. Dutrow

Aaron S. Bell
University of Oklahoma
Sponsored by Dr. David London

Jennifer E. Campbell
Williams College
Sponsored by Dr. Reinhard A. Wobus

Stanley Dalbec
University of Hawai'i at Manoa
Sponsored by Dr. Julia E. Hammer

Sarah Lynn Durham
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Sponsored by Dr. Richard D. Warner

Ashley E. Shuler
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Paula Marie Zelanko
University of Maryland
Sponsored by Dr. Michael Brown

The Mineralogical Society of America

2006 Grants for

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*from the Edward H. Kraus Crystallographic Research Fund
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STUDENT RESEARCH IN MINERALOGY AND PETROLOGY

from an endowment created by MSA members



Selection is based on the qualifications of the applicant, the quality, innovativeness, and scientific significance of the research of a written proposal and the likelihood of success of the project. There are three US\$5000 grants with no restrictions on how the funds may be spent, as long as they are used in support of research. Application instructions and forms are available from the MSA home page, <http://www.minsocam.org>, or the MSA offices. Completed applications must be received by June 1, 2005.



International Mineralogical Association

FROM THE PRESIDENT

The arrival of *Elements* on the mineralogy–geochemistry scene presents IMA with an unprecedented opportunity to reach its members and provides a means for its members to communicate with each other. Of course, by no means all members of IMA are members of the current group of societies supporting *Elements*, but most will be able to see the magazine through their institutional subscription to one of the technical journals produced by the consortium. The editors of *Elements* hope that other societies, particularly from countries where English is not the main language, will join and make use of the opportunities for widening communication that *Elements* offers. Like the predominantly English-speaking founding group, they can use *Elements* as a pointer to their national, own-language website to provide detailed information to members.

IMA is supported by small subscriptions, based on membership, from 37 mineralogical organizations, the largest with more than one thousand members, the smallest with less than ten. The oldest of these national mineralogical societies were founded in the early second half of the nineteenth century when many of the important mineral species were being established on the basis of crystal morphology and physical properties, a time when analytical chemistry was extremely primitive. The newer science of geochemistry grew up in a world in which travel and communication were more developed, and most geochemical organizations had an international character from the outset. The IMA was founded to improve contact between its historically fragmented members. Its best known activities are its quadrennial general meetings, the next in Kobe, Japan, in 2006, and the work of its Commission on New Minerals and Mineral Names. Its commissions and working groups regularly sponsor or organize

sessions at other meetings, such as the recent International Geological Congress in Florence and the forthcoming Goldschmidt Conference in Moscow, Idaho, and many of these lead to special publications or thematic journal issues. IMA has a new website (ima-mineralogy.org), which can connect you to each of the member organizations.

So, do we need an IMA, and can it do its job more effectively? We certainly need an international organization as a focus for the worldwide activities of mineralogists. The word 'international' in the title is essential to raise travel funds in many countries where science is less well developed. But our quadrennial meetings have been nothing like as successful as the annual geochemical Goldschmidt meetings, which often attract more than twice the number of delegates, even though the scientific territory the two organizations cover is a continuous solid solution. I fear that one reason for this is the current scientific dominance of an English-speaking world, whose members see the 'I' in IMA (or, for that matter, IGC) as implying that participants will have to sit through large numbers of lectures delivered in less than perfect English. If this influences your choice of annual big meeting, I can only suggest that the greater gains for mankind of a truly international scientific community is a factor you should consider, even if it entails a little extra effort.

IMA has long suffered from lack of a communications channel. *Elements* gives us the opportunity to be regularly in the public eye, and we will provide news of the activities of commissions and of

meetings in which we are involved. My personal view (not shared, I should say, by all members of Council) is that the IMA is bureaucratic out of all proportion to its modest size. The members of commissions are chosen as representatives of the supporting societies rather than for their scientific standing or ability to inspire. I think they would do a better job if composed of like-minded experts and enthusiasts in each field, and if they were responsible for their own membership. Commissions would not be required to involve every national organization, but would have the duty to serve the whole community. Their membership would be subject to the approval of Council, which would ensure that the international community was represented as widely as possible.

