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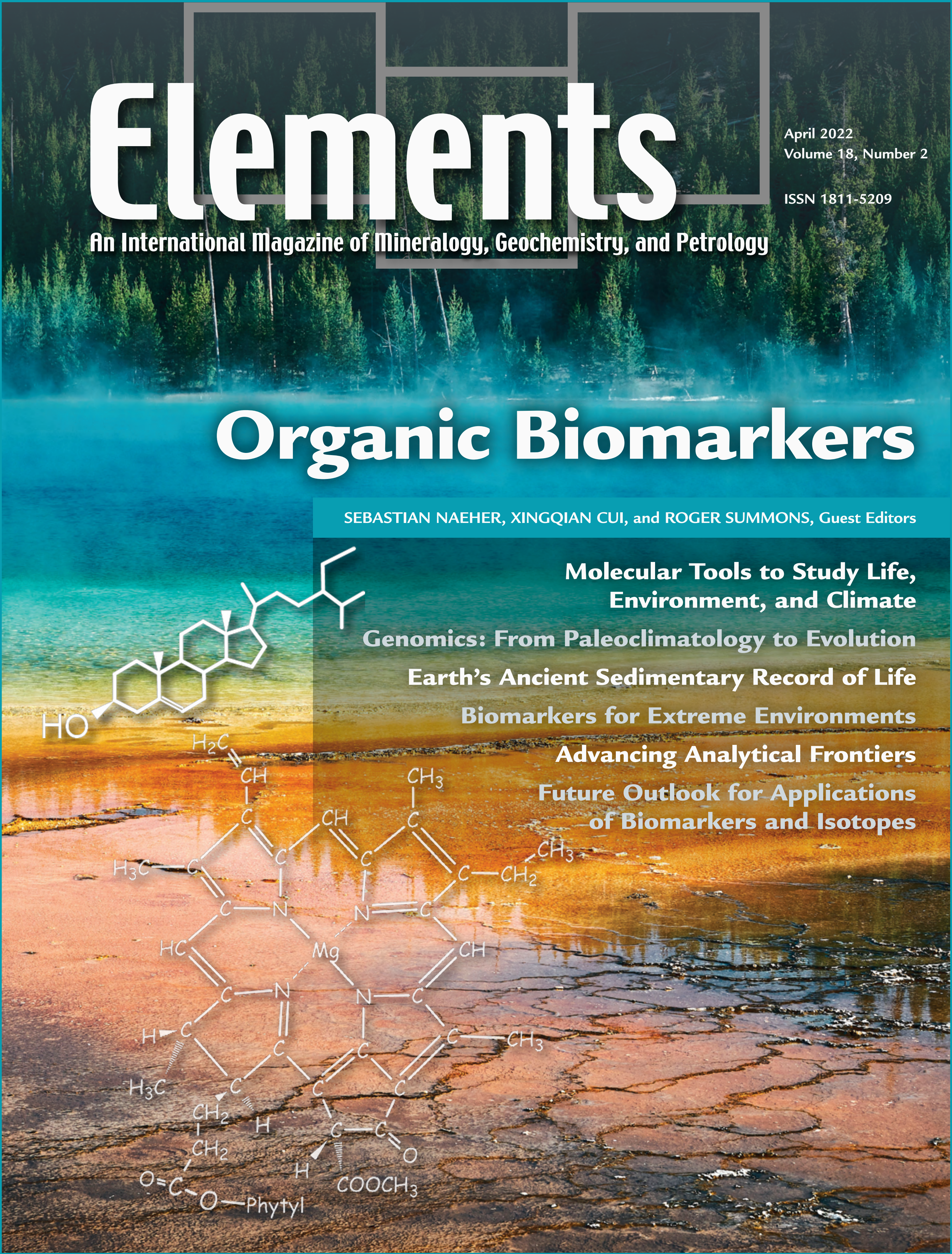
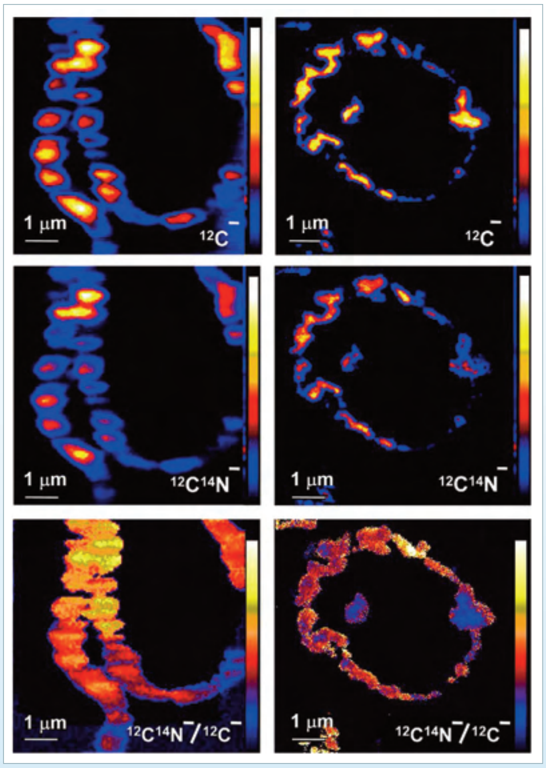


Organic Biomarkers

SEBASTIAN NAEHER, XINGQIAN CUI, and ROGER SUMMONS, Guest Editors

- Molecular Tools to Study Life, Environment, and Climate
- Genomics: From Paleoclimatology to Evolution
- Earth's Ancient Sedimentary Record of Life
- Biomarkers for Extreme Environments
- Advancing Analytical Frontiers
- Future Outlook for Applications of Biomarkers and Isotopes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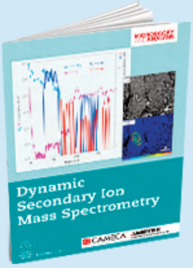
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Volume 18, Number 2 • April 2022

Grand Prismatic Spring,
Yellowstone National Park,
Wyoming USA

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

Elements is published six times a year. Individuals are encouraged to join any one of the participating societies to receive *Elements*. Institutional subscribers to any of the following journals—*American Mineralogist* and *The Canadian Mineralogist*—also receive one copy of *Elements* as part of their subscription. Institutional subscriptions are available for US$180 (US$195 non-US addresses) a year in 2022. Contact the executive editor (editorialteam.elements@gmail.com) for information.

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Organic Biomarkers

Guest Editors: **Sebastian Naeher**, **Xingqian Cui**, and **Roger Summons**

DEPARTMENTS

PARTICIPATING SOCIETIES

The Mineralogical Society of America is for individuals interested in mineralogy, crystallography, petrology, and geochemistry. Founded in 1919, the society promotes—through research, education, and publications— the understanding and application of mineralogy by industry, universities, government, and the public. Membership benefits include *Elements* magazine, access to the electronic version of the *American Mineralogist*, as well as discounts on journals, Reviews in Mineralogy & Geochemistry series, textbooks, monographs, reduced registration fees for meetings and short courses, and participation in a society that supports the many facets of mineralogy.

Website: **www.minsocam.org**

Contact: business@minsocam.org

Society News Editor: Ann Benbow (abenbow@minsocam.org)

The Mineralogical Society of the UK and Ireland is an international society for all those working in the mineral sciences. The society aims to advance the knowledge of the science of mineralogy and its application to other subjects, including crystallography, geochemistry, petrology, environmental science and economic geology. The society furthers its aims through scientific meetings and the publication of scientific journals, books, and monographs. The society publishes *Mineralogical Magazine* and *Clay Minerals*. Students receive their first year of membership free of charge. All members receive *Elements*.

Website: **www.minersoc.org**

Contact: info@minersoc.org

Society News Editor: Kevin Murphy (kevin@minersoc.org)

The Mineralogical Association of Canada was incorporated in 1955 to promote and advance the knowledge of mineralogy and the related disciplines of crystallography, petrology, geochemistry, and economic geology. Any person engaged or interested in these fields may become a member of the association. Membership benefits include a subscription to *Elements*, a reduced subscription to *The Canadian Mineralogist*, a 20% discount on volumes in the Topics in Mineral Sciences series (formerly the Short Course series), and a discount on the registration fee for annual meetings.

Website: **mineralogicalassociation.ca**

Contact: office@mineralogicalassociation.ca

Society News Editor: Johanne Caron (johanne.caron@ete.inrs.ca)

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

Website: **www.clays.org**

Contact: cms@clays.org

Society News Editor: Bhabananda Biswas (Bhabananda.Biswas@newcastle.edu.au)

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

Website: **www.geochemsoc.org**

Contact: gsoffice@geochemsoc.org

Society News Editor: Kevin Johnson (kjohnson@geochemsoc.org)

The European Association of Geochemistry was founded in 1985 and is a non-profit organization dedicated to promoting geochemistry internationally. The society is a dynamic association that organizes the Goldschmidt Conference® in Europe, publishes *Geochemical Perspectives* and *Geochemical Perspectives Letters*, recognizes scientific excellence through awards; supports early career scientists; sponsors workshops and conferences in Europe; organizes distinguished lecture and outreach programs; publishes job opportunities, newsletters and blogs; and partners with other learned societies to strengthen geochemistry internationally.

Website: **www.eag.eu.com**

Contact: office@eag.eu.com

Society News Editor: Alice Williams (awilliams@eag.eu.com)

The International Association of GeoChemistry (IAGC) has been a preeminent international geochemical organization since 1967. Its principal objectives are to foster cooperation in the advancement of applied geochemistry by sponsoring specialist scientific symposia and the activities organized by its working groups and by supporting its journal, *Applied Geochemistry*. The administration and activities of IAGC are conducted by its council, comprising an executive and ten ordinary members. Day-to-day administration is performed through the IAGC business office.

Website: **www.iagc-society.org**

Contact: businessoffice@iagc-society.org

Society News Editor: Chris Gardner (BusinessOffice@IAGC-Society.org)

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

Website: **www.sfmc-fr.org**

Contact: sfmc@ccr.jussieu.fr

Society News Editor: Mary-Alix Kaczmarek (mary-alix.kaczmarek@get.omp.eu)

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

Website: **www.appliedgeochemists.org**

Contact: office@appliedgeochemists.org

Society News Editor: John Carranza (ejmcarranza@gmail.com)

The Deutsche Mineralogische Gesellschaft (DMG; German Mineralogical Society) was founded in 1908 to "promote mineralogy and all its subdisciplines in teaching and research as well as the personal relationships among all members." Its great tradition in geoscience is reflected in the list of honorary fellows, which include M. v. Laue, G. v. Tschermak, P. Eskola, C.W. Correns, P. Ramdohr, and H. Strunz. Today, the subdisciplines in the DMG are also bridging the gap with other communities, such as materials science, solid state chemistry/physics, and the environmental sciences. The DMG especially tries to support young researchers, e.g., to attend conferences and short courses. Membership benefits include the *European Journal of Mineralogy*, *Elements*, and *GMit*.

Website: **www.dmg-home.org**

Contact: post@dmg-home.org

Society News Editor: Klaus-Dieter Grevel (klaus-dieter.grevel@rub.de)

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

Website: **www.socminpet.it**

Contact: segreteria@socminpet.it

Society News Editor: Costanza Bonadiman (bdc@unife.it)

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

Website: **geoanalyst.org**

Contact: jmc@bgs.ac.uk

Society News Editor: Alicia Cruz-Uribe (alicia.cruzuribe@maine.edu)

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

Website: **www.ptmin.pl**

Contact: ptmin@ptmin.pl

Society News Editor: Anna Pietranik (anna.pietranik@uwr.edu.pl)

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

Website: **www.ehu.es/sem**

Contact: npvsem@lg.ehu.es

Society News Editor: Nuria Sanchez Pastor (secretaria@semineral.es)

The Swiss Geological Society was founded in 1882 and comprises specialist groups in geophysics, mineralogy and petrology, sedimentology, tectonics, and paleontology. The society is part of the Swiss Academy of Sciences and promotes the advancement and dissemination of Earth sciences in Switzerland. The society coorganizes the annual Swiss Geoscience Meeting (SGM) and publishes the *Swiss Journal of Geosciences* (*SJG*), which is now fully "open access". Members receive discounts for publishing in the *SJG* and participating at the SGM.

Website: **https://geolsoc.ch**

Contact: office@geolsoc.ch

Society News editor: Julien Allaz (julien.allaz@erdw.ethz.ch)

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

Website: **meteoriticalsociety.org**

Contact: meteoritical.org/contact

Society News Editor: Cari Corrigan (corriganc@si.edu)

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

Website: **jams.la.coocan.jp**

Contact: KYL04223@nifty.ne.jp

Society News Editor: Tomoaki Morishita (moripta@se.kanazawa-u.ac.jp)

The International Association on the Genesis of Ore Deposits (IAGOD) was established in 1963 to promote international cooperation and to increase knowledge in the field of the genesis of ore deposits: it is affiliated with the International Union of Geological Sciences (IUGS). The society organizes quadrennial symposiums and cosponsors sessions at the International Geological Congress and SGA Biennial Meetings. The IAGOD working groups and commissions promote ore deposit research and sponsor an international speaker series. Membership includes reduced fees at our meetings, discounted subscriptions to our flagship journal *Ore Geology Reviews* and other publications, and a subscription to *Elements*.

Website: **www.iagod.org**

Contact: http://iagod.org/node/87

Society News Editor: Simon Jowitt (simon.jowitt@unlv.edu)

Affiliated Societies

The International Mineralogical Association, the European Mineralogical Union, and the International Association for the Study of Clays are affiliated societies of *Elements*. The affiliated status is reserved for those organizations that serve as an "umbrella" for other groups in the fields of mineralogy, geochemistry, and petrology but that do not themselves have a membership base.

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ORGANIC GEOCHEMISTRY'S LOOMING TEST

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John Eiler

If the Mars Sample Return program goes as planned, 11 years from now, a canister containing 40-some samples of lake sediments and other rocks from the surface of Mars will land in Utah, and, after a (hopefully brief!) period of worrying about the imagined dangers of extraterrestrial microbes, these samples will be released for study in Earth's laboratories. All sorts of scientists will approach these samples with all sorts of goals, but the question with arguably the biggest stakes, the broadest interest, and the greatest potential consequences will be whether these rocks contain incontrovertible evidence of present or past life on Mars.

Over the last 26 years, several studies of Martian meteorites have tried to answer this question, with results that depend on what you think counts as 'evidence', and what it takes for you to rank that evidence as 'incontrovertible'. Personally, I am unconvinced by any of the putative biosignatures found so far in the fragments of Mars impact ejecta that have landed on Earth. But returned samples will include sediments collected from well-described locations, and just might hold a discovery even a fussy reader like myself would accept: a living organism, a fossil eye ball, or clearly non-terrestrial proteins, nucleic acids, or similarly complex biomolecules.

On the other hand, these sorts of game-changing discoveries are long shots. The best evidence of life we should expect to find will be organic molecules and macromolecular materials, which we already know are present in Gale crater mudstones, surfaces of rocks in Jezero crater, and in trace amounts in some Martian meteorites. These organics just might be the trace residues of past Martians. Or, they might be something less exciting, like organics from chondritic meteorites, or products of Fischer-Tropsch chemistry or other forms of abiogenesis. Deciding which of these options it is will fall on the community of scientists represented in this issue of *Elements*, and that role will put them in a very visible hot seat. Are they—and we—ready for it?

The biomarkers that figure prominently in the papers in this issue mostly consist of compounds we have found in living, culturable organisms, generally only modestly changed by diagenesis, catagenesis, and metamorphism. How will such arguments work when confronted with molecules that just might have a biological function but that cannot be linked to any known organism? All of the papers in this volume brush up against this question, but Schubotz, Sephton, and Derenne take it on directly, pointing to possible extraterrestrial biosignatures based on chirality, molecular complexity, and isotopic properties. These may be enough to make the case if organics returned from Mars are diverse and exquisitely preserved.

However, in situ analyses of rocks in Gale Crater, made by the SAM experiment on the Curiosity rover, revealed cyclic compounds rich in Cl and S—likely products of intense surface alteration in the chemically hostile environment at the surface of Mars. What will we do with organics that are more like volcanized rubber than intact biomolecules? This is a profoundly difficult challenge—one we have never really solved after decades of studies of kerogenous materials in ancient terrestrial rocks. What distinctive properties of biomolecules survive during such extreme transformations, and how can they be mined out of refractory organic materials? My prejudiced best guess is that distinctive site-specific and multiply-substituted isotopic structures will be the most complex remnants that can be identified and interpreted. But perhaps a better chemist than myself will think of other ways to recognize moieties of past biomolecules in the soot and kerogen and assorted other gunk left behind after billions of years of Mars-surface alteration. The important point is that we have a decade to think about this question and prepare; this is the time to face these possibilities and approach them in the spirit of a grand challenge.

John Eiler
Principal Editor

ABOUT THIS ISSUE

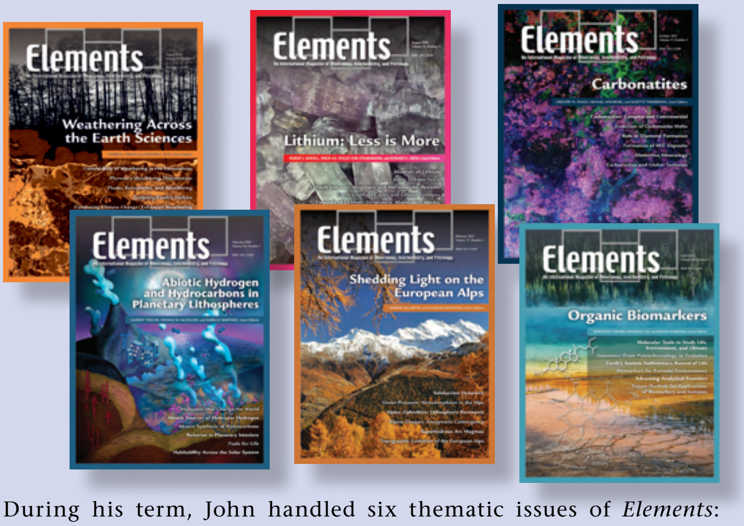
Life on Earth produces innumerable structurally diverse biomolecules that are ubiquitous in the environment. Such organic compounds are diagnostic indicators of biotic and abiotic processes in water, soils, sediments, sedimentary rocks, petroleum systems, and mineral deposits.

In this thematic issue, the authors introduce applications of biomarkers to study fundamental biogeochemical processes and the utilization of organic molecules and their compound-specific isotope signatures as proxies for paleoenvironmental and climate reconstructions. Organic geochemists also search for molecular signatures to study life evolution and early Earth history, life in extreme environments such as hydrothermal systems and the deep-crustal biosphere, and to detect extraterrestrial life forms on other planets.

The science of biomarkers spans a multidisciplinary research field with far-reaching interactions with biology (and astrobiology), chemistry, environmental and earth sciences. Major advancements in this research field have arisen from the development of innovative genomic tools and high-resolution techniques, and this issue provides a future outlook into applications of biomarkers and isotopes in Earth and environmental sciences.

FAREWELL JOHN EILER

Please join us in thanking outgoing principal editor, John Eiler, for his service as *Elements*' geochemistry principal editor (2019–2021), which comes to a close with this issue. John is a highly acclaimed geologist and geochemist at Caltech (USA), and has received numerous prestigious awards throughout his career.



During his term, John handled six thematic issues of *Elements*: “Weathering Across the Earth Sciences” (August 2019, v15n4); “Abiotic Hydrogen and Hydrocarbons in Planetary Lithospheres (February 2020, v16n1); “Lithium: Less is More” (August 2020; v16n4); “Shedding Light on the European Alps” (February 2021; v17n1); “Carbonatites” (October 2021; v17n5); and “Organic Biomarkers (April 2022; v18n2). We wish John all the best in his future endeavors!

Richard Harrison, **Becky Lange**,
Janne Blichert-Toft, **Esther Posner**, and **Jodi Rosso**

CALL FOR THEMATIC PROPOSALS

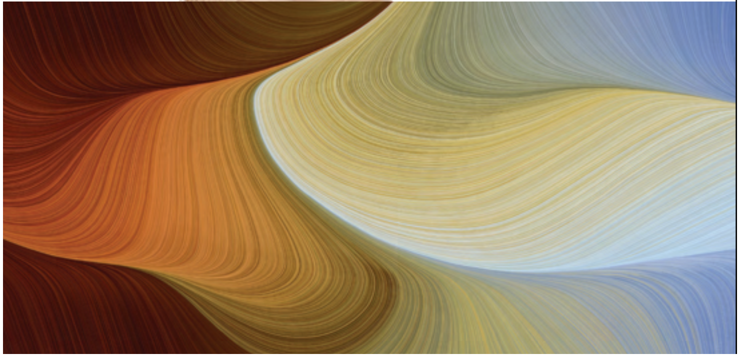
Would you like to read about a certain topic in *Elements*? Do you think your research area would make a great thematic issue? Contact the *Elements* editorial team and/or submit a proposal!