Running IMA is not easy. Many of the problems fall on the shoulders of our hard-working secretary, Maryse Ohnenstetter, and dogged treasurer, Kase Klein. It is frequently difficult to get answers from national representatives and even from chairs of commissions. No less than 10 out of 37 member organizations are currently behind with payment of dues for 2004 (some for several years). So let me end with a rallying call to you, the mineralogists who own IMA: it is only going to be as effective as you make it. Come to the Kobe meeting, support the work of the commissions and working groups, do your bit for mineralogy international!

Ian Parsons, President of IMA,
2002–2006

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Li-Phosphate Minerals and Storage Batteries

Examples of the use of minerals in technological applications abound, and “materials mineralogy” has remained one of many exciting frontiers in the science. A frequent feature of *Elements* will be discussions and updates on recent mineralogical studies that focus on or are relevant to the materials applications of minerals.



Triphylite in a matrix of microcline, quartz, and muscovite, Chandlers Mills, New Hampshire. PHOTOGRAPH COURTESY OF SMITHSONIAN INSTITUTION (NMNH SPECIMEN #R9228), PHOTOGRAPHER KEN LARSEN.

The minerals of the lithiophilite (LiMnPO_4)–triphylite (LiFePO_4) series, for which there exists a complete solid solution in nature, provide our first example. Lithiophilite–triphylite occur in rather restricted environments—evolved granitic pegmatites enriched in both Li and P—and thus are relatively uncommon. These phases are isostructural with olivine and are therefore commonly referred to as having an olivine-type structure.

Recently, there has been considerable interest in the Li-phosphate olivine, triphylite, as a storage

cathode for rechargeable lithium batteries (Andersson et al. 2000; Chung et al. 2002; Huang et al. 2001; Padhi et al. 1997a, 1997b; Prosini et al. 2001; Yamada et al. 2001a, 2001b; Yang et al. 2002). Keys to the use of triphylite in batteries are its electrical and ion (Li) conductivities. Triphylite, as well as other phases with an olivine structure, is an electrical insulator, which is the main impediment to its use in batteries. Chung et al. (2002), however, have shown that controlled cation nonstoichiometry combined with doping can increase the electrical conductivity of triphylite by as much as 10^8 times, well above that of Li storage cathodes currently used in commercially available

batteries. They postulated that in a conventional cell design, triphylite may yield the highest power density yet developed in rechargeable Li batteries. Furthermore, they speculated that the same doping mechanism for increasing electrical conductivity in triphylite will apply to other olivine-structure phases, such as lithiophilite. Structural changes in triphylite due to solid solutions with iron may have significant effects on its solid electrolyte properties, including rates of Li diffusion and activation energies. Thus, knowledge of structural changes that result from solid solutions are important in the development and design of Li-phosphate storage cathodes. In a recent study by Losey et al. (2004), single-crystal X-ray diffraction experiments were performed on natural lithiophilite–triphylite samples with Fe/(Mn+Fe) ratios of 6, 27, 50, 79, and 89 (referred to as Trip06, etc.). The atomic arrangement of each sample was refined to elucidate the structural changes with composition in this series.

The octahedrally coordinated cations in the lithiophilite–triphylite series are completely ordered between the *M1* and *M2* sites. Only Li occupies the *M1* site, whereas the *M2* site is occupied by divalent Mn, Fe, and in some cases, Mg. The complete ordering of cations in these minerals is in contrast to the majority of olivine-structure phases, in which there is extensive disorder among the octahedrally coordinated cations. Although Mn and Fe occupy only the *M2* site in the lithiophilite–triphylite series, the solid solution between these two constituents affects both the *M2* and *M1* sites.