Thematic proposals are short documents that include:

- Proposed issue title
- Proposed guest editor name(s) and full contact information
- Overall scope (1–2 paragraphs describing the topic and why it is important to cover in *Elements*)
- Proposed articles with brief descriptions, proposed authors, and their institutions (introductory article + five articles preferred)
- Summary of related coverage previously published elsewhere, if applicable

More information can be found on the *Elements* website (http://elementsmagazine.org/publish-in-elements/)

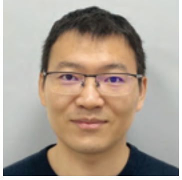
WE LOOK FORWARD TO RECEIVING YOUR PROPOSAL!



Meet the Authors

Jochen J. Brocks is a professor of geobiology at the Research School of Earth Sciences at the Australian National University. He was a Junior Fellow of the Harvard Society of Fellows from 2001 to 2004. He is fascinated by biological processes in deep time from the origin of life to mysterious ecosystems in Earth's earliest oceans. To find clues about ancient ecosystems, he studies molecular fossils preserved in billion-year-old sedimentary rocks. Currently, he and his students investigate the question of when and why complex cells and multicellular creatures appeared on Earth.

Marco Coolen is a research-focused tenured associate professor of molecular palaeoecology at Curtin University (Perth, Australia). He has played a pioneering role in establishing the use of preserved sedimentary ancient DNA (sedaDNA) signatures to reconstruct changes in lake and marine ecosystems and in the trophic interactions between its members in the context of paleoenvironmental and recent anthropogenic perturbations. Furthermore, his lab studies the activity, limitations, and evolution of the deep biosphere and to what extent sedimentary palaeomicrobiomes represent long-term genomic archives of marine biogeochemical cycling processes. Coolen was recently appointed as a Science Committee representative of "Biosphere Frontiers" at the Australia-New Zealand IODP Consortium (ANZIC).



Xingqian Cui is an associate professor of organic geochemistry and geobiology at the School of Oceanography, Shanghai Jiao Tong University (China). After completing his PhD at the University of Florida (USA) in 2016, he worked as a postdoc in the Summons Lab at Massachusetts Institute of Technology (USA) before moving to Shanghai in 2020. He has established himself as an expert in biomarkers and their compound-specific stable and radiocarbon isotopes. His research foci include organic carbon dynamics in modern land surface and platforms, as well as provenances and indications of fossil molecules in ancient ecosystems.

Sylvie Derenne is a distinguished senior scientist at CNRS in Paris (France) after a career dedicated to the insoluble organic matter in various "geomaterials" such as sedimentary rocks, soil, natural waters, and extraterrestrial materials. She aims to decipher their molecular structure by combining various techniques of analytical chemistry to understand their formation pathway and behaviour in the environment. She has been the Associate Editor of *Organic Geochemistry* for 16 years, and received the CNRS silver medal and Treibs Award of the Geochemical Society.

Katherine L. French is a research geochemist in the Central Energy Resources Science Center at the U.S. Geological Survey in Denver, Colorado (USA). She received a B.S. in chemistry from Yale University (2009), completed a Ph.D. in geochemistry from the MIT/WHOI joint program in oceanography (2014), and was an Agouron postdoctoral fellow at WHOI (2016). She focuses on molecular characterization of sedimentary organic matter, developing improved analytical methods, and enhancing understanding of biomarkers in the sedimentary record. She has applied her research to geobiology of early Earth and Phanerozoic anoxia, organic matter transport from land to sea, and petroleum systems.

Christian O. E. Hallmann is a professor of organic geochemistry at the university of Potsdam and a section head at the German Research Center for Geosciences (GFZ). He studied geology and paleontology at the University of Cologne and received a PhD from Curtin University, Australia, in 2009. Before moving to Potsdam, he was a postdoc at MIT and led an independent research group, shared between the Max Planck Institute for Biogeochemistry and the University of Bremen (MARUM). Apart from exploring new methodological approaches, his principal interest lies in the co-evolution of life and environmental conditions on the early Earth and evolving lipid biosynthesis.

Amy M. McKenna is an analytical environmental and petroleum chemist and Research Faculty III in the Ion Cyclotron Resonance user facility at the National High Magnetic Field Laboratory, an NSF-funded laboratory. Since 2009, her research has focused on analytical method development for complex organic mixtures, such as geochemical fluids, shale oil, petroleum, asphaltenes, weathered oil, and natural organic matter that utilize FT-ICR mass spectrometry.

Sebastian Naeher earned his MSc from the University of Mainz (Germany) and PhD from Eawag/ETH Zurich (Switzerland) followed by postdoctoral fellowships at Université Pierre et Marie Curie (France), Curtin University (Australia), and MARUM (Germany). Since 2016, he is the Organic Geochemist and Lead Scientist of the GNS/VUW Organic Geochemistry Laboratory at GNS Science in New Zealand. His research focuses on biomarkers and compound-specific stable isotopes to reconstruct environmental and climate changes in lakes, coastal and marine environments, soils, sedimentary rocks (deep time), and petroleum. He serves as the Associate Editor for *Biogeosciences* and two Royal Society of New Zealand science journals.

Florence Schubotz completed her undergraduate and graduate studies in marine and environmental sciences in Oldenburg and Bremen (Germany) in 2009. She then moved to the USA as an Alexander von Humboldt Feodor-Lynen Fellow to study lipid biomarkers and the metabolism of thermophilic organisms living in hot springs and hydrothermal vents at the Massachusetts Institute of Technology. She returned to Germany in 2014 to the MARUM – Center for Environmental and Marine Sciences where she is now a senior scientist investigating microbial life and its biosignatures in extreme environments including the Earth's crust, hydrothermal systems, petroleum seeps, and the oligotrophic ocean.

Mark Sephton is Professor of Organic Geochemistry at Imperial College London (UK). He is an astrobiologist who develops new techniques for the detection of prebiotic chemistry and life in the Solar System. In recognition of his work on extraterrestrial samples, asteroid 7552 'Sephton' currently orbits between Mars and Jupiter. He is a science team member for the NASA Mars 2020 Perseverance rover mission that will collect samples of Mars for return to Earth, and the Europa Clipper mission that will use mass spectrometry to search for evidence of habitability and life in the subsurface ocean of Jupiter's icy moon.

Roger Summons is Schlumberger Professor of Geobiology in the Department of Earth, Atmospheric and Planetary Sciences at the Massachusetts Institute of Technology (MIT). He is a biogeochemist who studies molecular and isotopic fossils to illuminate the history of life on the Earth. He was born in Sydney, Australia, and attended the University of New South Wales at the Wollongong University College, now the University of Wollongong, where he was awarded B.Sc. (1969) and Ph.D. (1972) degrees in chemistry. After postdoctoral work in the Genetics Department at Stanford University, he held positions at the Australian National University and Geoscience Australia before joining MIT as a professor of geobiology in 2001. He is a fellow of the Australian Academy of Science, the American Geophysical Union, The Royal Society of London, and is a member of the National Academy of Sciences.

Laura Villanueva is a senior scientist at the Royal Netherlands Institute for Sea Research and associate professor in the Department of Geosciences at Utrecht University, the Netherlands. Her work focuses on marine geomicrobiology, specifically in the diversity and physiology of microorganisms in oxygen-depleted systems. She applies genomics and evolutionary molecular biology to determine the microbial sources of lipid biomarkers of interest for paleoclimate interpretations. In the last years, she has also focused on membrane lipids of Archaea and the implications for the formation of membranes in the first life forms.

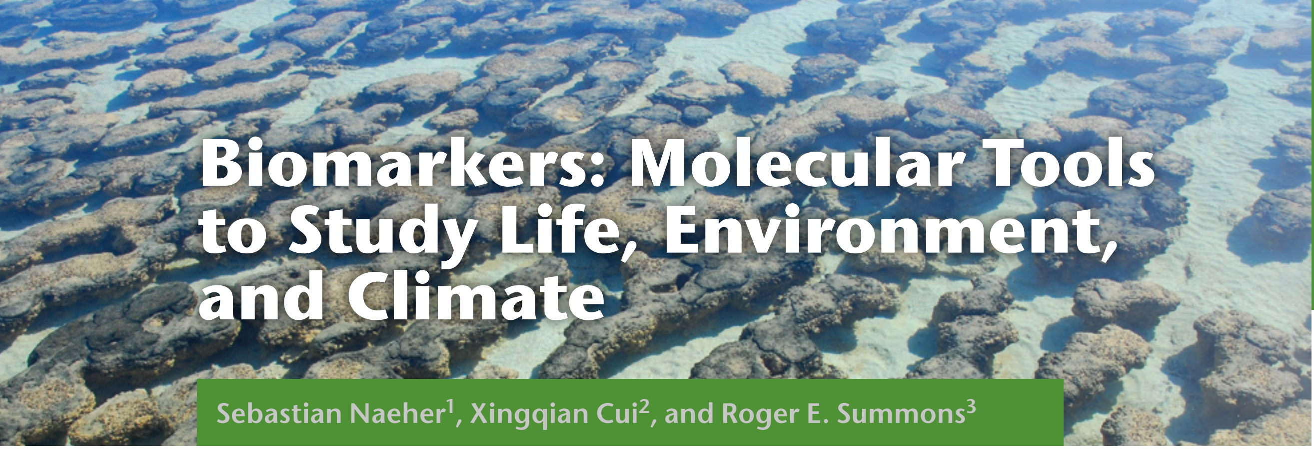
John K. Volkman is a former Chief Research Scientist with CSIRO Oceans and Atmosphere based in Hobart, Tasmania, Australia, where he led large interdisciplinary programs involving geochemistry, biogeochemistry, genetics, and environmental studies. John has published over 230 papers in the fields of organic geochemistry, environmental pollution, and marine natural products. He is well known for his research on algal and bacterial biomarkers, which have underpinned a number of paleoenvironmental proxies. In 2010, he was the recipient of the Alfred Treibs medal from the Geochemical Society and he is currently Co-Editor-in-Chief of the international journal *Organic Geochemistry*.

Lars Wörmer is a senior research scientist at MARUM – Center of Marine Environmental Sciences, University of Bremen (Germany). He holds a degree in Environmental Sciences and a PhD from Universidad Autónoma de Madrid (Spain). Lars has pioneered the implementation of mass spectrometry imaging (MSI) of molecular proxies and biomarkers in the Earth Sciences and is currently the scientific co-leader of the Geobiomolecular Imaging Lab at the University of Bremen. The MSI technique can obtain images of the spatial distribution of molecules with micrometer-resolution, which can be used to explore sedimentary archives or modern microbial ecosystems with unprecedented resolution and detail.

Paul D. Zander is a postdoctoral researcher at the Max Planck Institute for Chemistry in Mainz, Germany. He completed his BSc in Environmental Science and MSc in Geology at Northern Arizona University (USA). In 2021, he received a PhD in Climate Sciences from the University of Bern (Switzerland). His research experience includes environmental reconstructions from lake sediments, geochronology of lake sediments, biomarkers, and tephra. His recent focus is on applying ultra-high-resolution spectroscopy and imaging techniques to varved sediments.

DR PATRICK ROYCROFT IS THE NEW CURATOR OF GEOLOGY AT THE NATIONAL MUSEUM OF IRELAND

Dr Patrick Roycroft served as the copyeditor and proofreader for *Elements* for the last seven years (2014–2021), but departed in January 2022 to become the Curator of Geology at the National Museum of Ireland (NMI). Patrick did his undergraduate work at Trinity College Dublin, his PhD at University College Dublin (UCD), and two post-docs: the first as an EU Marie Curie Fellow in Marseille (France), the second back at UCD. His PhD thesis was on his discovery of new optical zoning textures in muscovite and their petrogenetic implications. Patrick is a Fellow of the Mineralogical Society of Great Britain and Ireland and, in 2021, was elected to the International Commission on the History of Geological Sciences (INHIGEO). In 2015, he wrote *648 Billion Sunrises: A Geological Miscellany of Ireland* (Orpen Press) and, in recent years, has published on cotterite and on clarifying the etymology of the mineral name "apatite" (while copyediting the "Apatite" issue of *Elements*). As the new NMI Curator of Geology, Patrick now also has to grapple with fossils—which he enjoys doing!



Biomarkers: Molecular Tools to Study Life, Environment, and Climate

Shark Bay Microbialites: Flagpole Landing, Hamelin Pool, Western Australia. PHOTO: ROGER SUMMONS.

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Life on Earth produces innumerable structurally diverse biomolecules. Biomarkers, a subset of these compounds, are sufficiently specific in the structure that they serve as tracers of organisms present in the environment or preserved in the geological record. Biomarkers can be used as proxies for organisms and the biogeochemical processes they mediate or to which they respond. They can help to document and understand processes that are otherwise difficult to study, and their fossil derivatives can be used to reconstruct past ecosystems, environmental conditions, and climate variations. Biomarker science interfaces with biology, chemistry, environmental, and Earth sciences, and provides valuable opportunities to learn more about how the Earth system has evolved over time.

KEYWORDS: biomarker; lipid; stable isotope; organic matter; environmental reconstructions; climate change

INTRODUCTION

A multitude of organic molecules, mostly originating from biological sources, can be found in the environment. Geochemists define biomarkers as organic molecules with enough structural complexity and specificity (e.g., elemental composition, carbon number, chemical structure, stereochemistry, isotope composition) to be assigned to specific organisms or groups of organisms (FIG. 1A). Traditionally, to serve as a biomarker, an organic compound had to be sufficiently stable to be preserved in the environment, either in its original, intact form or with minimal modifications such that it could be traced to an original precursor. However, the revolution in molecular biology since the late 20th century has demonstrated that transiently stable biomolecules, specifically DNA and proteins, can be detected and traced to their origins with great fidelity (Villanueva and Coolen 2022 this issue). The term biomarker is not exclusive to geochemistry and is also used in molecular biology, medicine, pharmacology, and forensics to describe compounds that have some form of diagnostic utility for disease or health conditions. Here, we focus on biomarkers from plants or microbes with diagnostic utility in the environmental and Earth sciences.

This review focuses on the non-hydrolysable (i.e., not reactive with water) and more recalcitrant class of biomolecules known as lipids because of their resistance to chemical or biological degradation. These biomarkers can be readily detected with great sensitivity in aquatic settings (FIG. 2), sediments, soils, rocks, and petroleum, typically by applying mass spectrometry in combination with a separation technique such as gas or liquid chromatography.

Lipids are a small fraction of the biomass of most organisms and organic matter in the environment and exhibit a great variety of molecular structures. Although not necessarily chemically related, lipids are operationally defined as being insoluble in water and soluble in organic solvents. They include fatty acids, natural oils, waxes, steroids, pigments, and the intact polar lipids (IPLs) and triglycerides present in all known organisms (FIG. 1A). The carbon skeleton is the most durable part of these and other biomolecules and has the greatest potential to be preserved in sedimentary rocks and as petroleum over long periods of geological time. This simple fact implies that biomarkers can be used to relate organisms in today's world with those of the past. This finding forms the basis of the "biomarker principle" (Gaines et al. 2008) that started in the 1930s with Alfred Treibs' discovery of chlorophyll-derived pigments from algae that were preserved in an ancient bituminous oil shale.

A major distinction between organic chemistry and organic biogeochemistry is the limited variety of organic structures in the biosphere relative to the almost unlimited number that is feasibly possible. This limit is a consequence of the commonality in the biosynthetic pathways shared across the many forms of life that produce biomarkers. This constraint on the nature and number of biomolecules is central to the whole biomarker concept.

Biomarker Discovery

Biomarker discoveries have consistently coincided with advances in analytical technologies and perceptions of utility. Some researchers, largely motivated by curiosity about Earth's history, recognised the potential of applying our understanding of the identity, sources, and natural variability of compounds found in living organisms and in contemporary environments to study ancient biota, the evolution of life, and past environmental changes. Others have been motivated to understand the composition and origins of petroleum, detection of pollution and its sources,

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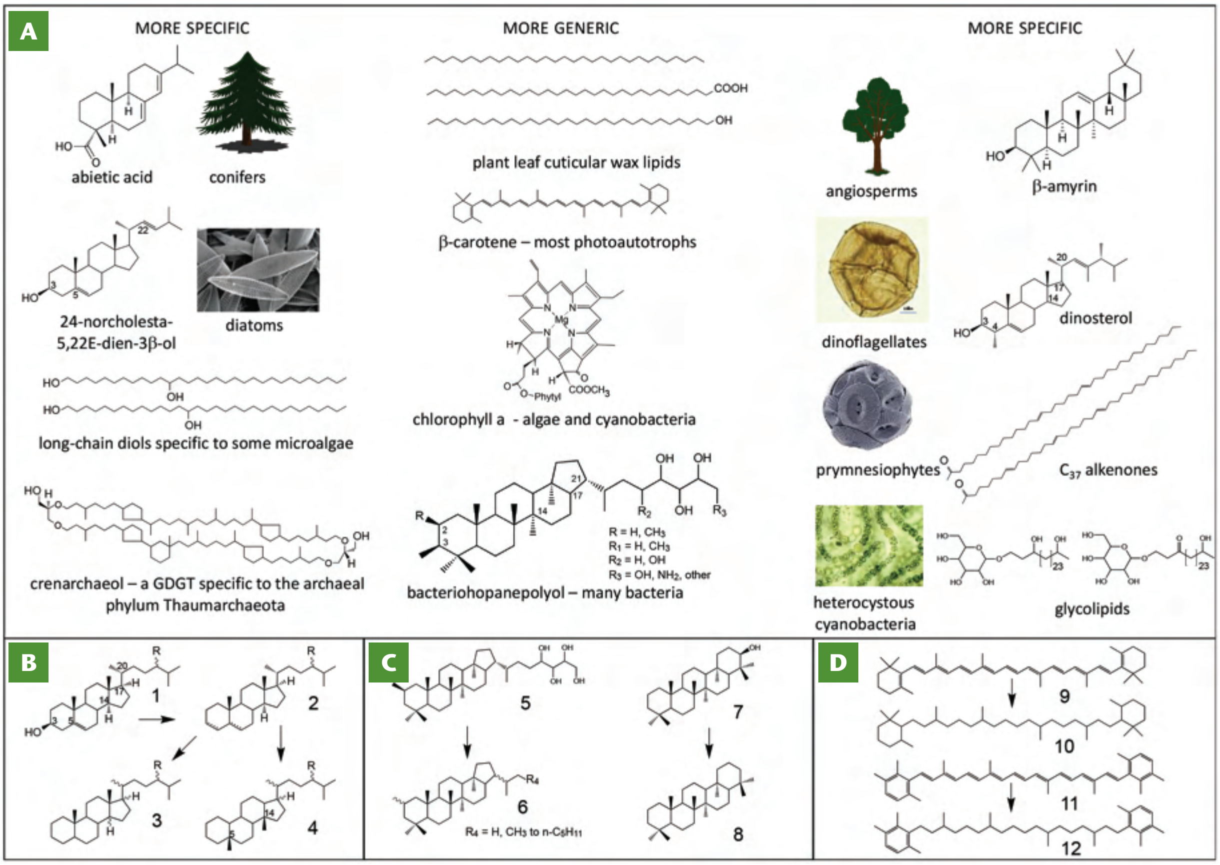

FIGURE 1 A snapshot showing the structures of some of the biomarkers discussed in this article. (**A**) Biological lipids used for paleoenvironmental and paleoclimate reconstruction, grouped according to their relative specificity. (**B**) Some of the key steps in diagenesis of sterols (1) leading to sterenes and steradienes (2), which can then be reduced to steranes (3) or rearranged and reduced to diasteranes (4). (**C**) Diagenetic transformation of triterpenoids represented by 2-methylbacteriohopane tetrol (5) being reduced to 2-methylbacteriohopanes (6), and tetrahymanol (7) being converted to gammacerane (8). (**D**) Reduction of β-carotene (9) to β-carotane (10) and isorenieratene (11) to isorenieratane (12). Many of these transformations are mediated by sedimentary sulfide and proceed through organo-sulfur compound intermediates.

or to discern the nature of organic materials preserved in sites of archaeological interest.

The field of natural products chemistry presented many early clues regarding the types of molecules that might be useful as biomarkers. For example, the study of sterols in nature and their diverse patterns of side-chain alkylation and ring modifications provided a foundation for identifying the sources of steroids present in sediments (Volkman 1986). In other cases, sediment analyses have revealed the presence of lipids, extended hopanoids for example, for which a precursor in an organism was only identified many years later (Rohmer and Ourisson 1976).

Biomarker Preservation

The relative stabilities of different classes of biomarker molecules define how, why, and where they can be used. Until recently, biopolymers such as DNA and proteins could not be used due to their hydrolysable and transient nature in the environment and due to associated analytical challenges. However, proteins and DNA can sometimes survive for thousands of years and—given advances in sequencing technologies, contamination control, and the availability of large DNA databases—major advances in their utility as biomarkers are expected in the near future (Villanueva and Coolen 2022 this issue).