The substitution of Fe^{2+} ($r = 0.78$ Å; Shannon 1976) for Mn^{2+} ($r = 0.83$ Å) in the lithiophilite–triphylite series suggests, by Vegard’s law, that a concomitant shortening of the octahedron bond lengths should occur. Although the shortening of the bond lengths involving *M2* is expected, the bond-length variations in that polyhedron also induce variations in the *M1* polyhedron, occupied solely by Li. The *M1*-O1 and *M1*-O2 bond lengths decrease, whereas the *M1*-O3 bond length increases with increasing Fe-for-Mn substitution. This change occurs with no substitution of cations for Li in the *M1* site. These structural changes in the lithiophilite–triphylite solid solution may have an effect on the activation energy for Li diffusion, and thus the rate of diffusion. The activation energy of Li diffusion is directly related to the energy necessary to break all the *M1*-O bonds. Bond-valence considerations indicate that Li is more underbonded in lithiophilite and thus is less stable in the *M1* site in this end member. Consequently, breaking the six *M1*-O bonds will be energetically easier in lithiophilite, which in turn will lead to greater rates of Li diffusion, making lithiophilite a potentially better storage cathode.

Although members of the lithiophilite–triphylite series are rather rare minerals of restricted geological significance, the physical and chemical properties that make them amenable to applications in battery manufacturing, may someday turn out to be of great societal and economic importance.

This text is based in part on the article published by Losey et al. (2004)

John Rakovan

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2005

April 3–7 8th International Conference on the Biogeochemistry of Trace Elements, Adelaide, Australia. Details: 8th ICOBTE Conference Secretariat, Attn: Sandra Wildman, CSIRO Land & Water, Private Bag No. 2, Glen Osmond 5064, South Australia. E-mail: 8thICOBTE@csiro.au; fax: +61-8-8303-8572; web page: www.clw.csiro.au/conferences/8thicobte/

April 10–13 107th Annual Meeting & Exposition of the American Ceramic Society, Baltimore, MD, USA. Details: Mark Mecklenborg. Tel.: 614-794-5829; e-mail: mmecklenborg@ceramics.org; web page: www.ceramics.org/meetings/am2005/default.asp

April 17–21 Third Study of Matter at Extreme Conditions (SMEC), Miami, FL, USA. E-mail: hennesse@fiu.edu; web page: www.cesmec.fiu.edu/SMEC2005/index.php

April 25–29 European Geosciences Union (EGU) Second General Assembly, Vienna, Austria. Details: EGU Office, Max-Planck-Str. 13, 37191 Katlenburg-Lindau, Germany. Tel.: +49-5556-1440; fax: +49-5556-4709; e-mail: egu@copernicus.org; web page: www.copernicus.org/EGU/ga/egu05/ind ex.htm

April 25–30 Asia Pacific Winter Conference on Plasma Spectrochemistry, Chiang Mai, Thailand. Details: Ramon Barnes, ICP Information Newsletter, P.O. Box 666, Hadley, MA 01003-0666, USA. Tel.: 413-256-8942; fax: 413-256-3746; e-mail: wc2005@chem.umass.edu; web page: www.unix.oit.umass.edu/~wc2005

May 5–7 4th International Colloquium on Magmatism, Metamorphism and Associated Mineralizations, Agadir, Morocco. Web page: http://3ma.esta.ac.ma

May 15–18 GAC-MAC: Halifax 2005, Halifax, Nova Scotia, Canada. Details: hfx2005@gov.ns.ca; web page: www.halifax2005.ca/

May 20–25 Goldschmidt 2005, Moscow, Idaho, USA. E-mail: gold2005@uidaho.edu; web page: www.uidaho.edu/gold2005