At the next level of preservation potential are the IPLs, which include phospholipids and sulfolipids (i.e., lipids possessing functional groups containing phosphorous or sulfur), glycolipids (i.e., bound to carbohydrates), and other types that, with proteins, form cell membranes. The IPLs are comprised of a hydrocarbon-based core (fatty acid or long-chain alcohol) that is linked through glycerol to a hydrolysable headgroup. Their chemotaxonomic (i.e., biological classification through molecular structures) and ecophysiological (i.e., environmental impact on organisms) diagnostic value stems from particular combinations of headgroup identity, the nature of the hydrocarbon backbone (straight-chain, branched, isoprenoidal, or cyclic), the way the hydrocarbons are bonded to the glycerol (ester, ether, or both), and the stereochemical configuration of the glycerol moiety (Summons and Lincoln 2012). Because most IPL headgroups are hydrolysable, as are the ester bonds linking fatty acid chains to the glycerol, IPLs only survive for a limited time once an organism dies. Nevertheless, and despite this fragility, they can be used to specifically characterise the living components of an environment.

Clear distinctions exist in IPL structure across the tree of life. Bacteria and eukaryotes synthesise IPLs with polymethylenic (straight or simple branched) hydrocarbon chains ester-bonded to the *sn*-1,2 hydroxyl groups of glycerol. Some phyla of thermophilic bacteria (e.g., Aquificae, Thermotogae) may have one or more chains linked through ether bonds. In contrast, archaea synthesise isoprenoidal alkyl chains, which are linked to the *sn*-2,3 hydroxyls of glycerol through ether bonds. Archaeal core lipids are therefore hydrolytically stable and chemically distinctive. The terminal carbon atoms of the hydrocarbon chains of ether lipids in bacteria and archaea can become joined by C–C bonds creating membrane-spanning glycerol dialkyl glycerol tetraether lipids (GDGTs) (FIG. 1A). The structural diversity described above is merely a snapshot of the predominant kinds of lipids with intermediate stability, which form the building blocks of membranes.

Many classes of non-hydrolysable lipids—including fatty acids, alcohols, ketones, and hydrocarbons—are even more recalcitrant. These can be subdivided into those with polymethylenic hydrocarbon chains, polyisoprenoidal branching patterns, or cyclic molecules with one or more rings. A further source of variability and information are stereochemical features that are encoded during biosynthesis and result in different spatial, three-dimensional configurations of organic compounds (FIG. 1A).

Diagenesis

An important aspect of biomarker science is the concept of diagenesis. This complex topic encompasses molecular transformations in the aftermath of cell death due to microbial activity, oxidation, reduction and, ultimately, temperature increases (FIGS. 1B–1D). Bacteria will attack most biomarkers over time, especially those with functional groups. Destruction can be complete in the presence of oxygen or greatly retarded in its absence. Organic molecules can also become cross-linked to form macromolecules ultimately resulting in kerogen.

The availability of sulfide is an important ingredient in diagenesis and is especially important in marine environments where sulfide is generated from seawater sulfate by sulfate-reducing bacteria (Wakeham et al. 1997). Generally, sulfide promotes organic matter preservation because it is toxic to many organisms that would otherwise destroy it. Sulfide also acts as a cross-linking and hydrogenating agent that promotes kerogen formation and chemically reduces labile compounds (Hebting et al. 2006). Diagenesis is an ongoing process throughout the conversion of a sediment into a lithified sedimentary rock, and the changes that occur in organic compounds follow predictable trajectories.

The diagenesis of sterols (FIG. 1B) is an extensively studied topic due to the immense variety of distinct compounds that can arise from a single precursor such as cholesterol. Reduction of sterols affords stanols that can then dehydrate, forming sterenes. These can then undergo isomerisation, rearrangement, or aromatisation. Dehydration plus reduction produces 5α(H)-cholestane and 5β(H)-cholestane which, under the influence of the increasing temperature and pressure of burial, can isomerise further. Despite these structural transformations, the products remain diagnostic of their precursors. In rare cases, it has been possible to identify products of multiple cholesterol diagenesis pathways in a single rock sample due to exceptional preservation (Melendez et al. 2013).

Isotopic Compositions

Lipids and their preserved diagenetic products contain carbon and hydrogen, often together with oxygen, nitrogen, and sulfur. These elements have stable isotopes that exhibit natural variabilities that are informative, useful, and measurable. Carbon isotopes convey information regarding carbon fixation pathways biosynthesis and, potentially, atmospheric pCO_2 (Schubert and Jahren 2012). The H and O isotopic compositions of biomarkers encode information about hydrological cycles including humidity, precipitation, and altitude (Sachse et al. 2012). Nitrogen isotopes are strongly influenced by trophic (i.e., feeding/nutrition) relationships between organisms. All of these isotopes can be measured on bulk materials or at the level of individual molecules via compound-specific stable isotope analysis (CSIA) (Hayes et al. 1990). Since its development in geochemistry, CSIA has been widely adopted in biochemistry, forensics, archaeology, and product authentication among others. Further technological innovations are aimed at measuring position-specific C-isotope data within molecules and isotope "clumping" in certain compounds.

METHODOLOGIES FOR BIOMARKER CHARACTERISATION IN ORGANISMS AND THE ENVIRONMENT

As mentioned, lipids are operationally defined as compounds that are soluble in organic solvents and insoluble in water. Thus, lipids are extracted from a sample using solvents, assisted by heat, pressure, ultrasonication, or microwaves. Combinations of solvent and the type of mechanical assistance are chosen to optimise efficiency and protect labile components. The extraction solvents are then carefully removed to obtain the total lipid extract in the case of organisms and environmental samples, or "bitumen" in the case of ancient rocks. Often these extracts comprise only a minor component (~1%–10%) of the total organic matter present in a typical environmental sample with the solvent-insoluble remainder comprising hydrolysable macromolecules such as carbohydrates, proteins, DNA, and RNA.

The analytical pathway is then largely dictated by the compound classes in the total lipid extract that are being targeted. Liquid chromatography (LC) is widely used as a pre-concentration/purification approach in the analysis of lower molecular weight lipid classes such as sterols, alkenones, fatty acids, and hydrocarbons. These separations can be conducted on short open columns of silica gel (flash chromatography) using pre-prepared cartridges loaded with purpose-designed solid phases or more elaborate LC separations. Resulting lipid fractions are then analysed by gas chromatography mass spectrometry (GC–MS), which is suitable for stable and volatile compounds. Analyses of functionalised compounds, especially sterols and fatty acids, can be further enhanced by chemical derivatisation to improve the fidelity of subsequent GC–MS analyses. High-performance liquid chromatography (HPLC) and more versatile mass spectrometers have vastly widened the analytical window to include larger, less volatile, and less stable molecules. High-resolution mass spectrometry using time-of-flight and ion-trap mass analyses have largely replaced the previously expensive magnetic sector instruments in this application. For reliability, ease of use, and low cost, single or triple quadrupole mass analysers are the optimal instruments.

Analysis of fossil hydrocarbons in ancient sediments and oils typically follows a well-established protocol so that results can be compared to historical data sets that were largely acquired by scientists working in the petroleum industry (Peters et al. 2005). In this approach, the solvent extract of sediment (bitumen) is treated as if it was a crude oil. Intractable, high molecular weight components (asphaltenes) are dispersed into pentane or heptane where they are insoluble and precipitate, whereas maltenes (low-molecular hydrocarbons) remain in solution. Elemental sulfur, a common and intrusive component, is then removed using activated copper. Column chromatography can be used to separate the saturated, aromatic, and polar compounds (i.e., N-, S- and O-containing molecules; NSO) based on their different polarities. Gas chromatography with mass spectrometry and, increasingly, coupling of two or more MS techniques in tandem (MS–MS) then enable identification and quantification of an array of alkane, isoprenoid, steroid, and triterpenoid isomers that are useful for evaluating the thermal histories of sedimentary basins and for correlating oils with their

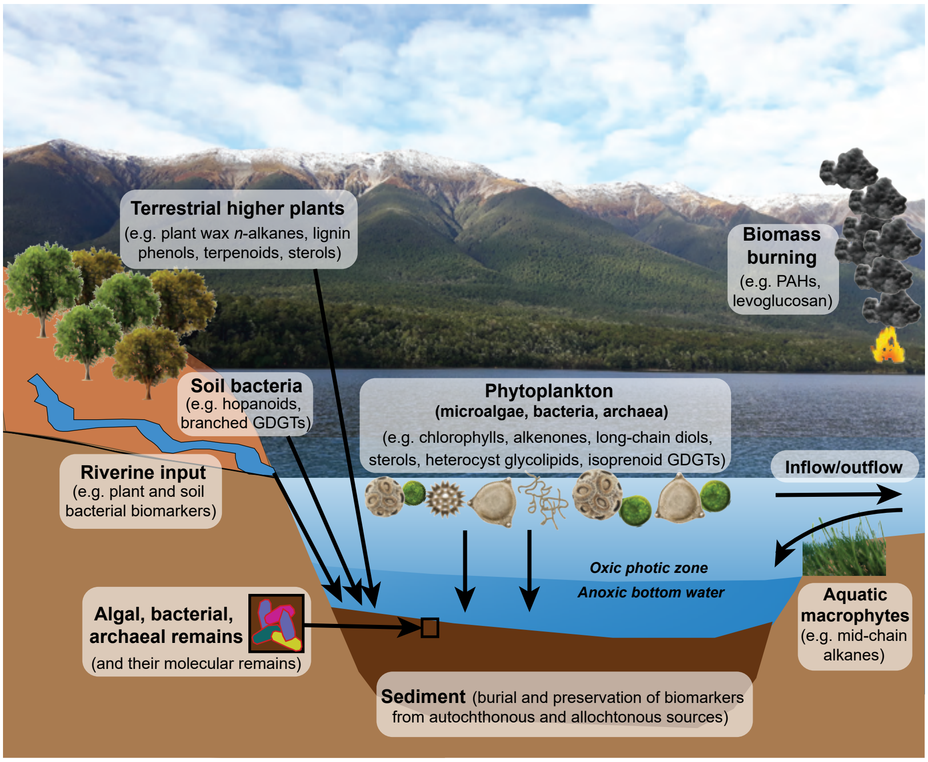

FIGURE 2 Illustration of biomarker sources, transport, and preservation in aquatic and terrestrial environments. Abbreviations: polycyclic aromatic hydrocarbons (PAHs); glycerol dialkyl glycerol tetraethers (GDGTs).

sources (Peters et al. 2005). Biomarker hydrocarbons have been particularly useful for optimising aspects of petroleum discovery and production, especially in recent years by facilitating production from unconventional reservoirs.

Biomarkers also can be retrieved from otherwise intractable macromolecular organic matter (e.g., kerogen, asphaltene, NSO fractions) using chemical degradation, pyrolysis, or hydropyrolysis. In the latter, *in situ* and kerogen-bound biomarkers released by high-pressure catalytic hydrogenation can be compared to co-occurring soluble and moveable bitumen to identify similarities and differences and to test whether or not the hydrocarbons are native to the sediment layer being analysed (Love et al. 2008). In marine kerogens and bitumens, a significant fraction of the biomarker hydrocarbons may be tied up in the form of organosulfur compounds. Macromolecular organosulfur compounds can be rendered into individual components using Raney Nickel desulfurisation, a valuable method for tracking the processes at work during early diagenesis (Hebting et al. 2006).

For analyses of IPLs and light-sensitive pigments, minimal pre-treatment is usually preferable prior to LC–MS analysis. Technical developments and cost reductions have allowed MS–MS and high-resolution tools to replace prior chromatographic separations by taking advantage of their far superior mass discrimination capabilities to resolve and identify individual components of complex mixtures (McKenna et al. 2022 this issue). Liquid chromatography–mass spectrometry methods have revolutionised analysis of high-molecular polar and involatile compounds such as chlorophylls, bacteriohopanepolyols, heterocyst glycolipids, and others (Talbot et al. 2016; Bauersachs et al. 2021).

Techniques for spatially resolved analysis of biomarkers in sedimentary sequences and molecular imaging of organic compounds have also become widely available in recent years including secondary ion mass spectrometry, laser-pyrolysis GC–MS, matrix-assisted laser ionisation time-of-flight mass spectrometry, and methods further discussed in McKenna et al. (2022 this issue).

BIOMARKER CLASSES AS INDICATORS OF ORGANIC MATTER SOURCES

Biomarkers originate from all forms of life: archaea, bacteria, and eukarya all produce molecules that are distinctive to particular taxa, in cases down to individual species (FIGS. 1A and 2). Hence the molecular composition of an environmental sample can be used to evaluate relative contributions of organic matter sources to a particular sample. Biomarkers have also become an important complement to environmental DNA as a means of documenting microbial communities and ecological relationships (Villanueva and Coolen 2022 this issue).

Distributions of Alkanes, Fatty Acids, and Alcohols as Source Indicators

The *n*-alkanes are almost ubiquitous in sediments and typically occur together with *n*-fatty acids and *n*-alcohols. The acids and alcohols, biosynthesised by bacteria and eukaryotes, are typically dominated by even-carbon-numbered chain lengths, whereas *n*-alkanes, formed by decarboxylation of acids, are dominated by odd-numbered homologs. This pattern is the basis of the carbon preference index (CPI), with high values reflecting a strong dominance of either even or odd carbon numbers and values close to one reflecting slight or no predominance of even or odd (Peters et al. 2005). Low CPI values indicate microbial degradation and alteration of biomarkers in young geological settings such as soils, peatlands, and even some sediments. Petroleum typically has low CPI values because hydrocarbon cracking upon thermal maturation leads to a smoothing of the alkane distributions, and often shows characteristic "humps" in chromatograms (i.e., nearly continuous elution of a variety of compounds from a chromatographic column over an extended period), the so-called unresolved complex mixture. High CPI values of *n*-alkanes are typical of environmental samples that have not been heated and reflect input of vascular plant leaf wax (typically with strong preference for C_{27}, C_{29}, and C_{31}), aquatic macrophytes (typically with C_{21}, C_{23}, or C_{25} preferences), or *Sphagnum* moss (specifically C_{25}). Low molecular weight *n*-alkanes with odd-carbon-number preferences (C_{15}, C_{17}, C_{19}) are typical of cyanobacteria or microalgae. Some cyanobacteria (e.g., *Calothrix*) synthesise distinctive branched alkanes. As an example of how additional indices of *n*-alkane proportions may be applied, the P_{aq} index (i.e., ratio of $(C_{23} + C_{25})/(C_{23} + C_{25} + C_{29} + C_{31})$ *n*-alkanes) is used to estimate relative contributions of aquatic macrophytes (mainly mid-chain length homologues) versus higher plant (mainly long-chain homologues) input to environmental samples. Similarly, the average chain length (ACL) parameter for *n*-alkanes reflects vegetation changes based on the differing predominant carbon chain lengths of *n*-alkanes produced by different plant types.

Terpenoid Biomarkers for Protists, Vascular Plants, and Animals

Sterols (Fig. 1B), or sterol surrogates such as tetrahymanol (Fig. 1C), are essential components of the cell membranes of all eukaryotes, that is protists, plants, and animals. The C_{27} sterols are typical source indicators of animals such as zooplankton and red algae. The C_{28} sterols are prevalent in prasinophyte green algae, diatoms, and fungi. The C_{29} sterols are typical for higher plants and green algae. C_{30} sterols are indicators of pelagophyte algae and sponges. Steranes, degradation products of sterols, are prevalent in sediments, rocks, and petroleum and provide a window into the transitions of the dominant types of phytoplankton that lived in the oceans of the past.

In addition to having diagnostic leaf waxes, vascular plants have evolved a rich assemblage of pathways for the production of diverse chemicals that are useful for life in terrestrial ecosystems (Fig. 1A). These include compounds that encourage pollination, resist insect predation, or repair injury. The biochemistry of plant terpenes is central as it has given rise to diagnostic biomarker compositions such as the prevalence of diterpenes in conifers and triterpenes in flowering plants. As with steroids, these compounds display secular and spatial variations in the geological record that inform aspects of the origin and dispersal of vegetation in the past. Prime examples include the odoriferous terpenes prevalent in, but not exclusive to, conifers (e.g., pinenes), the oleanoid triterpenes (e.g., β-amyrin, lupeol) that can be used to track the expansion of angiosperms from the Late Cretaceous onwards, and the cadalene-based resins characteristic of the dipterocarp flora that dispersed across South Asia in the Paleogene.

Reconstructing Phytoplankton Communities, Redox Conditions, and Nutrient Cycling with Photosynthetic Pigments

All photosynthetic organisms use pigments for light-harvesting and photoprotection. These pigments (chlorophylls, carotenoids) (Figs. 1A and 1D) are widespread indicators of photosynthetic algae, bacteria, and plants, and their preserved remains serve to reconstruct microbial community composition, primary productivity, and water column redox conditions (Keely 2006). The recent development of hyperspectral imaging of sediment cores for detailed analysis of pigment stratigraphic distribution, with up to the interannual resolution, is further discussed in McKenna et al. (2022 this issue).

Intact pigments are rapidly transformed by diagenesis into a large variety of chlorins (e.g., pheophytins, pheophorbides), porphyrins, maleimides, and carotanes. Their C- and N-isotopic compositions can distinguish phytoplanktonic communities and disentangle dominant nitrogen acquisition pathways (e.g., nitrate uptake versus nitrogen fixation) in aquatic systems (Ohkouchi and Takano 2014).

Green and purple sulfur bacteria (GSB and PSB), which perform anoxygenic photosynthesis, simultaneously require hydrogen sulfide as an electron donor and anoxia in the upper water column. This state is known as photic zone euxinia and such conditions exist in present-day fjords and stratified water bodies such as the Black Sea. The GSB and PSB synthesise diagnostic bacteriochlorophylls (bacteriochlorophylls *c*, *d*, *e*) and carotenoids (isorenieratene, chlorobactene, and okenone). Such pigments and their diagenetic transformation products (e.g., porphyrins, maleimides, aryl isoprenoids) are typically viewed as indicators of oxygen-limited conditions or episodes such as oceanic anoxic events (Hallmann et al. 2022 this issue).

Bacterial and Archaeal Biomarkers

Bacteria and archaea are widespread and abundant in aquatic environments, sediments, and soils and dominate in situations where eukaryotes are excluded by extremes of temperature or pH (e.g., many hydrothermal systems, see Schubotz et al. 2022 this issue). Their presence in modern environments can be distinguished exclusively on the basis of the chemistry of their IPLs although this distinction becomes more difficult as diagenesis progresses. Some biomarkers, such as bacteriohopanepolyols, are specific to bacteria and diagenetically transform to hopanols, hopanoic acids, and hopane hydrocarbons (Fig. 1C), which are some of the most geochemically stable, abundant biomarkers present in the sedimentary record. Archaea, on the other hand, are notable for their ether-linked membrane lipids such as archaeols and the membrane-spanning isoprenoidal glycerol dibiphytanyl glycerol tetraethers (iGDGTs) (Fig. 1A), which are analogous to branched glycerol dialkyl glycerol tetraethers (brGDGTs) in bacteria. Interestingly, and despite the antiquity and prevalence of archaea in many modern environments, archaeal biomarkers are relatively rarely reported in ancient sediments.

PALEOCLIMATE INDICATORS

Molecular indicators of climate have become increasingly valuable and widely applied, especially when used in combination with inorganic climate proxies or where alternatives (e.g., $\delta^{18}O$ paleothermometers, Mg/Ca ratios, or carbonate clumped isotopes) are absent or confounded.

Alkenones as Surface Water Paleothermometers in Lakes and Oceans

The application of biomarkers for reconstructing past sea and lake surface water temperatures began in the late 1980s when it was discovered that the proportions of sedimentary alkenones (long-chain C_{37}–C_{39} ketones with two, three, and four double bonds; Fig. 1A) differed systematically with the water temperature used in laboratory cultures of haptophyte algae (Brassell et al. 1986). The unsaturated ketone index ($U^{K'}_{37}$) reflects the relative increase of di-unsaturated relative to tri-unsaturated C_{37} alkenones in warmer waters. This index has been refined and optimised to account for geographical location, haptophyte community composition and dominance of particular species, or particular temperature calibrations (i.e., mean annual versus seasonal temperature). Differences in alkenone distributions in marine and freshwater environments demonstrate how biomarkers provide distinctive information on past depositional settings. Alkenone indices may also be influenced by other factors such as the phylogeny of the haptophyte producers, salinity, light regime, nutrient limitations, and degradation. With care and calibrations appropriate for the environment being studied, reliable temperature reconstructions are readily accomplished.