May 23–27 AGU Joint Assembly, New Orleans, Louisiana, USA. Details: AGU Meetings Department, 2000 Florida Avenue NW, Washington, DC 20009, USA. Tel.: 202-777-7333; fax: 202-328-0566; e-mail: meetinginfo@agu.org; web page: www.agu.org/meetings/sm05/

May 28–June 2 American Crystallographic Association (ACA) Annual Meeting, Walt Disney World, FL, USA. Details: Ed Collins, Program Chair. E-mail: edward_collins@med.unc.edu; web page: www.hwi.buffalo.edu/ACA/future-meetings.html

May 31–June 3 Workshop on Oxygen in Asteroids and Meteorites, Flagstaff, AZ, USA. Details: Dave Mittlefehldt, NASA Johnson Space Center. Tel.: 281-483-5043; e-mail: david.w.mittlefehldt@nasa.gov; web page: www.lpi.usra.edu/meetings/am2005/am2005.1st.html

June 11–15 42nd Annual Meeting of The Clay Minerals Society, Burlington, Vermont, USA. Details: Peter C. Ryan, Geology Department, Middlebury College, Middlebury, Vermont 05753,

USA. Tel.: 802-443-2557; e-mail: pryan@middlebury.edu; web page: www.claysonline.org/HomeAnnualMeeting.html

June 13–17 European Association of Geoscientists and Engineers, 67th Annual International Conference and Exhibition, Madrid, Spain. Details: Sandra Hermus, Conference Assistant, Standerdmolen 10, 3995 AA Houten or PO Box 59, 3990 DB Houten, The Netherlands. Fax: +31 30 6343534; web page: www.eage.nl/conferences/index2.phtml?confid=17

June 19–22 American Association of Petroleum Geologists and Society for Sedimentary Geology Joint Annual Meeting and Exhibition, Calgary, Alberta, Canada. Details: AAPG Conventions Dept., PO Box 979, Tulsa, OK 74119, USA. Tel.: 918-560-2679; fax: 918-560-2684; e-mail: convене2@aapg.org; web page: www.aapg.org/cal-gary/globalroundup.cfm

June 19–28 EMU School: Mineral Behaviour at Extreme Conditions, Heidelberg, Germany. E-mail: EMU2005@min.uni-heidelberg.de; web page: http://www.univie.ac.at/Mineralogie/EMU/emus_7.htm

July 3–9 7th International Eclogite Conference, Seggau, Austria. Details: Alexander Proyer, IEC-7 Organizing Committee, Institute of Earth Sciences, Department of Mineralogy and Petrology, University of Graz, Universitaetsplatz 2, A-8010 Graz, Austria. Fax: +43 316 380 9865; e-mail: iec-7@uni-graz.at; web page: www.uni-graz.at/IEC-7/

July 6–9 ECROFI XVIII: European Current Research on Fluid Inclusions, Siena, Italy. E-mail: bonelli5@unisi.it or ecrofiXVIII@unisi.it; web page: www.unisi.it/eventi/ECROFI XVIII

July 11–15 Role of Volatiles and Atmospheres on Martian Impact Craters, The Johns Hopkins University, Maryland, USA. Details: Nadine Barlow, Northern Arizona University. Tel.: 928-523-5452; e-mail: nadine.barlow@nau.edu; web page: www.lpi.usra.edu/meetings/volatiles2005/volatiles2005.1st.html

July 31–August 3 5th International Dyke Conference (IDC-5), Rovaniemi, Finland. Details: Dr. Jouni Vuollo, Geological Survey of Finland, PO Box 77, FIN-96101 Rovaniemi, Finland. Tel.: +358 (0)205 504206; fax: +358 (0)205 5014; e-mail: jouni.vuollo@gtk.fi; web page: http://idc5.gsf.fi/

July 31–August 5 Gordon Research Conference on Inorganic Geochemistry and Ore Deposits, Proctor Academy, Andover, New Hampshire. Details at www.grc.uri.edu/programs/2005/inorggeo.htm

August 7–11 10th International Platinum Symposium, Oulu, Finland. Details: Dr. Tuomo Alapieti, University of Oulu. Tel.: +358-8-553 1432; mobile: +358-40-504 4599; fax: +358-8-553 1484; e-mail: tuomo.alapieti@oulu.fi; web page: http://platinumsymposium.oulu.fi/

August 8–11 Earth System Processes 2, Calgary, Alberta, Canada. Details: Chris Beaumont, e-mail: chris.beaumont@dal.ca; Don Canfield, e-mail: dec@biology.ou.dk; web page: www.geosociety.org/meetings/esp2/

August 18–21 Society for Geology Applied to Mineral Deposits, 8th Biennial Meeting, Beijing, China. Details: 8th SGA Biennial Meeting, Dr. Jingwen Mao – Secretary, Institute of Mineral Resources, Chinese Academy of Geological Sciences, 26 Baiwanzhuang Road, Beijing 100037, China. Tel.: +86 10 68 32 73 33; fax: +86 10 68 33 63 58; e-mail: mail@sga2005.com; web page: www.sga2005.com/

August 21–27 Claysphere: Past, Present and Future, 13th International Clay Conference, Waseda University, Tokyo, Japan. Details: Prof. T. Sakamoto, Secretary General 13th ICC, Faculty of Science, Okayama University of Science, 1-1, Ridai-cho, Okayama 700-0005, Japan. Tel.: +81-86-252-8922, e-mail: icc13@das.ous.ac.jp; web page: www.soc.nii.ac.jp/csj2/13ICC/

August 23–26 3rd Federation of European Zeolite Associations (FEZA) Conference, Prague, Czech Republic. E-mail: feza2005@jh-inst.cas.cz; web page: www.jh-inst.cas.cz/~feza2005/

August 23–27 7th International Symposium on the Geochemistry of the Earth's Surface (GES-7), Aix-en-Provence, France. Details: Jean-Dominique Meunier, CEREGE, Europôle Méditerranéen de l'Arbois – BP 80, 13545 Aix-en-Provence cedex 4, France. Tel.: (+33) 442 971 524; fax: (+33) 442 971 540; e-mail: ges7@cerge.fr; web page: www.cerege.fr/GES7/index.htm

August 23–31 XX Congress of International Union of Crystallography, Florence, Italy. Details: Congress Secretariat, XX Congress and General Assembly of the International Union of Crystallography, c/o Dipartimento di Energetica, University of Florence, via S. Marta 3, 50139 Firenze, Italy. Tel.: +39-055-4796209; fax: +39-055-4796342; e-mail: iucr@iucr2005.it; web page: www.iucr2005.it

August 28–September 1 American Chemical Society 230th meeting, Washington, DC. Details: 2005 ACS Meetings, 1155 – 16th St NW, Washington, DC 20036-489, USA. Tel.: 202-872-4396; fax: 202-872-6128; e-mail: natlmtgs@acs.org

August 29–September 2 Structure, Tectonics and Ore Mineralization Processes (STOMP), James Cook University, Townsville, Australia. E-mail: Timothy.Baker@jcu.edu.au or Thomas.Blenkinsop@jcu.edu.au; Web page: www.es.jcu.edu.au/STOMP/

September 10–11 Symposium on Agate and Other Forms of Cryptocrystalline Quartz, Colorado School of Mines, Golden, CO, USA. Details: Peter Modreski, U.S. Geological Survey. Tel. 303-202-4766, e-mail: pmodreski@usgs.gov

September 11–16 6th International Symposium on Applied Isotope Geochemistry (AIG-6), Prague, Czech Republic. E-mail: aig6@natur.cuni.cz; web page: http://www.aig6.cz

September 12–13 Micro-organisms and Earth Systems: Advances in Geomicrobiology, University of Keele, UK. Details: Society for General Microbiology, Marlborough House, Basingstoke Road, Spencers Wood, Reading RG7 1AG, UK. E-mail: j.hurst@sgm.ac.uk; web page: www.sgm.ac.uk/meetings