Reconstructing Aquatic and Terrestrial Paleoclimate with GDGTs

There are two classes of GDGTs, one originating from archaea and the other from soil bacteria (Fig. 1A), and both serve as important proxies of past water (Schouten et al. 2002) and air temperatures (Weijers et al. 2007). The TEX_{86} index (tetraether index of tetraethers consisting of 86 carbon atoms) is based on the ratios of particular iGDGTs derived from Thaumarchaeota. Global and regional correlations of this index to surface water temperature in oceans and some large lakes have been firmly established although complexities exist. The ring index is an alternative proxy based on a weighted average of iGDGT cyclopentane moieties and can help determine if TEX_{86} temperature estimates are influenced by additional factors.

In terrestrial environments, bacterial GDGTs containing methylated, branched chains (brGDGTs) are proxies for average air temperatures, and calibrations are available for soils and peat. These compounds additionally serve as indicators of past air temperatures in aquatic systems with high terrestrial input. Soil pH also can be estimated using the cyclisation ratio of branched tetraethers.

The ring index of hydroxylated isoprenoid GDGTs is a new, increasingly used indicator that also has been shown to be correlated with surface water temperature in lakes and oceans (Lü et al. 2015).

Long-Chain Diols as Surface Water Paleothermometers in Lakes and Oceans

A third class of molecular paleothermometers are long-chain (C_{26}–C_{32}) diols (two alcohols), derived from eustigmatophyte algae and *Proboscia* diatoms. The C_{28} 1,13-, C_{30} 1,13-, and C_{30} 1,15-diols (Fig. 1A) show a strong correlation with water temperature that is expressed as the long-chain diol index. This proxy can be used for reconstructions of surface water temperatures in lakes and oceans. The newest global marine calibration of the long-chain diol index shows a strong correlation with annual mean sea surface temperature but performs best if environments with low salinity and high contributions of *Proboscia* diatoms are excluded, as both influence long-chain diol distributions (de Bar et al. 2019).

Reconstructing Water Temperature with Heterocyst Glycolipids in Freshwater Lakes

Heterocyst glycolipids are cell wall components specific to the heterocysts in nitrogen-fixing cyanobacterial orders Nostocales and Stigonematales. Heterocyst glycolipids consist of carbohydrate groups bonded to long-chain diols, triols, keto-ols, and keto-diols via glycosidic linkages (Fig. 1A). In laboratory cultures, the amount of keto-ols and keto-diols decreases with increasing temperature relative to their corresponding diol and triol counterparts. The heterocyst diol index of 26 carbon atoms and other related heterocyst glycolipid–based indices are correlated to growth temperature in cyanobacterial cultures and are promising surface water temperature indicators in freshwater lakes (Bauersachs et al. 2021).

Reconstructing Water and Air Temperatures with Bacterial Hydroxy Fatty Acids

Another promising paleotemperature proxy is based on 3-hydroxy fatty acids (3-OH-FAs), which are membrane lipids with 10 to 18 carbon atoms, mainly derived from gram-negative bacteria that are widespread in aquatic and terrestrial environments. The ratio of 3-methyl to normal C_{15} 3-OH-FAs (RAN_{15} index) and C_{17} 3-OH-FAs (RAN_{17} index) is correlated with mean annual air temperature in soils, whereas the ratio of 3-methyl to normal C_{13} 3-OH-FAs (RAN_{13} index) in marine surface sediments is correlated with sea surface temperature. First applications of these indices were based on local datasets, but the potential for a global calibration has also been demonstrated (Wang et al. 2021).

RECONSTRUCTING PALEOENVIRONMENTS, HUMAN IMPACT, AND AGE FROM BIOMARKERS

Precipitation, Aridity, and Biomass Burning

The H-isotopic composition (δ^2H or δD value) of plant wax *n*-alkanes is sensitive to the availability of moisture to plant leaves and has been used as an important indicator of past precipitation (Sachse et al. 2012) and changes in vegetation composition.

Aridity increases the frequency and intensity of wildfires. During natural fires, charcoal serves as a local indicator of biomass burning, whereas volatile products such as highly condensed polyaromatic hydrocarbons (PAHs) may be transported over long distances in the atmosphere and eventually deposited. Such "fire-indicator" biomarkers have been reported from soil, sediment, and ice core records. However, combustion PAHs may also originate from anthropogenic ignition of coals and other fossil organic matter. In contrast, levoglucosan is considered the most specific indicator of natural fire, as it is derived from burning cellulose (Simoneit 2002).

Stratification and Salinity

Water column stratification indicators are tetrahymanol and its fossil derivative gammacerane (Fig. 1C). The rationale behind these indicators is that bacteria tend to congregate at the haloclines or chemoclines of salinity- or redox-stratified water columns. Bacterivorous ciliates feeding on these communities use tetrahymanol as a sterol surrogate with the result that gammacerane will accumulate in the sediments below such features. Archaeal lipids can also serve as salinity proxies (Turich and Freeman 2011).

Biomarker Tracers of Water Quality and Human Impact

Eutrophication is the process by which a body of water becomes progressively enriched with minerals and nutrients. Typically induced by anthropogenic pollution, land-use changes, and agricultural practices, eutrophication leads to enhanced biological productivity and algal blooms, which can be reconstructed from sediments deposited from that water using phytoplanktonic pigments and other algal biomarkers. Sewage pollution is one possible contributing factor of eutrophication, which can be traced by specific fecal biomarkers such as coprostanol, a stanol produced by the gut microbiota of humans and some other large mammals. Fecal steroids are also valuable for archaeological investigations where they can distinguish human coprolites from those of other primates (Sistiaga et al. 2015).

Petroleum pollution is indicated by compounds that are typically found in crude oil, gas condensates, or gasoline, which have a clear forensic fingerprint. The *Deepwater Horizon* oil spill in the Gulf of Mexico in 2010 is a prime example where water column hydrocarbon distributions changed with time due to the original event followed by natural bioremediation and human efforts in spill clean-up (Farrington et al. 2021).

Age-Diagnostic Biomarkers and Compound-Specific Radiometric Dating

Age-specific biomarkers are based on diagnostic organic compounds produced by specific groups of organisms that are indicative of their evolutionary emergence based on the geologic fossil record (e.g., oleanane as an indicator of angiosperm plants since the mid-Cretaceous). Compound-specific radiocarbon measurements have revolutionised age determination by distinguishing the ages of different compound classes, as opposed to conventional dating of bulk sediment or plant material in sediments (Ingalls and Pearson 2005). Biomarkers, purified in sufficient quantities by GC or LC can be converted via CO_2 to graphite and dated by accelerator mass spectrometry. Radiocarbon measurements can also constrain residence times of different compound classes in the environment and have improved our understanding of permafrost degradation, climate feedbacks, and timescales of terrestrial organic matter transport from continents into the ocean (Eglinton et al. 2021).

CONCLUDING REMARKS

Biomarkers and their isotopic signatures are invaluable biogeochemical indicators that enable studies of changes in oceanic phytoplankton communities, the colonisation of terrestrial environments, climate variations of the past, and human impacts on contemporary landscapes. Biomarkers can be indicators of water and air temperatures, precipitation, redox conditions, salinity, stratification, or pH in aquatic and terrestrial environments. Human impacts through pollution and land-use changes can also be revealed. Biomarkers and compound-specific radiocarbon dating afford timescales of environmental processes and important insights into early life evolution and resource evaluation.

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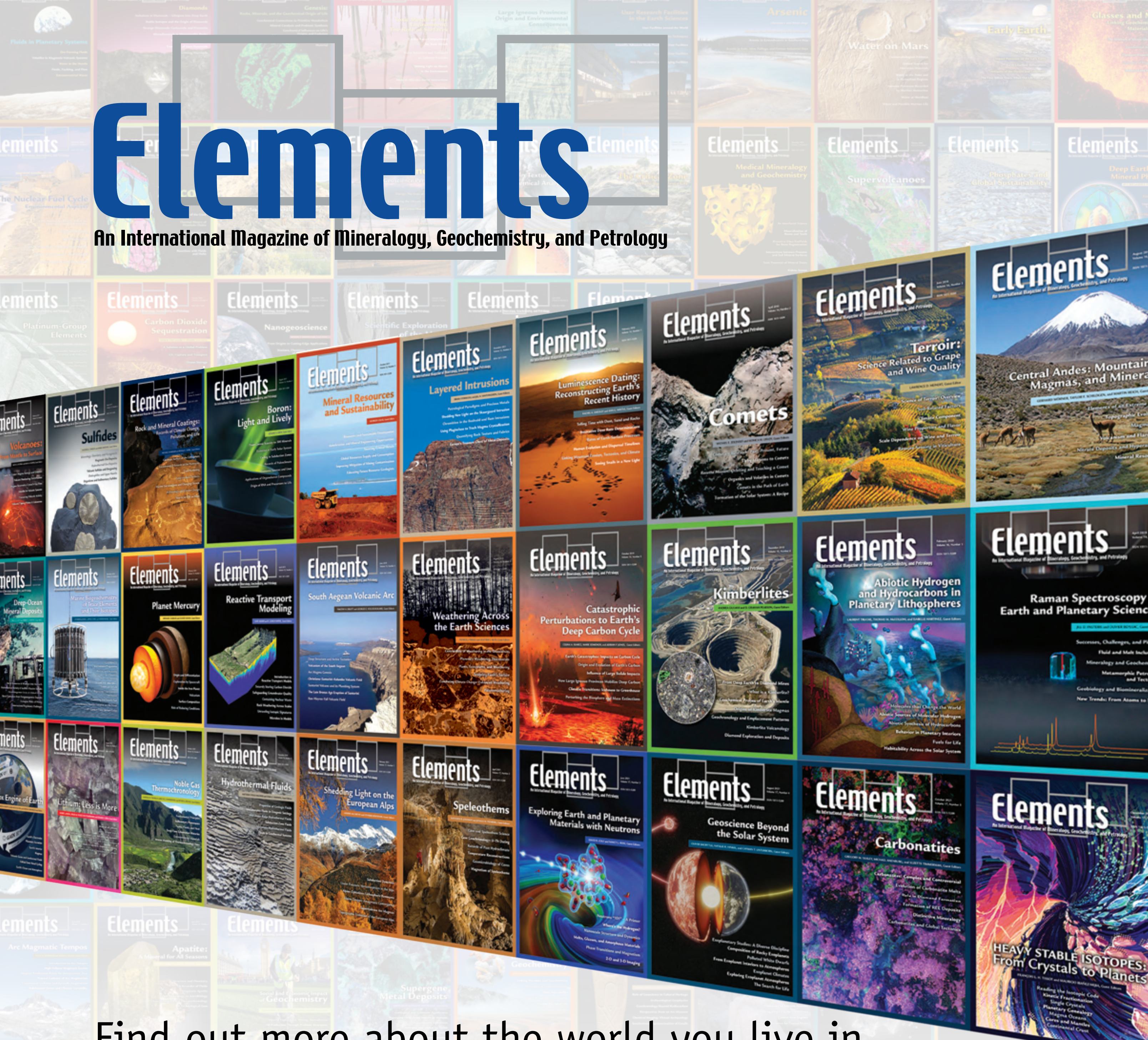

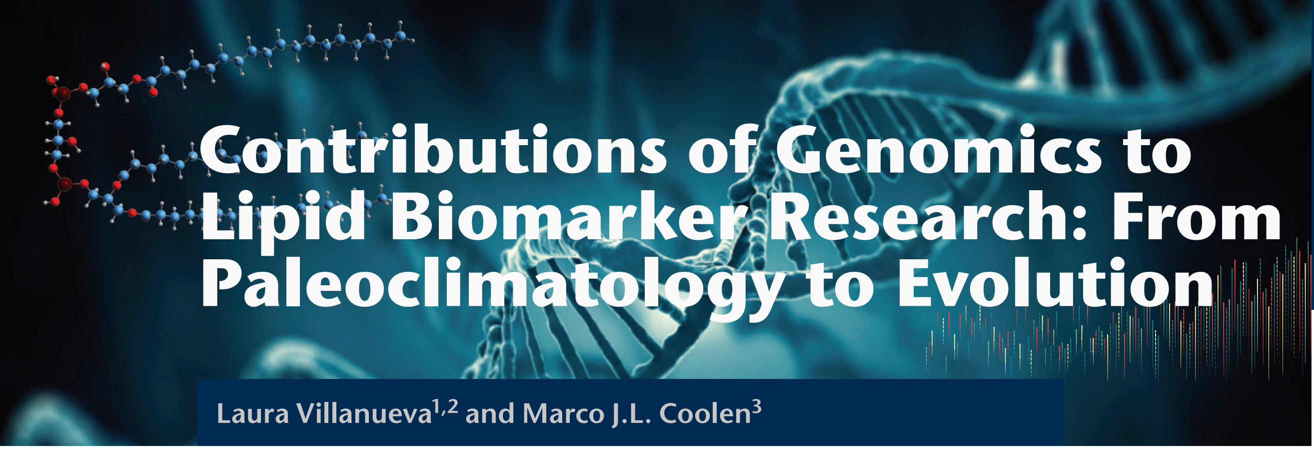

Contributions of Genomics to Lipid Biomarker Research: From Paleoclimatology to Evolution

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Lipid biomarkers can be preserved over long geological timescales. They are widely used as taxonomic markers of past and present microbial communities and as parts of organic paleoclimate proxies. However, questions remain regarding the precise biological sources and evolution of the acquisition of specific lipids, and why and how they are synthesized. In the last two decades, the use of DNA-based approaches has proven to be key in unraveling some of these questions. As methodological approaches improve, (paleo) genomics increasingly supports lipid biomarker research. Here, we provide an overview of the usefulness of DNA-based approaches over the years, including ancient sedimentary DNA research and phylogenomics, and a perspective on the upcoming challenges of this field.

Keywords: lipid biomarkers; ancient sedimentary DNA; paleomicrobiology; lipid biosynthesis; phylogenomics

INTRODUCTION

Microbial lipids have been widely used as markers of the presence of specific microorganisms in both present and past ecosystems, and as proxies for the reconstruction of past environments and climates (Naeher et al. 2022 this issue). In some instances, the biological source (i.e., precursor) of a microbial lipid biomarker is unknown, in which case they are referred to as "orphan biomarkers." The identification of a lipid biomarker directly from pure (only one microorganism) or enriched (with higher abundance of the target microorganism) laboratory culture is the most definite way to confirm a biomarker's biological source. Nevertheless, it is not possible to assure that other microorganisms, which have not yet been screened for their lipid biomarker composition, are also potential sources of a lipid biomarker of interest. These caveats introduce a certain level of uncertainty to the application of lipid biomarkers in past and present environments. Ideally, given a lipid biomarker of interest, we would like to address the following questions: which organism(s) produced the biomarker? How, where, and when was the lipid biomarker produced? Since when has this lipid biomarker been synthesized and how was it acquired? Studies based on the current microbial ecology of the biological sources of specific lipid biomarkers have proven to be very useful to determine the distribution, diversity, seasonality, and metabolic potential of lipid biomarker producers, and to correct interpretations made on the presence of those lipid biomarkers in the sedimentary record. This information has been obtained using complementary approaches that target microbial molecules other than lipids, i.e., nucleic acids, such as DNA (deoxyribonucleic acid) or RNA (ribonucleic acid).

GENOMIC BIOMARKERS

The complete set of DNA of a (micro)organism is called its genome. A genome is composed of genes that encode for structural transcripts—such as ribosomal RNA (rRNA) that functions as structural components of ribosomes—and functional genes that encode for messenger RNA (mRNA). The latter transcripts are translated within the ribosomes into proteins, notably enzymes involved in a wide scale of cellular metabolic processes. Some of these genes are present in most microbial taxa and play an important role in cellular functioning. Based on evolutionary differences in the nucleotide positions, sequencing analysis of these taxonomic marker genes can identify the various members that are present in complex environmental microbial populations and track their evolutionary history. Here, we define those as "genomic markers". Gene encoding for 16S rRNA, the structural component of the small subunit of the prokaryotic ribosome, functions as a "molecular clock" that can be used to track when and how different organisms diverged. This is also the most frequently used taxonomic marker gene for identifying bacterial and archaeal community members in environmental samples and reconstructing phylogenies (i.e., history of the evolution of a species or group). The counterpart for eukaryotic organisms is the 18S rRNA gene. Apart from ribosomal RNA coding genes, other genes can be used as "functional genes" to indicate the potential roles that the microorganisms carrying these genes play in important biogeochemical cycling processes. The majority of "functional genes" also have been proven to be excellent taxonomic markers and thus help elucidate the composition and diversity of environmental microbial communities.

COMBINING rRNA/FUNCTIONAL GENES & LIPID BIOMARKERS

Nucleic acids (i.e., DNA, RNA) have a shorter preservation potential than lipid biomarkers based on their lower inherent stability and degradation mechanisms (Fig. 1).

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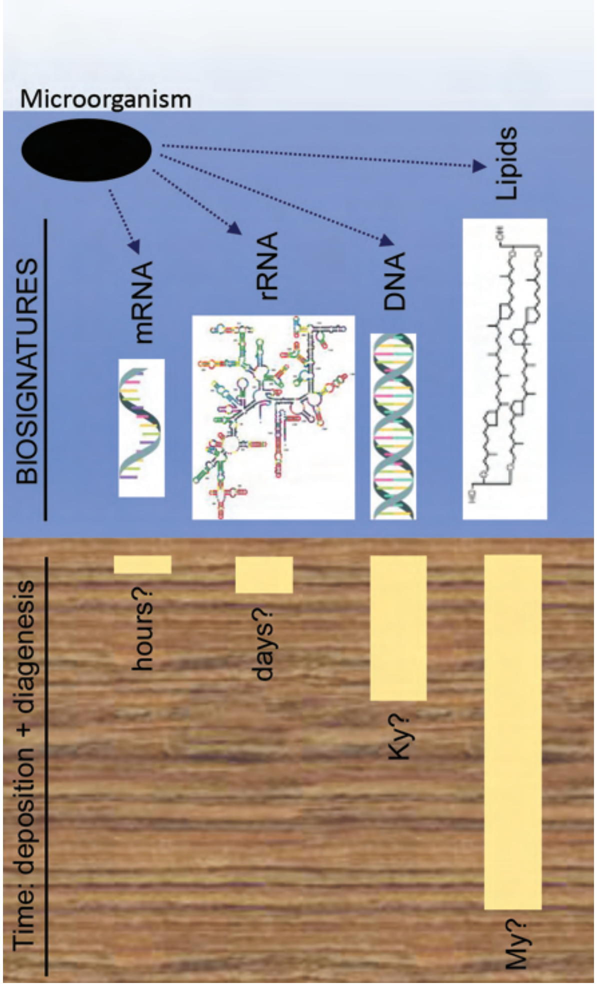

FIGURE 1 Preservation potential or turnover time of different microbial biosignatures or biomarkers including messenger RNA (mRNA), ribosomal RNA (rRNA), DNA, and lipids (core or intact polar lipids). The yellow bars represent environmental lifetimes (deposition + diagenesis time) in a log-based time axis not drawn to scale.

RNA molecules can degrade in a matter of minutes or hours after cell death, whereas DNA can be preserved for longer time scales, especially under rapid sediment burial, low temperature, or oxygen-poor conditions (as detailed below).

A major advantage of the use of lipid molecules as biomarkers is their great preservation potential (see FIG. 1 and Naeher et al. 2022 this issue). Nevertheless, they are limited in taxonomic resolution and can be synthesized by multiple sources, making it difficult to assign a certain lipid molecular structure to a specific microbial producer. In contrast, despite their lower preservation potential, "genomic markers" are excellent taxonomic and/or functional markers, allowing the identification of member species of complex microbial communities, and addresses the questions "who is there?" and "what are they potentially doing?"

The first studies combining lipid and DNA-based biomarkers (i.e., the 16S rRNA gene) aimed to better understand the relationship between microbial communities and their modern environments ("microbial ecology"). The lipid biomarkers used in those studies were phospholipid-derived fatty acids (PLFAs), which are chemotaxonomic markers of bacteria and eukaryotes that can be used as biomarkers of microbial physiological status, viability, and to a certain degree (limited by the low molecular diversity of PLFAs) to elucidate microbial diversity. The fact that PLFAs rapidly degrade after cell death makes them excellent indicators of viable (alive) microorganisms with an intact cell membrane; however, this characteristic invalidates them as lipid biomarkers for paleo interpretations. To identify potential biological sources, microbial ecology studies based on PLFAs were shortly thereafter complemented with DNA-based biomarkers, i.e., 16S rRNA (e.g., Stephen et al. 1999) to compensate for the low taxonomic potential of lipid biomarkers.

Sequencing analysis of the 16S rRNA gene remains widely used in combination with other lipid biomarkers that have longer preservation lifetimes than PLFAs. This combination approach has proven to be very useful to identify or confirm potential biological sources of a specific lipid biomarker, which can facilitate the paleo-interpretation of those biomarkers in studies of ancient materials in which DNA is not preserved. Nonetheless, conclusions derived from these combined DNA-lipid biomarker analyses should be taken with caution, as even in dynamic microbial systems the turnover time of these molecules can be different. Namely, DNA was shown to be more persistent (FIG. 1) after cell death than phospholipids and represents both living and non-viable microorganisms.