September 12–16 68th Annual Meteoritical Society Meeting,

Gatlinburg, Tennessee, USA. Details: Kimberly Taylor (LPI Meeting Coordinator), Program Services Department, Lunar and Planetary Institute, 3600 Bay Area Boulevard, Houston, TX 77058-1113, USA. Tel.: 281-486 2151; fax: 281-486 2160; e-mail: metsoc2005@utk.edu or taylor@lpi.usra.edu; web page: http://geoweb.gg.utk.edu/2005/metsoc2005.html

September 12–16 22nd International Meeting on Organic Geochemistry (22 IMOG), Seville, Spain. Details: Viajes El Corte Ingles, Teniente Borges 5, Seville 41002, Spain. Tel.: +34 954506605; fax: +34 954223512; e-mail: secretary@imog05.org; web page: http://www.imog05.org

September 19–23 From Tropics to Tundra: 22nd International Symposium of the Association of Exploration Geochemists, Perth, Western Australia. Details: Promaco Conventions Pty Ltd, ABN 68 008 784 585, PO Box 890, Canning Bridge, Western Australia 6153. Tel.: +61 8 9332 2900; fax: +61 8 9332 2911; e-mail: promaco@promaco.com.au; web page: www.promaco.com.au/conference/2005/iges

September 25–28 Materials Science & Technology 2005 (MS&T '05), Pittsburgh, PA, USA. Contact: TMS Meetings Services, 184 Thorn Hill Road, Warrendale, PA 15086. Tel.: 724-776-9000, ext. 243; e-mail: mtgsv@tms.org

October 16–19 GSA Annual Meeting, Salt Lake City, Utah, USA. Details: GSA Meetings, Box 9140, Boulder, CO 80301-9140, USA. Tel.: 303-447-2020, ext. 164; fax: 303-447-1133; e-mail: meetings@geosociety.org; web page: www.geosociety.org/meetings/index.htm

November 6–11 International Gondwana 12 Conference, Mendoza, Argentina. Details: Gondwana 12, Centro de Investigaciones Geológicas, Calle 1 # 644, B1900TAC La Plata, Argentina. Tel./Fax: +54 221 4215677; e-mail: gondwana@cig.museo.unlp.edu.ar; web page: http://cig.museo.unlp.edu.ar/gondwana

November 13–15 Geology Forum 05: Focus on Exploration, Cape Town, South Africa. Details: B. Wills, Minerals Engineering Int., 18 Dracaena Ave., Falmouth, Cornwall TR11 2EQ, UK. Tel.: 44 (0)7768 234 121; e-mail: bwills@min-eng.com; web page: www.min-eng.com/geologyforum05/index.html

December 5–9 American Geophysical Union Fall Meeting, San Francisco, California, USA. Details: E. Terry, AGU Meetings Department, 2000 Florida Avenue NW, Washington, DC 20009 USA. Tel.: 202-777-7335; fax: 202-328-0566, e-mail: eterry@agu.org or meetinginfo@agu.org; web page: www.agu.org/meetings

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March 12–16 The Minerals, Metals & Materials Society Annual Meeting & Exhibition, San Antonio, TX, USA. Contact: TMS Meetings Services, 184 Thorn Hill Road, Warrendale, PA 15086, USA. Tel.: 724-776-9000, ext. 243; e-mail: mtgsv@tms.org; web page: www.tms.org/Meetings/Meetings2006.asp

March 26–30 American Chemical Society 231st Annual meeting, Atlanta, GA, USA.

From the Managing Editor

It has been heartwarming to read the positive feedback and the useful suggestions many of you have sent. It made all the hard work worthwhile. My favorite message was this one: «Wow... Quel magazine! Il est très beau maman. Félicitations! J'espère qu'il sera un succès monstre. Beau travail.» It was from my son David, who is doing an MSc in geology at McGill University.

If you sense, from reading Ian Parsons' editorial, that the editorial team works well together, you are right. Indeed, we feel privileged that we get along so well and that we can happily come to a consensus on just about every issue that comes our way.

DIAMONDS AND GLAMOUR

While working on this issue, I learned a lot about diamonds and the unique contribution their study has made to our understanding of the mantle. Studying diamonds can be a glamorous occupation at times, as this picture of George Harlow attests. When George sent me the picture for fun, I begged him to allow me to use it.



George Harlow at a dinner held just prior to the opening event for the exhibition *The Nature of Diamonds* in October 1997. COURTESY OF THE AMERICAN MUSEUM OF NATURAL HISTORY

AND THEN THERE WERE SEVEN

So much has happened since I was closing the inaugural issue, in a race against time to have the issue on hand for the Geological Society of America meeting. Just as I was putting the

finishing touches to the issue, I received an e-mail message from Terry Seward informing us that the European Association for Geochemistry (EAG) Council had voted to join *Elements*. We were able to add a last-minute news item. During the GSA meeting, we learned that the International Association of GeoChemistry (IAGC) Council had also voted to join the *Elements* effort, and members of both EAG and IAGC did receive the inaugural issue. We welcome these two societies and their members, and you can read their news on pages 110 and 112.

ELEMENTS' WEBSITE

Elements now has its own website, which is also linked to the website of each of the participating societies. Take a moment to browse through it. We have posted the inaugural issue on the website as a sample copy. We welcome comments. www.elementsmagazine.org

THANKS

Thanks to all who have contributed time and talent to this issue, to George Harlow and Rondi Davies, guest editors, and all the authors; to the society news editors Seth Davies, Mel Gascoyne, Andrea Koziol, Daniel Kontak, Adrian Lloyd Lawrence, Kathryn Nagy, Eric Oelkers; to contributors Ross Angel, Peter J. Heaney, Ian Parsons, Jean-Claude Petit, John Rakovan, Nancy Ross, Paul Ribbe, Quintin Wight; and to copy editor Thomas Clark.

Pierrette Tremblay

2006 (cont'd)

May 4-6 Society of Economic Geologists 2006 Conference, Keystone, Colorado, USA. Web page: www.segweb.org/meeting.htm

June 3-7 Joint 43rd Annual Meeting of The Clay Minerals Society and Annual Meeting of the Groupe Français des Argiles (French Clay Group), Oléron Island, France. Details: Sabine Petit, Université de Poitiers, CNRS Hydr'ASA, 40 Av. du Recteur Pineau, 86022 Poitiers Cédex, France. Tel.: 33-(0)5-49-45-37-56; e-mail: sabine.petit@hydrasa.univ-poitiers.fr; web page: www.clays.org

July 16-23 Zeolite '06, Socorro, New Mexico, USA. Details: Dr. Robert Bowman. E-mail: bowman@nmt.edu; web page: <http://cms.lanl.gov/zeo2006.html>

July 23-28 19th International Mineralogical Association (IMA) Meeting, Kobe, Japan. Details: Prof. T. Yamanaka. E-mail: b61400@center.osaka-u.ac.jp; web page: www.congre.co.jp/ima2006/

August 26-27 GIA Gemological Research Conference, San Diego California, USA. Contact information: Dr. James Shigley, jshigley@gia.edu, or Brendan Laurs, blaurs@gia.edu

August 27-September 1 16th Annual V.M. Goldschmidt Conference, Melbourne, Australia. e-mail: goldschmidt2006@tourhosts.com.au; web page: www.goldschmidt2006.org

August 27-September 1 17th International Mass Spectrometry Conference (IMSC), Prague, Czech Republic. Web page: www.imsc2006.org/