A next generation of multi-proxy studies combined analysis of lipid biomarkers and 16S rRNA gene sequencing with profiling of functional genes, elucidating not only taxonomic diversity (who is there?) but also the metabolic potential of the source organisms (what are they potentially doing?). As an example, members of the Thaumarchaeota phylum (formerly known as marine crenarchaeota) were identified and taxonomically placed in the tree of life as a novel marine archaeal group based on 16S rRNA gene analysis. They were later confirmed to have a metabolism based on carbon fixation (i.e., chemolithoautotrophs) and ammonia oxidation. Incubation studies of samples enriched in Thaumarchaeota and spiked with isotopically labeled bicarbonate confirmed that this archaeal group synthesizes archaeal tetraether lipids, glycerol dibiphytanyl glycerol tetraethers (GDGTs) with zero to four cyclopentane rings, and the specific thaumarchaeotal lipid biomarker crenarchaeol, which has four cyclopentane and one cyclohexane ring in its structure. These discoveries paved the way for the development of the sea surface temperature (SST) proxy, TEX$_{86}$, based on the GDGT distribution of Thaumarchaeota. Later studies also confirmed that Thaumarchaeota carry the functional marker gene, *amo*A, which encodes for the ammonia monooxygenase enzyme that is involved in the first step of ammonia oxidation. The detection of this "functional gene" in microbial ecology studies (along with 16S rRNA gene and lipid biomarkers) has allowed not only the detection of this microbial group and its diversity, but also the indication of its potential role within the global biogeochemical cycle of nitrogen.

However, the combined analysis of lipid biomarkers and profiling of environmental 16S rRNA and functional genes does have inherent limitations: (i) one can only link all three markers to the same source organism in environmental samples if prior knowledge is available regarding the taxonomic and functional diversity as well as the lipid biomarker composition of related taxa (e.g., from cultivation experiments); (ii) the analysis of single taxonomic marker genes does not provide a complete view of the metabolic or functional potential of the targeted microorganism; and (iii) differences in preservation potential complicate direct comparisons of the DNA and lipid data.

LIPID BIOSYNTHETIC PATHWAYS

Some of these issues can now be partly addressed thanks to recent technological advances that have drastically reduced the cost of DNA sequencing and increased the availability of very extensive genomic databases for data comparison, in addition to the continuing development of advanced bioinformatics and biostatistical toolsets for processing, interpreting, and visualizing large sequencing datasets. For example, the random sequencing of all the genes of all microorganisms present in an environmental DNA sample (shotgun metagenomes) and subsequent reassembly of these fragments into full genomes (i.e., metagenome assembled genomes) using advanced bioinformatics tools makes it possible to determine the genetic pathways involved in the biosynthesis of a specific lipid biomarker, and to identify the source organism(s) without the need for cultivation. Nevertheless, in most cases, information is still lacking regarding the genes encoding for enzymes involved in a specific lipid biomarker biosynthetic pathway. When this approach is applied to an unknown lipid biosynthetic pathway, the genome of the relevant microorganism(s) must be determined before "candidate" genes can be identified that are potentially involved in that pathway. Once those candidate genes have been identified, based on their position within the genome or its resemblance to previously described biosynthetic processes, the activity of those genes must be confirmed. The activity of candidate lipid biosynthetic genes can be confirmed by removing or incapacitating the candidate gene in the targeted microorganism (processes referred to as deletion, mutation, or "genetic knock-out") and by observing a loss of function (e.g., the inability to make the lipid biomarker). Alternatively, or in cases where this is not possible, one can artificially incorporate and express the candidate gene in another microorganism (e.g., *Escherichia coli*) that is more easily subject to genetic manipulation, and then observe a "gain of function" (new capacity to make the lipid biomarker); this method is referred to as "heterologous gene expression" (Fig. 2). These approaches also have been successfully applied to determine enzymatic steps leading to specific lipid biomarkers.

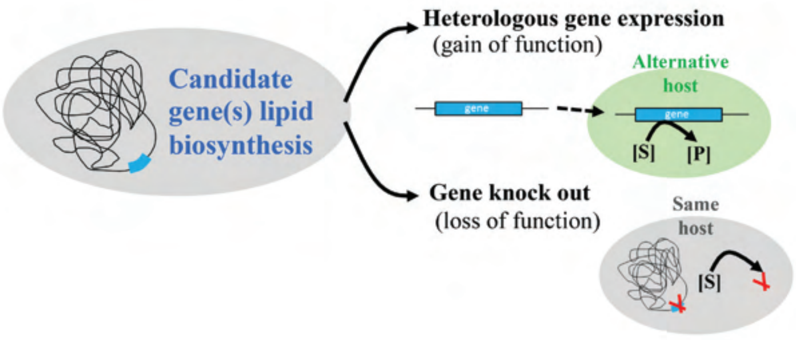

Figure 2 Methodological options for confirming the activity of candidate genes involved in a specific lipid biosynthetic pathway. Heterologous gene expression involves the addition of a candidate gene to an alternative microbial host that is genetically more treatable (e.g., *E. coli*), in which the gene expression will lead to a gain of function. By performing a gene knock-out, the targeted gene is deleted from the original microorganism (same host) and loss of the function or formation of the lipid or intermediate should be lost. Abbreviations: S = substrate; P = product of the enzymatic reaction.

Targeting Lipid Biosynthetic Pathways of Well-Known Lipid Biomarkers

One of the most remarkable cases of the use of genomics to clarify the origin and diversity of biological sources of lipid biomarkers is that of hopanoid lipids (i.e., polycyclic terpenoids located in bacterial membranes), which are thought to be functional analogues to eukaryotic sterols and are involved in the maintenance of membrane stability. Hopanoid lipids are preserved as hopanes in the sedimentary record. The biosynthesis of these biomarkers requires the isoprenoid precursor, squalene, which is cyclized by a squalene–hopene cyclase encoded by the *shc* gene (Fig. 3). Hopanoids have been detected in a minor proportion of bacterial groups and the squalene–hopene cyclase encoding gene needed for hopanoid production is present in only approximately 10% of all bacteria (Pearson et al. 2007).

Among hopanoid biomarkers, 2-methylhopanes were initially considered to be biosynthesized by cyanobacteria, and their presence in sediments as old as 2,500 Ma was used as an indication of the advent of oxygenic photosynthesis (Summons et al. 1999). Nevertheless, the identification and confirmation of the gene required for hopanoid C-2 methylation, and the fact that it is not generally found in all cyanobacterial genomes and is present in other bacterial taxa, invalidate the use of 2-methyhopanes as biomarkers of the appearance of oxygenic photosynthesis on Earth (Welander et al. 2010).

A similar case is that of the 3-methylhopanoids, which are generally attributed to aerobic methanotrophic bacteria. However, the gene involved in hopanoid C-3 methylation is found in the genomes of microorganisms other than aerobic methanotrophic bacteria, suggesting 3-methylhopanoids cannot be used as biomarkers of aerobic methanotrophy in the past (Welander et al. 2012). A "genomic" approach for this lipid biomarker question has also been helpful to understand the physiological role of 3-methylhopanoids, because the "removal" (deletion) of the gene responsible for C-3 methylation from the obligate methanotroph *Methylococcus capsulatus* demonstrates that 3-methylhopanoids are required for membrane maintenance and cell survival under stationary conditions.

Other lipid biomarkers with well-characterized lipid biosynthetic pathways are sterols, which perform essential functions in the membranes of eukaryotes. Sterols are preserved as steranes in the geological record and have been used as biomarkers for the appearance of eukaryotes and the occurrence of oxygen on Earth (Brocks et al. 1999). The enzyme oxidosqualene cyclase (OSC) mediates the first committed step of sterol biosynthesis requiring oxygen (Fig. 3). Sterols also have been found to be produced by some bacterial groups, either by screening of pure cultures or inferred from the presence of bacterial OSC homologs in their genomes. An aerobic marine heterotrophic bacterium of the Bacteroidetes, *Eudoraea adriatica*, was predicted to harbor a bacterial OSC in its genome (Banta et al. 2017). Lipid analyses of *E. adriatica* and gene expression of its bacterial OSC in *E. coli* (Fig. 2) confirmed that this strain makes two isoarborinol-like lipids (eudoraenol and adriaticol) directly from an oxidosqualene precursor. This is particularly relevant because arboranes, degradation products of isoarborinol, have often been used as indicators of terrestrial input into aquatic environments, as these biomarkers were initially thought to be solely biosynthesized and to originate from specific angiosperm vegetation. Banta et al. (2017) confirmed the possibility of bacterial sources of arborane that had been previously suspected due to the occurrence of arborane biomarkers in Permian and Triassic sediments, which predates the origin of angiosperms.

Unraveling The Evolutionary Acquisition of Lipid Biomarkers

By targeting the lipid biomarker biosynthetic pathways, it is also possible to determine when a specific lipid biomarker was acquired through the course of evolution and to determine if that capacity has been transferred to other microbial groups by, for example, horizontal gene transfer. There are several examples in which the study of lipid biomarker biosynthetic pathways has led to the resolution of some evolutionary mysteries by the application of phylogenomics (analysis involving genomic data and evolutionary reconstruction).

For example, squalene synthase mediates the first committed step in the biosynthesis of sterols within the isoprenoid pathway, catalyzing the reaction from farnesyl diphosphate (FPP) to squalene (SQ) (Fig. 3). The evolutionary story of squalene synthase has allowed us to decipher the possible paths of squalene formation. The eukaryotic photosynthetic green algae *Botryococcus braunii* race B accumulates triterpenes (predominantly botryococcene) and has received attention because it is considered an ancient algal species dating back to at least 500 Ma, and is also one of the few organisms known to have directly contributed to oil and coal shale deposits. Due to their similar structure, botryococcene biosynthesis was expected to resemble that of squalene. The genome of *B. braunii* harbors a typical squalene synthase (SS) and three squalene synthase-like (SSL) encoding genes (SSL-1, SSL-2, SSL-3). Enzymatic studies proved that a combined activity of SSL-1 + SSL-3 leads to botryococcene, and of SSL-1 + SSL-2 to squalene biosynthesis (Niehaus et al. 2011). It has been estimated that SQ and the three SSL genes separated from a common ancestor ~500 Ma in a process of gene duplication and specialization. This enzymatic specialization is believed to regulate the flux of FPP into sterol biosynthesis independent from the flux into the biosynthesis of botryococcene, which accumulates in high amounts into the membrane of *B. braunii* to provide flotation and maximize its exposure to sunlight.

Biosynthetic Pathways of Lipid Biomarkers Used as Paleoclimate Proxies

The TEX_{86} SST proxy presents an example of the use of genomics to better constrain a paleoclimate proxy based on microbial lipid biomarkers. There is accumulating evidence that temperature is not the only variable affecting the Thaumarchaeota GDGT distribution (on which the TEX_{86} proxy is based) (e.g., Qin et al. 2015; Hurley et al. 2016). It is also known that TEX_{86} does not reflect SSTs but rather subsurface temperatures, and that archaea in the deeper water column may also contribute to the GDGT signal in sediments, potentially leading to a warm bias in TEX_{86} SST estimates. In this regard, some studies indicated that deeper waters are characterized by a higher abundance of GDGTs with two cyclopentane rings relative to those with three cyclopentane rings, and an increase in the crenarchaeol isomer (Taylor et al. 2013). This observation was further supported by the detection of different marine Thaumarchaeota groups inhabiting shallow and deep waters based on the use of the *amo*A "functional gene marker" and of gene coding for the enzyme involved in the first ether bond formation of the GDGT molecule (i.e., geranylgeranylglyceryl synthase) (Villanueva et al. 2015). The TEX_{86} signal may also be affected by input from other archaea, which could potentially synthesize GDGTs used in TEX_{86}. Previous studies have suggested a potential contribution to the GDGT signal by the marine euryarchaeota group II (MGII), which is present in oceanic surface waters. Because members of the MGII have not yet been cultivated, it is currently unknown which archaeal lipids they synthesize. Regardless, the lack of a homolog of the recently described GDGT cyclase encoding genes (Zeng et al. 2019) (Fig. 3) in the MGII genomes suggests that this archaeal group does not synthesize GDGTs with cyclopentane rings, which are involved in the TEX_{86} paleotemperature proxy. Further analysis of lipid biosynthetic genes of MGII genomes also suggested this archaeal group is potentially unable to synthesize "classical" archaeal membrane lipids (Villanueva et al. 2017), leaving unanswered questions regarding the diversity and evolution of membrane lipid acquisition in Archaea.

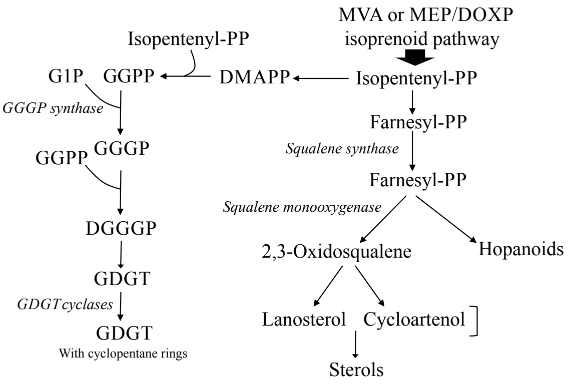

Figure 3 Overview of the lipid biosynthetic pathways discussed in the text and key enzymes. Abbreviations: DMAPP = dimethylallyl diphosphate; GGPP = geranylgeranyl diphosphate; GGGP = geranylgeranylglyceryl phosphate synthase; DGGGP = digeranylgeranylglyceryl phosphate synthase, G1P = glycerol 1-phosphate; GDGT = glycerol dialkyl glycerol tetraether; MVA = mevalonate; MEP/DOXP = 2-*C*-methyl-D-erythritol 4-phosphate/1-deoxy-D-xylulose 5-phosphate; PP = diphosphate

SEDIMENTARY ANCIENT DNA AND PALEOMICROBIOLOGY

Lake and marine sediments are comprised of organic and inorganic deposits and represent rich archives of temporal changes in both planktonic (autochthonous) and terrestrial (allochthonous) ecosystem members. The majority of paleoecological studies involve microscopic analysis of a relatively limited number of taxa that form or leave behind easily identifiable morphological remains in sediments. Lipid biomarkers can be preserved in the absence of morphological remains, but their taxonomic specificity is generally limited, as outlined above. A more recently developed approach targeting ancient DNA preserved in lake and marine sediments (i.e., sedimentary ancient DNA or *sed* aDNA) is rapidly increasing in popularity.

Sequencing analysis of preserved *sed* aDNA markers offers unprecedented detail into the composition of past biota, from individuals to complex ecosystems, and across all domains of life, including taxa that do not leave behind any other diagnostic remains (e.g., Coolen et al. 2013) despite the more limited preservation potential compared to lipid biomarkers and the need for stringent measures to prevent cross contamination with modern environmental DNA during sampling and sample processing in a dedicated clean lab facility. Paired with paleoenvironmental proxy data, *sed* aDNA can be used to question how aquatic and terrestrial ecosystems have responded to natural versus anthropogenic environmental perturbations (see Armbrecht et al. 2019 and references therein). Past plankton communities have been identified at the genus level from *sed* aDNA in ~270-Ka lake and ~1-Ma marine sediments under ideal depositional and post-burial conditions (e.g., low temperatures, anoxia, and/or adsorption of extracellular DNA to clay minerals) (e.g., Kirkpatrick et al. 2016).

Strategies Used to Study and Authenticate Sedimentary Ancient DNA

Following the extraction and purification of sedimentary ancient DNA, the past planktonic community composition (e.g., chloroplast-containing algae) can be studied through sequencing analysis of polymerase chain reaction (PCR)-amplified taxonomic marker genes (i.e., amplicon sequencing). Several bioinformatics "pipelines" (data processing algorithms) have been developed to process the resulting sequence datasets to ultimately generate a matrix with the total counts of unique taxonomically assigned amplicon sequence variants. These "species" × sample abundance matrices form the basis for biostatistical analysis to study past ecosystem responses to shifts in categorical (e.g., lithology, climate, or environmental stages) or quantitative environmental changes (e.g., paleosalinity, paleotemperature, paleoprecipitation) given that suitable paleoenvironmental datasets are generated in parallel (e.g., Coolen et al. 2013).

"Hybridization capture" is a method that offers great potential to selectively enrich *sed* aDNA from, for example, planktonic taxa that can inform about past ecosystem responses to paleoenvironmental changes (Armbrecht et al. 2021). This approach involves the selective binding of marker genes to magnetic beads, followed by magnetic separation, clean-up, gene amplification, and sequencing.

Moreover, the metabolic properties of environmental microbial communities, such as the role they play in elemental cycling, can be inferred from shotgun metagenomic sequencing, as mentioned earlier. Mostly applied to modern environments, this approach was recently used to reconstruct microbial populations and genes involved in nitrogen cycling during long-term expansion of the oxygen minimum zone in the Arabian Sea over the last 43,000 years (Orsi et al. 2017), and to reconstruct microbial communities that were involved in the sulfur cycle in the Black Sea during the Holocene (More et al. 2019). Importantly, shotgun metagenomic datasets can be analyzed using sophisticated bioinformatics tools, such as Mapdamage2 (Jónsson et al. 2013), to differentiate between altered, post-mortem ancient microbial DNA and intact DNA from sedimentary bacteria that are shaped by modern in situ environmental conditions (e.g., the availability of electron acceptors and donors as well as sediment porosity). As another example of authenticating ancient sedimentary microbial DNA, bioinformatic tools have recently been developed to calculate the growth rate of environmental bacteria by measuring genome replication rates from shotgun metagenomic data (Emiola and Oh 2018).

Examples of Combined Stratigraphic Analysis of Lipid Biomarkers and sed aDNA

The first study to combine lipid biomarker and *sed* aDNA data was performed on Holocene sediments of Lake Mahoney, Canada (Coolen and Overmann 1998). The water column of this permanently stratified saline lake contains an oxygenated photic zone and higher density anoxic and sulfidic bottom water. A dense population of purple sulfur bacteria (PSB) occurs at the transition between both waters (i.e., within the chemocline) where both light and toxic hydrogen sulfide (H_2S) is available for PSB to perform anoxygenic photosynthesis. The concomitant presence of the specific carotenoid okenone as well as 16S rRNA genes of PSB in the sedimentary record of Lake Mahoney reveal when the lake was stratified and experienced periods of anoxia, and that *sed* aDNA can be preserved and analyzed to identify the source of lipid biomarkers covering at least the last 10,000 years (Coolen and Overmann 1998).

The combined presence of *sed* aDNA and fossil carotenoids from past chemocline-dwelling green sulfur bacteria (i.e., chlorobactene and/or isorenieratene instead of okenone), indicative of permanently stratified and anoxic conditions, was subsequently used to reconstruct orbitally controlled changes in paleoproductivity that resulted in the deposition of organic-rich sediment intervals (i.e., sapropels) in the eastern Mediterranean Sea (Coolen and Overmann 2007). Similar findings have also been used to reconstruct environmental changes in the Black Sea associated with postglacial reconnection with the Mediterranean Sea via the Bosporus Strait (Manske et al. 2008) versus postglacial isolation of the brackish Antarctic Ace Lake from the Southern Ocean (Coolen et al. 2004).

Research over the last three decades has shown that the unsaturation level in long-chain alkenones produced by the calcifying haptophyte alga *Emiliania huxleyi*, a cosmopolitan oceanic plankton, is linearly related to growth temperature. Downcore changes in the alkenone composition were used to develop the so-called $U^{K'}_{37}$ proxy for past SST (Brassell et al. 1986). This index was initially developed and calibrated for *E. huxleyi*. However, parallel analysis of *sed* aDNA and alkenones revealed novel groups of non-calcifying "naked" haptophytes as invisible sources of fossil alkenones in the sedimentary records of the brackish Black Sea and Ace Lake, where the original alkenone SST proxies calibrated for *E. huxleyi* produced spurious results (Coolen et al. 2004, 2013). These studies then resulted in the development of novel, calibrated alkenone-SST indices to accurately reconstruct paleo SST from terrestrial settings.

As a final example, dinoflagellates are important plankton members that are traditionally identified from the sedimentary record based on microscopic analysis of calcareous or organic-walled cysts, or from the presence of the lipid biomarker dinosterol. However, 80% of dinoflagellate species produce cysts and dinosterol is only known from a relatively small number of species. Analysis of *sed* aDNA in Holocene sediments of Ellis Fjord near Ace Lake (Antarctica) revealed late-Holocene changes in the relative abundance of sea ice dinoflagellate *Polarella glacialis*, indicating changes in the extent of sea ice formation in this East Antarctic region during the Holocene. Other proxies failed to reproduce this result because *P. glacialis* does not produce the lipid biomarker dinosterol and its small organic-walled cysts escaped microscopic identification (Boere et al. 2009).