October 22-25 Geological Society of America Annual Meeting, Philadelphia, Pennsylvania, USA. Details: GSA Meetings Dept., PO Box 9140, Boulder, CO 80301-9140, USA. Tel.: 303-447-2020; fax: 303-447-1133; e-mail: meetings@geosociety.org; web page: www.geosociety.org/meetings/index.htm

December 11-15 American Geophysical Union Fall Meeting, San Francisco, California, USA. Details: E. Terry, AGU Meetings Department, 2000 Florida Avenue NW, Washington, DC 20009, USA. E-mail: eterry@agu.org; web page: www.agu.org/meetings

To get meeting information listed in the calendar, contact Andrea Koziol (Andrea.Koziol@notes.undayton.edu).

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NOTE FROM THE EDITORS: We follow up on Randy Cygan's suggestion to present an interesting picture to close each issue. Our first submission is from Ian Parsons. Readers are invited to submit interesting pictures, with a caption, to the managing editor.



of art ever. It is 3.86 m high and 2.33 m wide. The cabinet, of unsurpassed richness and splendour, was commissioned by Henry Somerset, 3rd Duke of Beaufort, whose family seat was at Badminton in southwest England, when he was only nineteen. It was made at the Grand Ducal workshops (Ufficio delle pietre dure) in Florence from 1720 to 1732. It remained in Badminton until 1990 when it was sold (again for a record price, £8.58 million) to the collection of the American philanthropist Barbara Piasecka Johnson (of the baby-powder family, another mineralogical connection!). In the recent auction, the cabinet was purchased by the Director of the Liechtenstein Museum in Vienna, on behalf of Prinz Hans-Adam II of Liechtenstein. It will be on permanent display in Vienna from spring 2005. I am indebted to Norman Butcher for drawing my attention to this spectacular contribution of mineralogy to the art world.

Ian Parsons



Detail of cabinet construction. PHOTOGRAPHS COPYRIGHT CHRISTIE'S 2005

This fabulous cabinet, constructed of ebony and gilt-bronze and incorporating lapis lazuli, agate, red and green Sicilian jasper, chalcedony, and amethyst, as well as a variety of polished rocks, was sold in December 2004 at Christie's of London for £19,045,250 (US\$36,662,106; Eu27,463,250), making it the most expensive nonpictorial work



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Barium	mg/kg	0.0032	0.0342
Boron	mg/kg	0.25	0.23
Iron	mg/kg	0.2038	0.213
Manganese	mg/kg	3.935	4.093
Silica	mg/kg	17.39	17.82
Strontium	mg/kg	0.318	0.334
Zinc	mg/kg	0.011	0.012



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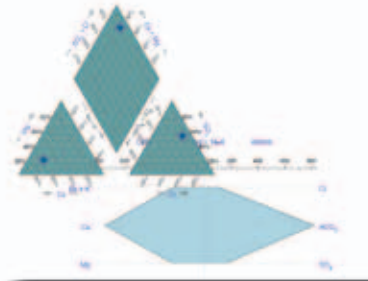
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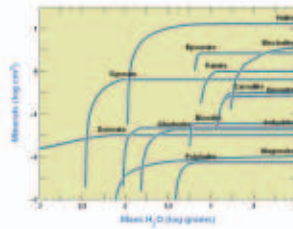
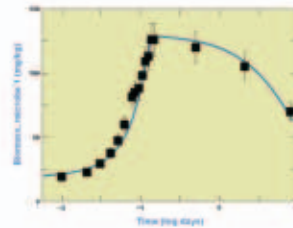


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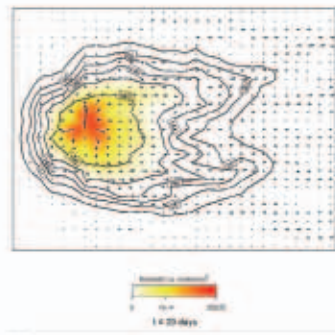
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