Taken together, the examples summarized above show that a parallel comparison of lipid biomarkers and *sed* aDNA profiles can be used to cross-validate the reliability of both approaches, identify the sources of lipid biomarkers, and refine the interpretation of paleoenvironmental reconstructions.

FUTURE CHALLENGES

Here, we have reviewed the studies that verify the usefulness of combining DNA and lipid biomarker analysis to better understand the microbial sources of these compounds and their physiology, in both present and past environments. Nonetheless, the definite confirmation of microbial sources of lipid biomarkers will depend on further methodological developments. For example, prior knowledge of physiological properties inferred from genome sequencing would aid the targeted development of cultivation methods and facilitate the confirmation of the lipid composition of yet-uncultured microorganisms. Further physiological studies in the laboratory would also be useful to determine under which conditions those lipids are synthesized. The improvement of computational methods will be key to predict lipid biosynthetic genes and, combined with novel gene editing tools (i.e., CRISPR), aid the confirmation of biosynthetic pathways that produce specific lipid biomarkers. Improvement of evolutionary reconstruction methods based on genomic data will also contribute to a better understanding of how and when certain lipid biomarkers were acquired. The study of *sed* aDNA will additionally benefit from the development of novel tools to lower the detection limit of *sed* aDNA and to explore its preservation potential in sedimentary records that have been deposited under less favorable conditions, such as long-term exposure to warm temperatures in understudied tropical lakes. The stratigraphic analysis of *sed* aDNA has the potential to serve as a unique opportunity to reconstruct ecosystem biodiversity across all domains of life and may provide a holistic overview of past biotic interactions and ecosystem functioning. This approach can also be applied to reconstruct their role in biogeochemical cycling processes within the overlying water column at the time of deposition. Studying the latter requires the development of experimental and/or bioinformatics approaches to accurately distinguish between members of an indigenous sedimentary microbiome, which are actively shaped by in situ environmental conditions, versus ancient microbial sources (i.e., the paleomicrobiome) of sedimentary DNA that originate from the overlying water column and are shaped by the prevailing environmental conditions at the time of deposition. A further challenge is to successfully recover ancient genomes and compare them with those of closely related modern taxa to reconstruct past evolutionary events that led to the present-day taxonomic diversity and physiological properties of planktonic ecosystems.

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Biomarkers in the Precambrian: Earth's Ancient Sedimentary Record of Life

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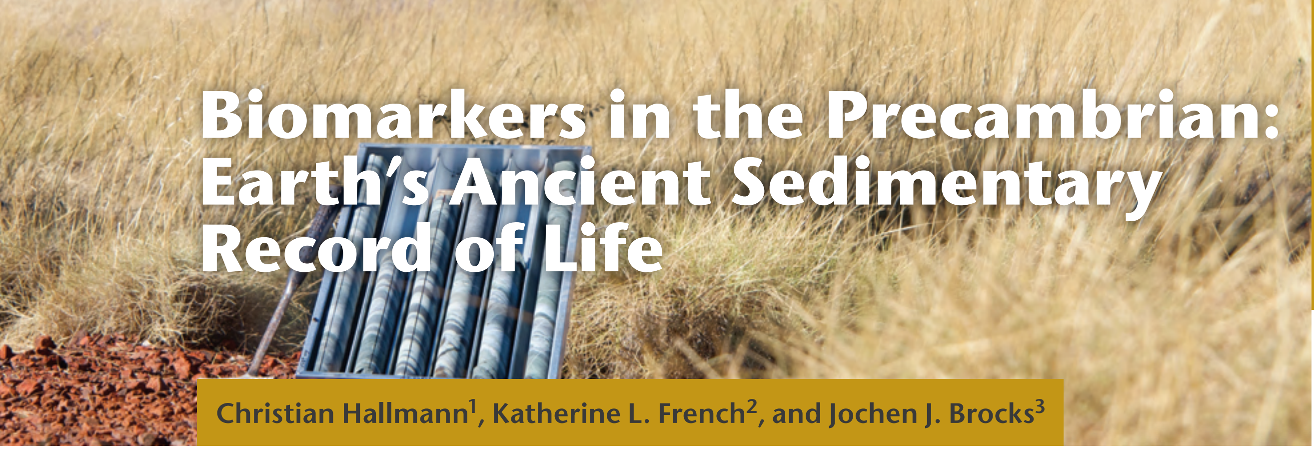

Cores of the Coucal Formation, Coonterunah Subgroup, from drill hole AIDP-1, in a field of Triodia ('Spinifex'). PHOTO: CHRISTIAN HALLMANN.

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The hydrocarbon remnants of biologically diagnostic lipids inform our understanding of Earth's early ecosystems, particularly where morphological vestiges of biology are absent or ambiguous. Yet both the analysis and interpretation of ancient biomarkers require scrutinous approaches. Here, we describe the status quo of Precambrian biomarker geochemistry with four examples that highlight current challenges and opportunities.

KEYWORDS: Precambrian; biomarker; Archean; animal evolution; steroid; hopanoid

INTRODUCTION

Fossil fats—taxonomically diagnostic hydrocarbons that are the sedimentary remnants of cellular lipids—are a vital tool for reconstructing past organismic diversity, ecosystem evolution, and environmental conditions. In deep time, they bridge a gap between microfossils and genomic information. While also valuable during younger intervals of Earth history, biomarker studies are indispensable when investigating Precambrian life and environments. Although the Phanerozoic (FIG. 1) witnessed the evolutionary emergence of the most manifest modern flora and fauna, it covers only ~15% of Earth history. Traces of early life and the processes that led to the modern Earth system are recorded in sedimentary rocks dating back to more than 3.5 billion years ago (Ga). However, Precambrian strata are largely devoid of skeletonized animal remains, and microfossils within such old sediments often have ambiguous links to modern organisms. The molecular remnants of early life therefore provide an important lens through which we can peer into the cradle of our modern biosphere.

Study of biomarkers from the ancient rock record faces limits. Biomarker preservation is largely restricted to fine-grained and organic-rich carbonates and shales, and biomarkers can be compromised directly by thermal destruction and indirectly by contamination, such as migrating fluids during the long residence times after deposition. Tectonic recycling reduces the availability of ancient sedimentary basins with increasing geological age. Only a small fraction of surviving deposits may host rocks amenable to biomarker studies because elevated temperatures and pressures experienced during sedimentary burial transform and degrade hydrocarbons. As the abundance of biomarkers decreases with progressive thermal alteration, samples become increasingly susceptible to secondary overprint by later hydrocarbon migration and contamination during sampling, storage, and handling, all of which may obfuscate the snapshot of early life encoded in fossil lipids. In addition, we continuously face challenging questions: Do we sufficiently understand how preservation biases, impacts, or distorts biomarker interpretations? Are specific biomarkers diagnostic for a group of organisms, or do they rather point to particular environmental conditions or biological processes? How do we know that organisms contributing specific biomarkers today also did so a billion years ago, and how can we recognize biomarkers that were produced by extinct biological lineages? Finally, how can we construct a reliable timeline of evolving lipid biosynthetic ability? To answer such questions, biomarker experts increasingly collaborate with molecular biologists, an interaction that is currently revolutionizing the field.

With the advantages and limitations of biomarkers in mind, what sketch of Precambrian ecosystems and environments can we draw here and now? In navigating issues of contamination, preservation, and biomarker interpretation, experience has shown that experience is exactly what is needed. Confidently distinguishing biomarkers from contaminant hydrocarbons stands at the end of a long corridor of trial-and-error. Here we attempt to provide a status quo on what fossil lipids tell us about the deep history of Earth.

THE ARCHEAN: BEYOND THE BIOMARKER PRESERVATION LIMIT

Archean (2.5–4.0 Ga) sedimentary rocks contain traces of Earth's incipient biosphere. Yet they are scarce, and metamorphism has significantly altered most of those that remain. Sparse stromatolites and microfossils testify to microbial life in the Archean, but their microbial source—and even biogenicity—is difficult to decipher. While biologically reminiscent stable isotope patterns and trace elements, recording biologically mediated environmental transformations, provide indirect evidence for early life, lipid biomarkers offer a direct and independent avenue to reconstruct the earliest ecosystems and their environments.

Gleaning information from biomarkers, however, requires their preservation (FIG. 2). This information is modified or erased as heat during burial breaks carbon bonds, cracking biomarkers into increasingly smaller fragments and partially reincorporating them into a macromolecular structure called kerogen. Most Archean rocks on Earth have experienced metamorphism that prevents biomarker preservation. The ~2.8–2.5 Ga Hamersley

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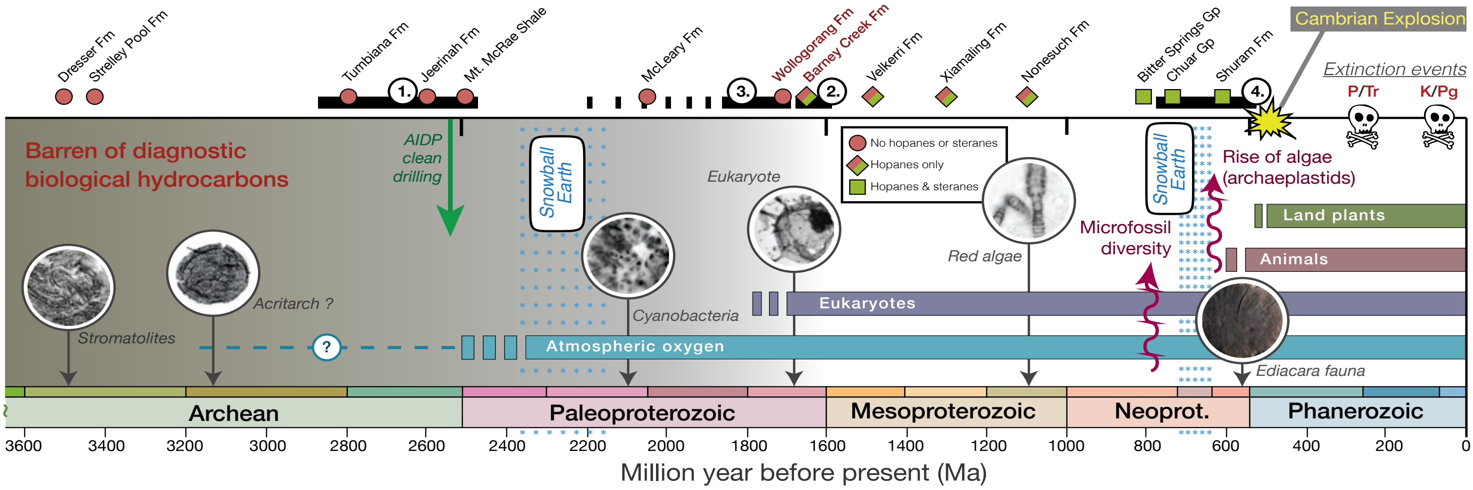

FIGURE 1 Schematic timeline of Earth history depicting crucial environmental and evolutionary events. Time intervals covered in individual sections of the text (1 - Archean, 2 - At the limit, 3 - Pushing limits, and 4 - Complex life) are indicated by black bars. Symbols at top denote sedimentary units without indigenous bacterial hopane or eukaryotic sterane biomarkers (red circles), with only indigenous hopanes (red/green diamonds), and with both hopanes and steranes (green squares). PHOTOGRAPHS ARE ADAPTED FROM ['ACRITARCH'] JAVAUX EJ ET AL. (2010) NATURE 463: 934-938; ['CYANOBACTERIA'] HOFMANN HJ (1976) JOURNAL OF PALEONTOLOGY 50: 1040-1073; ['EUKARYOTE'] JAVAUX EJ ET AL. (2001) NATURE 412: 66-69; ['RED ALGAE'] BUTTERFIELD NJ (2000) PALEOBIOLOGY 26: 386-404. PHOTO: CHRISTIAN HALLMANN.

(Western Australia) and Griqualand (South Africa) basins contain organic-rich strata that experienced a low degree of metamorphic alteration, leading previous studies to investigate these rocks for biomarkers to characterize Archean microbial communities and environments (e.g., Brocks et al. 1999; Waldbauer et al. 2009). The results were groundbreaking: methylhopane and sterane biomarkers implied that biological oxygen production (oxygenic photosynthesis) by ancestral cyanobacteria, along with oxygen-requiring eukaryotes, had evolved hundreds of millions of years prior to when Earth's surface became more permanently oxidized during the Great Oxidation Event (GOE; ~2.4 Ga). Additional support came from similar biomarker inventories discovered in mineral-encased droplets known as fluid inclusions in other rock strata predating the GOE (George et al. 2008). Yet subsequent studies cast doubt as to whether the biomarkers found in Archean and early Paleoproterozoic rocks were actually of that age. Large carbon-isotopic disagreements between extracted versus immobilized hydrocarbons (solid 'pyrobitumens') in the same rocks (Rasmussen et al. 2008) and higher biomarker concentrations on rock exteriors compared to their interiors (Brocks 2011) suggested that the extracted biomarkers were not co-deposited with the Archean host rocks. Rather, these observations implied that the biomarkers entered the rocks after deposition, either via petroleum migration pervading the samples or by contamination during and after drilling.

Subsequent field campaigns attempted clean drilling to minimize hydrocarbon contamination. The Agouron Griqualand Drilling Project (holes GKP and GKF in South Africa) and the NASA Astrobiology Drilling Program (hole ABDP-9 in Western Australia) used only water as a drilling fluid for most but not all of the drilling. While these cores were drilled to a higher standard of cleanliness than those used in previous campaigns, samples were sawed, stored, and collected for biomarker analyses without additional steps to minimize contamination or to monitor contamination via blanks. As a result, the exteriors of these core samples still exhibited signs of contamination with Phanerozoic hydrocarbons. The different biomarker patterns in sample interiors were interpreted both as indigenous Archean signatures (e.g., Waldbauer et al. 2009) as well as contaminants (Brocks 2011), further fueling the debate around the origins of the biomarkers extracted from Archean rocks.

In 2012, the Agouron Institute Drilling Program (AIDP) in Western Australia used only water for drilling, but unlike previous campaigns, biomarker samples were collected immediately after the cores reached the surface of the drill hole using hydrocarbon-clean sampling and storage methods (FIG. 3). Whole-core samples were sawed in half and into interior and exterior pieces using hydrocarbon-clean methods in a laboratory rather than in a core shed, as done previously. Blanks and negative control samples recorded contaminant introduction throughout the whole process (i.e., drilling, storage, and sawing), rather than during only a subset of processes. Negative control samples—highly metamorphosed, non-sedimentary rocks—would not contain biomarkers, except for those introduced via contamination. Corresponding core halves were analyzed by two independent laboratories to test the reproducibility of results. The AIDP study demonstrated that hopanes and steranes were below the detection limits of sensitive analytical instruments or comparable to trace abundances observed in blanks and negative control samples (FIG. 3) (French et al. 2015). These results also confirmed that the Archean rocks contain indigenous polyaromatic hydrocarbons (PAHs) and diamondoids ('nano-diamond' molecules) of high-temperature origin, but no hydrocarbons currently known to encode biological information.

While the upper limit for biomarker preservation is not precisely known and depends on multiple complex factors, the Archean rocks that have thus far been investigated for biomarkers are too metamorphosed to preserve diagnostic fossil lipids. We do not know that these rocks never hosted biomarkers indicative of early life and environments. We only know that any original lipids that may have been present have been lost to time and temperature, such that we cannot observe them today. An enhanced understanding of the thermal history of Archean basins on a finer lateral and stratigraphic scale may eventually reveal pockets that still preserve biomarkers, but we currently do not know whether such ventures would be fruitful.

Future studies of biomarkers in contamination-sensitive materials should leverage the lessons learned during the last two decades of Archean biomarker research, partic-

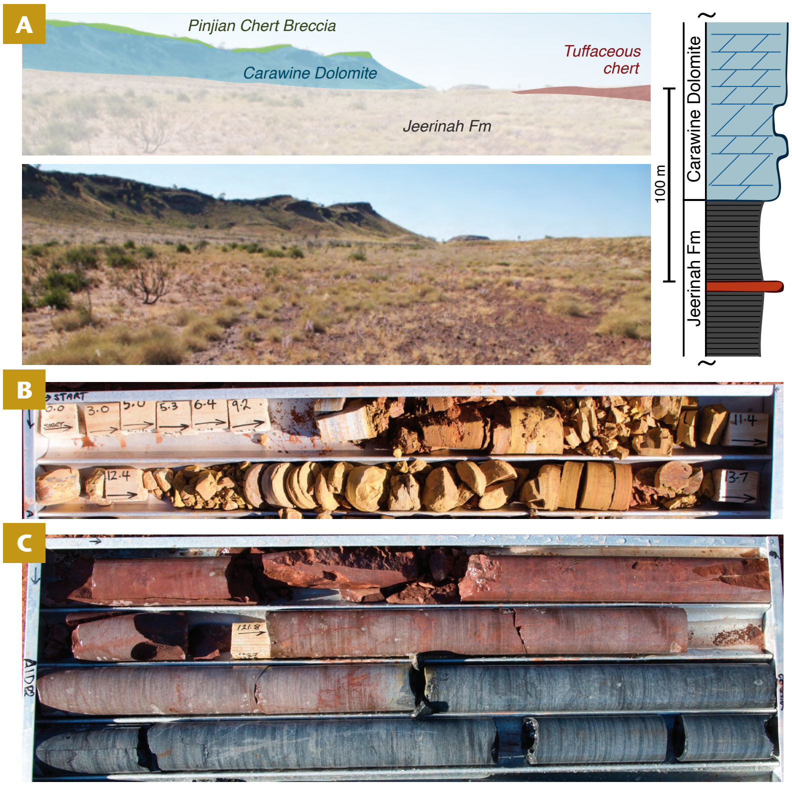

FIGURE 2 Weathering of Archean rocks on the Pilbara craton (Australia). Biomarker preservation depends not only on adequate thermal maturity. (**A**) Intense surface weathering on the Pilbara craton, particularly of pyrite-rich black shales (picture taken south of drill site AIDP-2 around 21°18.91110′S, 120°50.05109′E, looking east) necessitates clean drilling. (**B**) Extensive weathering and core loss in top ~15 m of drill hole AIDP-3. Downhole direction is from left to right and from top to bottom. (**C**) Red oxidation horizon in the Carawine Dolomite extending ~120 m into the subsurface as seen in drill hole AIDP-2. Downhole direction is from left to right and from top to bottom. PHOTO: CHRISTIAN HALLMANN.

ularly the strategies developed to minimize, track, and test for contamination. Ultra-clean drilling, sampling, storage, and laboratory preparation protocols are required to minimize the introduction of contaminant biomarkers. However, as petroleum products are ubiquitous, comprehensive blanks and negative control samples that record contamination over the entire life of the samples, as well as during specific processes, are essential for tracking the introduction of contaminants. Both strategies, contamination mitigation and comprehensive controls, are equally needed. Additional tests for distinguishing contaminants from authentic biomarkers include measuring gradients in hydrocarbon abundances within rock specimens to trace their migration into cracks and fissures (Brocks 2011), and comparing isotopic and molecular compositions of the solvent-extractable hydrocarbons to the solvent-insoluble organic matter (i.e., kerogen). Strategies used to resolve the Archean biomarker debate have now been successfully applied to biomarker studies in the Proterozoic, but they also promise broader application to biomarker studies of extreme environments on Earth and on other planets. Lastly, studies of critical sample material whose outcome may carry large evolutionary implications should adopt a null hypothesis where any encountered hydrocarbons are first considered to be non-indigenous.

AT THE LIMIT: THE OLDEST SYNGENETIC BIOMARKERS IN THE 1.64-GA BARNEY CREEK FORMATION

The Barney Creek Formation (BCF) hosts the oldest known (1.64 Ga), clearly indigenous biomarkers (Summons et al. 1988). Its organic-rich dolomites were deposited in deep local depressions along faults on a carbonate platform in the McArthur Basin, northern Australia. In contrast to Archean deposits, it is exceptionally well-preserved. Remarkably, some pockets of the BCF are only in the early stages of petroleum generation. This low degree of thermal alteration together with its organic-richness and unusual biomarker patterns demonstrate that the BCF biomarkers were co-deposited with the host rock.

The rich BCF biomarker assemblage is highly unusual (Brocks et al. 2005) with abundant bacterial hopanes in the absence of algal steranes, a pattern that continues into the Mesoproterozoic eon (e.g., Blumenberg et al. 2012; Flannery and George 2014) suggesting that photosynthetic primary production was performed almost entirely by bacteria until at least 1.1 Ga (Gueneli et al. 2018). The BCF also contains a distinctive distribution of abundant fossil pigments that are traditionally attributed to purple sulfur bacteria (PSB, Chromatiaceae) and green sulfur bacteria (GSB, Chlorobiaceae) (Summons and Powell 1986; Brocks et al. 2005). These bacteria photosynthesize without producing oxygen while inhabiting a niche that arises when anoxic, sulfidic waters intersect the sunlit part of the water column ('photic zone euxinia'). These organisms produce unusual carotenoid pigments as part of their light-harvesting system. For example, PSB synthesize okenone, which is a red-colored pigment possessing one terminal aromatic ring with methyl groups attached at carbon positions 2, 3, and 4, while the green-pigmented form of GSB produces chlorobactene, which has methyl groups attached at carbon positions 2, 3, and 6 (FIG. 4).

In contrast to the Archean, the emerging challenge for the BCF biomarkers is not whether they are contaminants, but how to interpret them. Specifically, what type of environment and which organisms facilitated the deposition of BCF biomarkers? The depositional environment provides essential context for interpreting biomarkers. Previous studies have interpreted the BCF biomarkers to represent a water column signal in a deep marine basin (Brocks et al. 2005). However, the BCF may have been deposited in a basin that was at times isolated from the global oceans or even a regionally expansive saline lake, which would require re-examining how the BCF is integrated into models of Paleoproterozoic marine redox conditions (French et al. 2020). Others have suggested that the anoxygenic photosynthetic biomarkers are not sourced from planktonic organisms but from microbial mats, implying that they reflect redox conditions in shallow sediments rather than the water column (Love and Zumberge 2021). Furthermore, cyanobacteria may have contributed to part of the fossil carotenoid inventory in the BCF (Cui et al 2020).

And yet, the old geological age of the BCF provides an opportunity. As molecular clocks (which are tools that use genetic differences in modern organisms to estimate when their last common ancestor lived) improve, we will be able to exclude some biological sources of biomarkers that emerged later in Earth history. For example, the recent suggestion that GSB evolved shortly before or even after the deposition of the BCF (Magnabosco et al. 2018) would guide our interpretation to consider other biological, even extinct, sources for the 2,3,6-trimethylated carotenoids currently assigned to GSB. We anticipate that future achievements in comparative genomics, phylogenetics, and molecular clocks will enhance our ability to reconstruct the phylogenetic diversity and history of lipid synthesis, possibly providing exciting new interpretations for the very oldest biomarker archives.

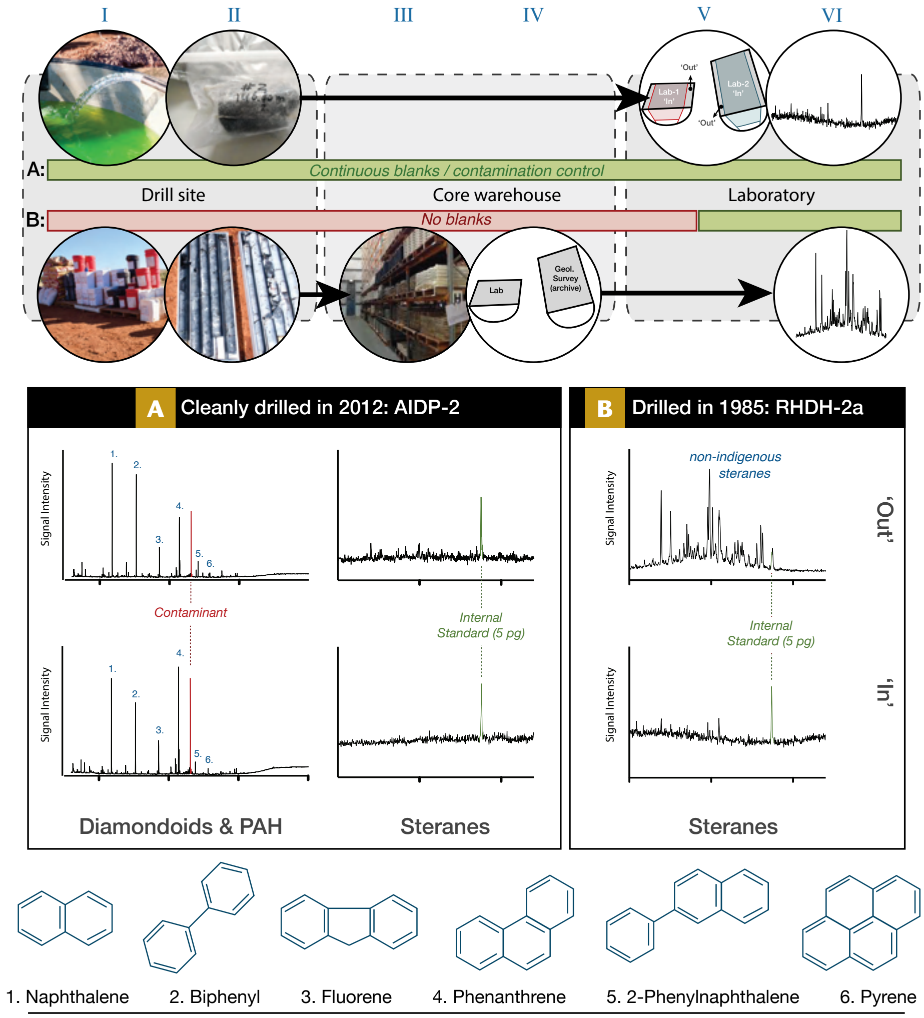

FIGURE 3 Hydrocarbon-clean drilling. (**TOP**) Procedural differences between (**A**) AIDP cores and (**B**) conventionally drilled cores such as the RHDH2A core. Differences include drilling with tracer-spiked clean water versus synthetic additives and lubricants [I], frozen storage in pre-cleaned Teflon bags under inert gas atmosphere versus open storage in core trays [II], accelerated transfer to the laboratory versus protracted storage in core warehouses [III], detailed sawing under controlled and clean lab conditions versus sectioning in the core warehouse [IV, V], and replicate analyses in different laboratories using extensive negative blank materials versus analysis under standard conditions [VI]. (**MIDDLE AND BOTTOM**) Molecular results illustrate the presence of contaminant-steranes in sample exteriors and indigenous diamondoids and polyaromatic hydrocarbons (PAHs) in sample exteriors and interiors.

PUSHING THE LIMITS BEYOND 1.64 GA: BIOMARKER DETECTION IN DEEP TIME

Almost two billion years of Earth history lie between the oldest biomarker-bearing rocks of the BCF and the earliest stromatolite evidence for microbial life, motivating the question of how far back in time can we push the biomarker record beyond 1.64 Ga to obtain a glimpse of Earth's earliest biosphere. Recent progress comes from an investigation of rocks stratigraphically underlying the BCF: the 1.73-Ga Wollogorang Formation (Vinnichenko et al. 2020), which does not carry a typical biomarker assemblage but contains the currently oldest known hydrocarbons that may retain some vestige of a biological molecular structure.

The Wollogorang Formation is highly thermally mature, such that kerogen generates small gas molecules rather than petroleum that contains larger biomarker structures. Catagenesis modifies and overprints biomolecular carbon structures so significantly, begging the question of what is the thermal alteration ceiling below which we still detect traces of molecules that retain biological information. During thermal alteration, biomarkers are cracked into smaller fragments, rings open or are aromatized, side chains are lost, rearranged, or shifted, and smaller molecules combine to form larger adducts. Hydrocarbons eventually lose all resemblance with their biogenic precursors. This thermal 'reshuffling' of carbon–carbon bonds also generates thousands of new products that were initially biogenic but no longer encode biological information. However, some of these products are structurally identical to compounds that we interpret as biomarkers. Modern mass spectrometry techniques are so sensitive and selective that we can detect the presence of such thermally generated compounds even in low concentrations within complex mixtures. How can we distinguish geologically generated molecules from their structurally identical biogenic counterparts? Comparing hydrocarbons from the 1.73-Ga Wollogorang Formation and the 1.64-Ga BCF illustrates the concept.

The pigments okenone and chlorobactene, which differ in the position of methyl groups on the aromatic ring (2,3,4 versus 2,3,6), break down to smaller fragments during sedimentary burial. The resulting trimethyl-aryl isoprenoids (TMAIs) (FIG. 4) are still biomarkers for phototrophic sulfur bacteria and photic zone euxinia because they retain the specific methylation positions seen in the original pigments (e.g., Summons and Powell 1986). The 2,3,4- and 2,3,6-TMAIs are clear bacterial signals in thermally well-preserved sections of the BCF because these are the only dominant TMAI isomers, even though other methylation patterns are possible. In contrast, where the BCF was more deeply buried and heated, the abundance of these two bacterial TMAI isomers drops, while other, reshuffled TMAIs emerge that do not share the same methylation pattern as the biogenic pigments, such as the 2,3,5-, 2,4,5-, and 2,4,6-TMAIs. In the most mature BCF sediments, these reshuffled TMAI isomers are more abundant than the 2,3,4- and 2,3,6-TMAI isomers. In this mixture, the 2,3,4- and 2,3,6-TMAIs could have originated from either the biogenic pigments, from the same abiogenic pathways that generated the co-occurring reshuffled TMAIs, or from a combination of these sources. Although still detectable using selective analytical techniques, we cannot distinguish whether the 2,3,4- and 2,3,6-TMAIs are direct bacterial remnants or are themselves reshuffled, abiogenic products formed during catagenesis, voiding these compounds as biomarkers in this case.

The black shales of the Wollogorang Formation were regionally heated by a volcanic sill. Organic matter in shales 30–70 m above the sill is too mature to have preserved hopanoid or steroid biomarkers. These samples exhibit the same 'reshuffling' pattern of TMAI isomers seen in overmature BCF sediments. Yet, the 2,3,6-TMAI isomer abundance increases relative to the other reshuffled TMAI isomers with progressive distance from the thermal effects of the volcanic sill. This trend suggests an increasing biogenic contribution of the 2,3,6-TMAI isomer as the thermal overprint decreases (Fig. 4). While the chemical structure of 2,3,6-TMAI itself ceased to be a biomarker in these overmature sediments, the trend between the reshuffled, abiogenic TMAI isomers in the overmature Wollogorang sediments and the relative ingrowth of the 2,3,6-TMAI with less thermal alteration may be regarded as the oldest known biomarker signal.

With additional complimentary approaches, we can start to tease out information regarding biosynthetic origins of putative biomarkers from other overmature sediments, possibly pushing the frontier towards even older geological sequences. Artificial laboratory maturation experiments on lipids will identify the smallest breakdown products that carry biological information as well as establish the boundaries where thermal overprinting extinguishes all remaining biosignature. Moreover, even when a chemical structure (i.e., spatial arrangement of atoms) is no longer biologically informative, the isotopic composition of these atoms may record biological information. For example, GSB incorporate CO_2 into their biomass using a biosynthetic pathway that generates organic matter unusually enriched in ^{13}C relative to that of most other primary producers. Subtle isotopic differences of TMAIs relative to other compounds may thus reveal a biogenic GSB contribution, even if the TMAIs are a biogenic and abiogenic mixture. However, this analysis is challenging, and it remains unknown at which maturity level such isotope signals are erased. One step higher on the ladder of analytical challenges stands the measurement of site-specific isotopes, i.e., the probability of each carbon atom in a molecule to be substituted by a heavy isotope, enabled by recent advances in ultra-high-resolution Fourier transform mass spectroscopy (e.g., Chimiak et al. 2021). Different enzymatic pathways impart different intra-molecular isotopic patterns, potentially differentiating biogenic compounds from those generated by abiogenic reactions during thermal maturation. The technological challenges of measuring such effects on individual compounds in ancient organic matter is formidable, and the thermal limits for the survival of site-specific isotopic signals remain unexplored. Nevertheless, such technology will likely open new pathways in the hunt for biogenic signals in the most ancient sediments and in samples returned from other planets.

COMPLEX MULTICELLULAR LIFE: NEOPROTEROZOIC ROOTS OF OUR MODERN ECOSYSTEMS

An increasing diversity of animal fossils throughout Cambrian (541–485.4 Ma) sediments reflects the rapid emergence of the crown group (i.e., all descendants from a most recent common ancestor) representatives of nearly all modern animal phyla. The 'Cambrian Explosion' of animal life stands at the root of our own existence, and the conditions and causalities surrounding the emergence of complex animal life count amongst the largest questions in geobiology. Answering these questions relies on getting the timing and order of evolutionary and environmental events correct.

The Early Cambrian animal fossils are immediately preceded by large and morphologically complex fossils of the Ediacara biota (Fig. 1). Most of these latter soft-bodied organisms had alien body plans and have been interpreted variably as failed evolutionary experiments, giant protists, fungi, and even terrestrial lichens, although paleontologists increasingly agree that some carry hallmarks of animals. Yet, most Ediacaran macrofossils remain enigmatic as they are usually preserved as molds and impressions lacking detail of internal structure and overall morphology. An advance was the discovery of Ediacaran fossils from the White Sea area (Russia) preserved as organic films. Bobrovskiy et al. (2018) found that the host sediments surrounding these fossils were generally rich in green algal C_{29} steroids typical for the Ediacaran (e.g., Grantham 1986; Hoshino et al. 2017); the organic films of individual macrofossils, however, revealed distinct molecular patterns compared to the sediment matrix. Fossils of *Beltanelliformis* (simple discs with concentric rings) were found to contain bacterial hopanoids and thus identified as spherical cyanobacterial colonies. Samples of *Dickinsonia*, one of the most iconic Ediacaran fossils that looks like a finely ripped oval bathmat up to 1.4 m in length, were estimated to contain at least 99.7% C_{27} steroids (possibly deriving from cholesterol), a distribution typical for animals. In contrast, the microbial mat that formed the substrate and food source of the analyzed *Dickinsonia* specimens again had a dominant C_{29} sterane signal, characteristic of green algae. The C_{27} steroid signature specifically found in the fossils, together with their morphology, placed 558-My-old dickinsoniids among animals (Bobrovskiy et al. 2018). The biomarkers from the fossils confirm that macroscopic organisms of the Ediacara biota did not belong to a single branch of life. Rather, they represent the synchronized evolution of several groups of organisms towards large size.

The record of body fossils of animal-like organisms starts around 575 Ma. Yet, most molecular clocks place the last common ancestor of all modern animals at a much earlier age, into the mid-Neoproterozoic around 800 Ma (e.g., Erwin 2021). It is unclear whether animals were simply small and inconspicuous for their first few hundred million years, or whether the molecular clocks suffer from large errors, perhaps due to a paucity of reliable calibration points (Budd and Mann 2020). Biomarkers have been used as a third, independent means to bridge the discrepancy between the animal fossil record and molecular clocks.

Unusual steroid molecules with 30 carbon atoms, which have been discovered throughout the Ediacaran and during the terminal stage of the global Snowball Earth glaciations in the preceding Cryogenian Period (720–635 Ma), led to the suggestion that animals could be traced further back in geologic time. Biological precursors to these sedimentary C_{30} steroid molecules, namely 24-isopropylcholesteroids (24-ipc) and 26-methylstigmasteroids (26-mes), are biosynthesized by some groups of sponges (McCaffrey et al. 1994; Love et al. 2009; Zumberge et al. 2018). When the molecular fossils of 24-ipc and 26-mes were found in Ediacaran rocks, they were interpreted to signify that basal animals date back to at least 635 Ma, bridging some of the time gap between molecular clocks and the fossil record. The widespread distribution and abundance of fossil sedimentary 24-ipc and 26-mes implies that early sponges were exceptionally abundant, covering most continental shelves during the Ediacaran. This discovery was transformational, providing a new scenario of animal evolution and the ecology of Ediacaran oceans (Love et al. 2009).

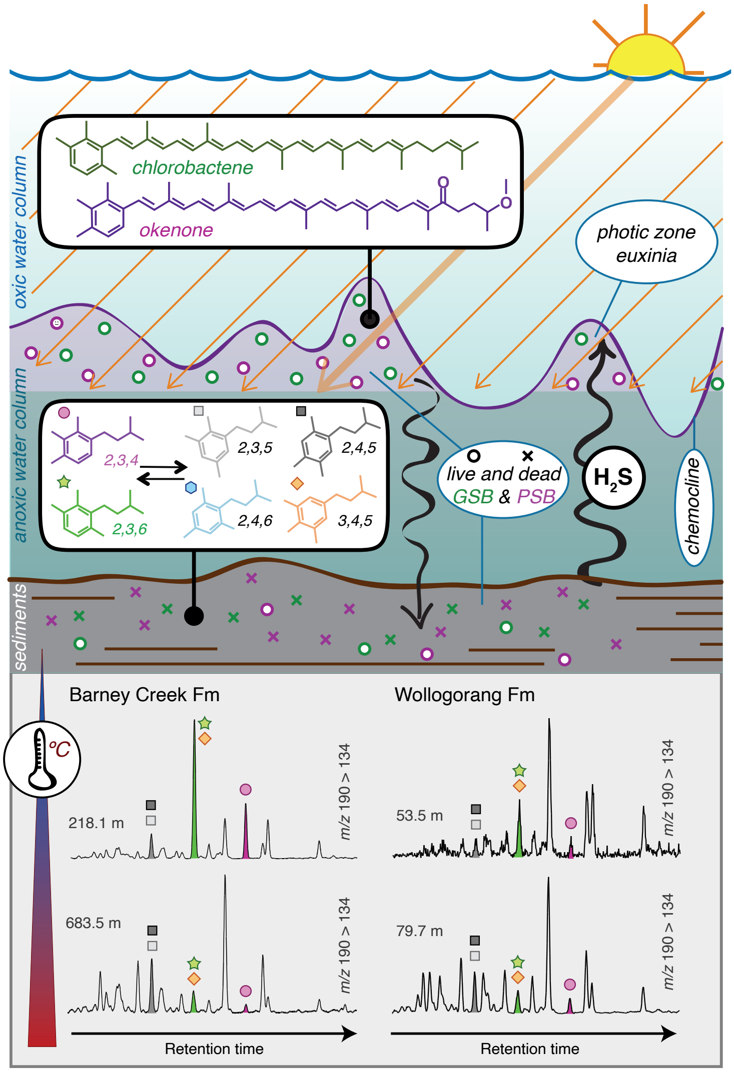

FIGURE 4 Production, breakdown, and preservation of okenone and chlorobactene. (TOP) The intersection of H_2S and the sunlit zone creates a niche for green and purple sulfur bacteria (GSB and PSB), whose intact pigments and fragmented trimethylaryl isoprenoid (TMAI)-remnants serve as biomarkers for this specific environmental condition. With increasing burial and thermal overprint, the 'green' and 'purple' biogenic TMAIs get lost among reshuffled (grey, blue, and orange) isomers. (BOTTOM) Chromatograms show that systematic patterns of changing C_{14} TMAI abundances can reveal the biomarker nature of some TMAIs, even if their structures alone do not allow for this conclusion.

However, a sponge origin for the C_{30} sterane signature observed in Precambrian sediments has several shortcomings. For example, while some sponges produce abundant precursor lipids to 24-ipc and 26-mes, most modern sponges do not. Furthermore, it remains unknown if Ediacaran sponges had the ability to produce the precursor compounds (Gold et al. 2016). These issues suggest that sponges may not be responsible for the bulk of fossil 24-ipc and 26-mes in Ediacaran sediments, thus requiring alternative and/or additional explanations.

The hydrogenation products of Rhizarian protists, which include foraminifera and radiolaria, were discovered to contain small quantities of fossil-equivalent 24-ipc and 26-mes in the same relative proportions as observed in Ediacaran sediments (Nettersheim et al. 2019), potentially posing an alternative source of these compounds in Precambrian sediments. However, subsequent laboratory studies revealed diagenetic alkylation of algal steroids as a further previously unrecognized source of fossil-equivalent 24-ipc and 26-mes, plausibly accounting for the occurrence of these molecules in Ediacaran sediments *and* the hydrogenation products of Rhizaria. Heating experiments mimicking geological conditions in the laboratory demonstrated that C_{30} steranes structurally identical to the putative sponge steranes can form via a chemical reaction from common green algal C_{29} sterol by the addition of a methyl group to the sterol side chain (Bobrovskiy et al. 2021). A hallmark of this abiogenic reaction is the progressive secondary addition of further methyl groups onto the molecule, resulting in a distinct series of methylsteranes. Such 'secondary' methylsteranes have been observed in Neoproterozoic sediments (van Maldegem et al. 2021), confirming that this process occurred in the geological past.

The high abundance, selective isomers, and variable relative distributions of the C_{30} steranes that occur in Neoproterozoic sediments add weight to a sponge origin for fossil 24-ipc and 26-mes, but the laboratory experiments together with the observed hallmarks of chemical alkylation in Neoproterozoic sediments provide a compelling argument favoring a diagenetic origin for these compounds. Although a contribution of sponges to fossil C_{30} steranes cannot be excluded at present, the diagenetic methylation of green algal C_{29} sterols, which were particularly abundant in the Ediacaran (e.g., Grantham 1986; Hoshino et al. 2017), currently provides the most parsimonious explanation for the C_{30} steroid record of the Neoproterozoic. As such, biomarkers have confirmed the presence of animals amongst the Ediacara biota, but unambiguous evidence for a deeper origin of animals remains elusive.

NEW DIRECTIONS, NEW HORIZONS

Fossil lipid hydrocarbons shape our understanding of early life on Earth. Biomarkers offer unique potential, but acknowledging and working with the many unknowns, inherent limitations, and known pitfalls of a biomarker approach is required to tap into the potential trove of information that biomarkers can reveal. New questions and opportunities flow from the topics described above such that we anticipate an exciting next decade pursuing these questions using recent analytical innovations. Continued collaboration between organic geochemists and molecular biologists will refine the taxonomic and environmental specificity of lipids. By incorporating molecular clocks, we may layer a temporal dimension to this knowledge. High-resolution cyclotron mass spectrometry of polar (sulfur-, nitrogen- and oxygen-containing) molecules that exist in parallel with fossil hydrocarbons are likely to contain a wealth of untapped information that we are just beginning to understand. Coupled with microscale laser methods, such techniques will allow molecular imaging, for instance of individual organic laminae or microfossils, at unprecedented resolution, which may revolutionize our understanding of biomarker provenance (e.g., allochthonous biomarkers associated with detrital particles) and the dynamics of environmental signals. Lastly, enhanced methods, such as position-specific isotope patterns in otherwise non-diagnostic molecular structures, and a continuous search for older and better-preserved rocks may eventually push the biomarker record deeper into time, bringing us closer to understanding Earth's earliest ecosystems. Meanwhile, the ancient hydrocarbon record of tectonically untouched deposits on Mars might hold information on the origin of life in our universe—a tantalizing possibility that will be tested using contamination-control and contamination-knowledge strategies shaped by the lessons learned while constructing and revising the record of biomarkers in Precambrian sediments on Earth.

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Biomarkers in Extreme Environments on Earth and the Search for Extraterrestrial Life in Our Solar System

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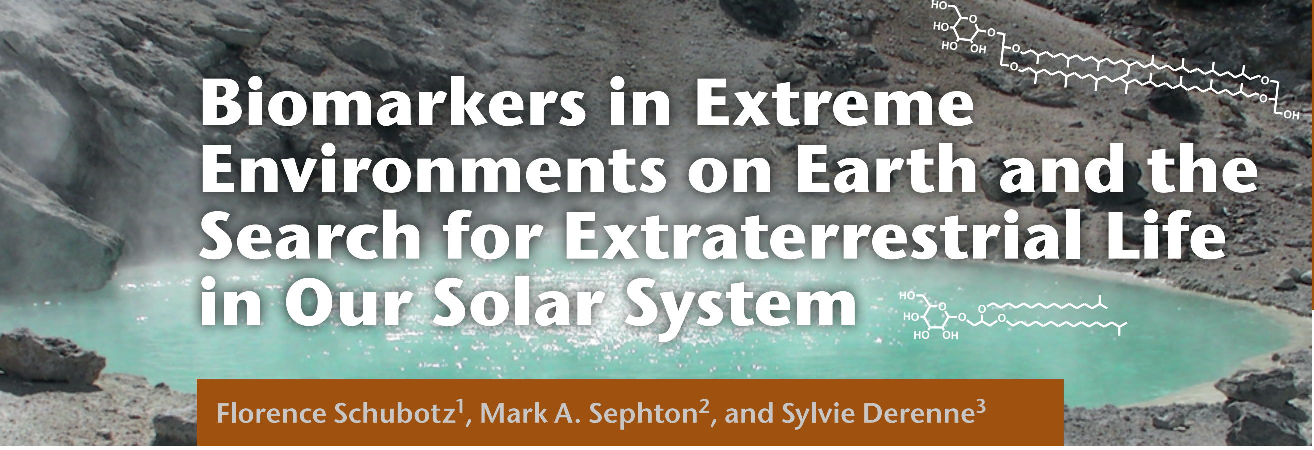

"Santa Blucia" hot spring, Yellowstone National Park (Wyoming, USA).

1811-5209/22/0018-0100$2.50 DOI: 10.2138/gselements.18.2.100

Our appreciation of the potential distribution of life in the Solar System has been impacted by the discovery that organisms are able to occupy the most extreme environments on Earth. The persistence of life in the deepest parts of oceans, the deep sedimentary and crustal biosphere accessed by deep drill holes, hot springs, deserts, and polar regions has led to diverse hypotheses regarding the potential for extraterrestrial life on other planets. This chapter provides an overview on how scientists explore the habitability of other planets and moons of our Solar System and far away in outer space and how future space missions aim to find evidence for extraterrestrial life.

Keywords: biosignatures; abiotic signatures; meteorites; ether lipids; isotopic fractionation; preservation

INTRODUCTION

Guided by our knowledge of how life has evolved on Earth, it is tenable to assume that possible extraterrestrial life in our Solar System may be similarly "primitive" as it was on Earth before the oxygenation of our atmosphere (Sasselov et al. 2020). In the search for biosignatures of such early life forms, we turn to extreme environments on Earth that may be analogous to extraterrestrial environments and which are still inhabited by organisms whose evolutionary development has remained relatively simple. Only four decades ago, the discovery of hydrothermal vents and associated flourishing oases of life on the seafloor far from sunlight opened up the possibility for life to be sustained solely from Earth's chemical energy. This discovery has illuminated new scenarios how terrestrial life may have emerged. Since then, our knowledge of where life can persist and remain viable includes some of the most inhospitable places imaginable: buried kilometers deep within the seafloor or within Earth's crust, at scorching temperatures over 120 °C, or below freezing at −20 °C. These exciting findings inspired current endeavors to search for extraterrestrial life in our Solar System, where many potential habitats would be considered extreme back on Earth, but are expected to be within modern understandings of the known environmental limits required by life.

For terrestrial life, the cell membrane is integral to protect an organism from the outside environment and enables the efficient functioning of cellular biochemical processes. If we consider the same principles of terrestrial biology to apply to other "living systems", alien life forms may therefore also use a lipid-based membrane consisting of organic molecules that have a high likelihood of preservation under favorable depositional settings. Some of the preserved lipids may be organism- and environment-specific with the potential to act as diagnostic biomarkers (Naeher et al. 2022 this issue; Hallman et al. 2022 this issue). Our knowledge of the diversity and characteristics of biomarkers in extreme environments is steadily increasing with advances in analytical technology and discoveries of novel species. Nevertheless, the detection of these signatures on extraterrestrial bodies or on samples returned to Earth faces several challenges and includes having sufficiently sensitive detection techniques and ensuring contamination-free sample recovery. These challenges are exacerbated by the need to identify extraterrestrial target sites where these biosignatures might be preserved. For this, we heavily rely on the information provided by Earth's geologic record (Hallman et al. 2022 this issue), but also experimental studies of organic matter decay and preservation to identify promising rocks and minerals where biomarkers of either extant or extinct extraterrestrial life may be found.

DISCERNING BIOTIC FROM ABIOTIC SIGNATURES

All forms of life on Earth share a number of common features, which serve as reference for the presence of life. Perhaps the most important distinction between biotic and abiotic signatures is that life is highly specific in the types of molecules it uses, while abiotic synthesis is undirected by enzymes. For instance, out of the hundreds of naturally occurring amino acids, life on Earth employs only 20 in the synthesis of proteins. It is a characteristic trait of living systems to form biochemically useful polymers from repeating subunits of a specific structure. In contrast, abiotic synthesis of organic matter results in the formation of small organic molecules and macromolecules whose architecture is a response only to chemistry and physical processes such as temperature and pressure (cf. Summons et al. 2008).

There are many organic molecules that can provide evidence for life, including nucleic acids, amino acids, sugars, or small metabolites; however, most of these compounds are not very stable over geologic timescales. Lipids are an ideal target for detecting extant or ancient life as they are common biological compounds with a wide structural variety and high preservation potential (Naeher

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Definition Box 1

Chirality: Mirror images that cannot be superimposed one upon the other.

Stereoisomer: Molecules with the same molecular formula and the same bonds, but different atom positions.

Isotope: Atoms with the same atomic number (same number of protons) but different masses (different number of neutrons).

Kerogen: Macromolecular organic material insoluble in organic solvents.

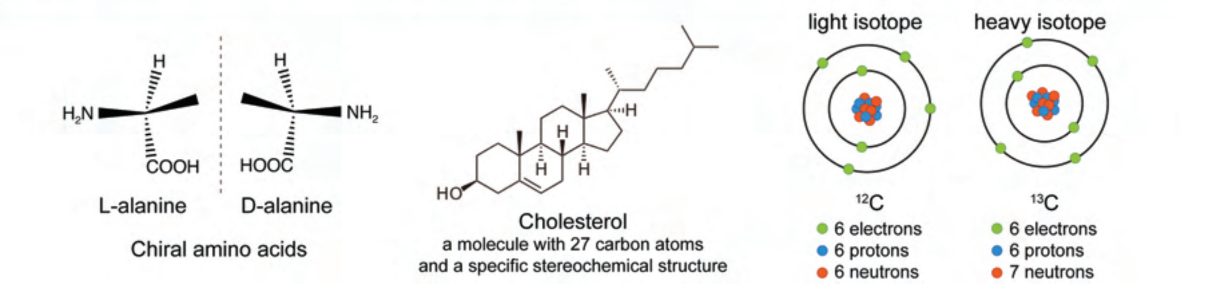

FIGURE 1 Overview of definitions used in the text with examples.

et al. 2022 this issue). Once detected, lipids represent a life signal with high specificity, providing information not only on the identity of their source organism, but also on its metabolic activity assisted by information encoded in stable isotopes. Covalent binding of organic molecules to a macromolecular network, where free and reactive counterparts are occluded by or bound to other molecules, such as is the case in kerogen, leads to an increase in preservation.

In the following sections, we define key attributes for assessing biological origins over potential abiotic signatures while keeping in mind that these may not be universal to all alien biochemistries.

Chirality

Highly specialized enzymes of living systems preferentially react with and produce specific structural isomers, resulting in a predominance of certain chiral compounds over others in biological products, such as the "left-handed" L-amino acids and "right-handed" D-sugars (FIG. 1). This predominance is most commonly referred to as L- or D-enantiomeric excesses of chiral amino acids and sugars. While the type of chirality may not be a strict requirement for life and the enantiomeric preference of L- or D-enantiomers may have been chosen at random on Earth, life elsewhere is similarly expected to express a certain preference during biochemical reactions.

Larger molecules are associated with a more complex variety of possible structures and increasing prevalence for structural isomer preference by biology. For instance, while a normal straight chain *n*-alkane with 10 carbon atoms has 136 isomers including stereoisomers, a C_{27} straight chain *n*-alkane has over six billion. The molecule cholesterol, which is synthesized by all animals, also has 27 carbons and 256 possible stereoisomers, but only one stereoisomer is used by biology (FIG. 1).

Molecular Complexity

Another defining feature of life is specific molecular architectures that are distinct from smaller molecules, displaying multiple isomers produced by abiotic reactions. Complex natural products, such as proteins, DNA, or polysaccharides, are generally constructed from repeating small sub-units, resulting in a highly ordered structure. Fatty acids and wax esters are polymers of acetate and thus called acetogenic lipids, while sterols, bacteriohopanepolyols, and archaeal ether lipids consist of fused isoprene units and are called isoprenoid lipids. The synthesis of acetogenic lipids leads to odd or even carbon chain preferences (i.e., excesses of even carbon number compounds over odd, or vice versa), while isoprenoid lipids have specific branching patterns (Naeher et al. 2022 this issue). Different lipids tend to cluster in discrete molecular weight ranges between C_{14} and C_{35} in contrast to distribution patterns of abiogenetically formed organic matter, where relative abundances are normally distributed and centered at low carbon numbers.

Isotopic Signatures

The acquisition of essential elements for the biosynthesis of biomolecules is associated with isotope fractionations as life generally uses lighter isotopes during enzymatic reactions and therefore discriminates against heavy isotopes. For carbon, these isotope fractionations are particularly significant during autotrophy, which is the process of fixing inorganic carbon into biomass. Different carbon fixation pathways exhibit different isotopic fractionations depending on their enzymatic machinery (Hayes et al. 2001). In contrast, the acquisition of carbon from organic molecules, called heterotrophy, results in only small isotopic variations, but this consistent fractionation can be used to reconstruct trophic relationships. Isotope fractionations during the biosynthesis of different biomolecules are distinct and depend on the enzymes involved and the isotopic compositions of the precursor molecule of the respective biopolymers. For instance, the isotopic compositions of acetogenic lipids differ from those of isoprenoid-based lipids, and lipids are distinct from proteins, DNA, and carbohydrates. The general preference of lighter isotopes during biochemical reactions makes the isotopic composition of organic molecules a helpful and confirmatory indicator for life. By contrast, a lack of enrichment in the light isotope of carbon can suggest an abiotic origin, while there are specific exceptions as further discussed below. For instance, laboratory experiments have demonstrated the abiotic generation of light methane under hydrothermal conditions with similar stable carbon isotope values as biological methane (Horita and Berndt 1999).

ORGANIC MATERIAL FOUND IN METEORITES: LIFE SIGNALS FROM OUTER SPACE?

Meteorites are the main source of extraterrestrial material on Earth and, next to laboratory experiments, they provide the basis for our current understanding of prebiotic chemistry. Of primary interest are carbonaceous meteorites that contain significant amounts of organic matter (up to 4 wt%) that has remained largely untouched since

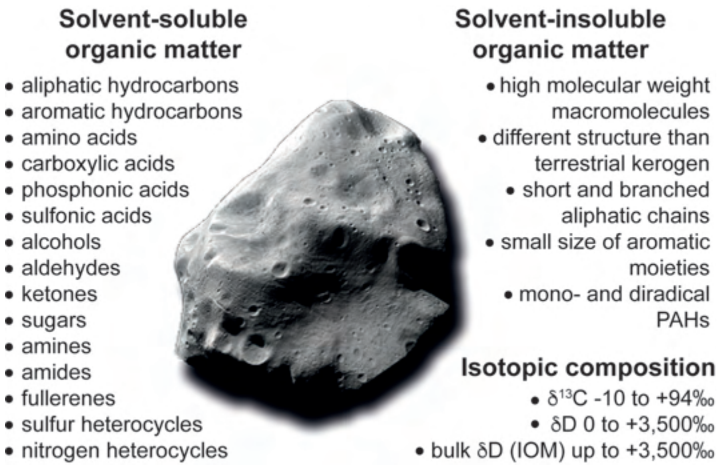

Figure 2 Characteristics of organic matter found in solvent-soluble and -insoluble fractions of carbonaceous meteorites. Isotopic ranges of solvent-soluble organic matter measurements include the analysis of amino acids, carboxylic acids, and aliphatic hydrocarbons for δD (see Pizzarello 2011 and references therein) and amines, amino acids, aldehydes, ketones, and carboxylic acids for δ^{13}C (see Simkus et al. 2019 and references therein). Bulk δD was determined on solvent-insoluble organic matter (IOM), while benzylic radicals of IOM can be as high as 96,000‰ (Gourier et al. 2008, see text for details). Abbreviation: PAH = polycyclic aromatic hydrocarbons.

the formation of the Solar System 4.6 billion years ago (reviewed in Sephton 2014). These meteorites consequently hold information on organic products that must have also been present on a prebiotic Earth and may be available also on other bodies in our Solar System for the potential emergence of carbon-based life. A small fraction of this organic matter is soluble in water and organic solvents and comprises low molecular weight compounds that resemble biologically important compounds found on Earth such as amino acids, nucleobases, carboxylic acids, phosphonic acids, sulfonic acids, and polyhydroxylated compounds, while low molecular weight aliphatic and aromatic hydrocarbons are also present in small amounts (Fig. 2) (Sephton 2014). Amino acid analyses of the Murchison meteorite, arguably the most famous carbonaceous meteorite, revealed the presence of more than 70 extraterrestrial amino acids. Support for an extraterrestrial source of these compounds was provided by their carbon isotopic compositions, which were richer in the heavy rare isotope, ^{13}C, than what was known from terrestrial organic carbon (Kvenvolden et al. 1970). In contrast, study of these extraterrestrial sources of biologically important molecules has also complicated the use of chirality as a biosignature, as some studies have shown that these abiotic compounds possess large enantiomeric enrichments commonly associated with biosynthesis. Moreover, laboratory studies reveal several cosmochemically relevant abiotic chemical processes that are enantiomerically selective (Glavin et al. 2019).

The majority of organic carbon in carbonaceous meteorites occurs as insoluble macromolecules that are challenging to analyze. Attempts to characterize the complex structure of the insoluble organic matter (IOM) include chemical and thermal degradation experiments, as well as non-destructive spectroscopic techniques. These analyses have revealed important distinctions from kerogen on Earth. In contrast to terrestrial kerogen, the meteorite IOM consists of small aromatic units, which are highly substituted and connected by short and branched aliphatic chains (Derenne and Robert 2010). These aromatic units bear mono- or diradicaloid species that are not observed on Earth and also show exceptionally strong enrichments in deuterium. The extremely heavy stable isotope values for hydrogen, up to +3,500‰ for bulk IOM and +96,000‰ in benzylic radicals of the IOM (Gourier et al. 2008), are a confirmatory characteristic for organic material found in meteorites and are outside the range of what is found on Earth. They are best explained by formation of this organic material in the protosolar nebula followed by spontaneous isotopic exchange during ion–molecule reactions between easily exchangeable hydrogen atoms of the IOM and abundant deuterium-rich ions (Remusat et al. 2006).

In summary, organic matter found in meteorites represents primitive prebiotic matter and not vestiges of extraterrestrial life, but its distribution and isotopic composition provide important information on the range of values that can be expected from abiotically synthesized organic matter in our Solar System. Notably, such enrichments in ^{13}C or D may not readily distinguish between abiotic or biotic compounds in extraterrestrial settings, as extraterrestrial biomass may be heavier than what is known from Earth and is dependent on the respective atmospheric and surface reservoirs.

CHALLENGES AND OPPORTUNITIES OF EXTRATERRESTRIAL ENVIRONMENTS

There are three main ingredients for an environment to be considered habitable: liquid water; an energy source, which could either be light or chemical energy; and accessibility to the building blocks of life, including C, H, N, O, P, and S. Ongoing discoveries of life in extreme environments on Earth have greatly expanded our views on where we can expect to find life elsewhere (Fig. 3). The observation that psychrophilic life is able to grow at subzero temperatures in brine has opened up the possibility that life may withstand the harsh and freezing conditions that persist on ice-covered bodies far from the Sun such as Enceladus or Europa (Hendrix et al. 2018). Furthermore, the presence of life in hyperarid and hypersaline environments such as evaporites on Earth has raised hopes that life may have been sustained under similar conditions on Mars. The discovery that piezophilic life even proliferates when buried over 2 km deep in marine sediments and over 4 km in the continental crust has turned much of the exploration for extraterrestrial life to the subsurface, particularly for those planets that have inhospitable surface conditions, such as the high ionizing radiation and highly oxidizing surface of Mars (Sasselov et al. 2020). Furthermore, there is compelling evidence that some subsurface systems can provide energy sources through water–rock reactions that can be exploited for biological processes. Particularly in the spotlight are ultramafic systems, which are composed of rocks that are rich in magnesium and iron. These petrogenic conditions result in very alkaline fluids that, when coming into contact with seawater, lead to chemical reactions that can initiate the abiotic synthesis of small organic compounds such as methane, organic acids, alcohols, and amino acids (McCollom and Seewald 2007). These systems have therefore been suggested as a likely place where life may have originated, particularly because ultramafic rocks were very prevalent on a young Earth. Similar to other deep-sea vents, these are sites where thermophilic and hyperthermophilic life is found, withstanding temperatures up to 120 °C and having ancient metabolisms such as methanogenesis, sulfate reduction, or acetogenesis (cf. Brazelton et al. 2006). Both Enceladus and Europa are considered to have a mafic or ultramafic rocky core overlain by a brine ocean, which is covered by ice. Together with observations of active geysers in the southern hemisphere of Enceladus, the evidence indicates some form of hydrothermal or gaseous activity, making these two moons very attractive target sites for astrobiology (Hendrix et al. 2018).

Definition Box 2

Thermophilic: "Heat-loving" organisms with optimal growth rates at temperatures between 41 and 122 °C.

Mesophilic: Organisms that grow at moderate temperatures with an optimum growth range from 20 to 45 °C.

Psychrophilic: "Cold-loving" organisms capable to grow and reproduce at temperatures ranging from -10 to +10 °C.

Piezophilic: "Pressure-loving" organisms with optimal growth rates at hydrostatic pressure at or above 10 MPa.

Halophilic: "Salt-loving" organisms, which can tolerate up to 30% salt content.

FIGURE 3 Overview of definitions used in the text with exemplary habitat pictures. (**A**) Hot spring at Yellowstone National Park (Wyoming, USA), a habitat for thermophiles. (**B**) Salt flats of Badwater Basin, Death Valley (California, USA), a habitat for halophiles. (**C**) Glacier ice in Antarctica, a habitat for psychrophiles. PHOTO: FLORENCE, CHRISTA, AND LUTZ M. SCHUBOTZ.

Terrestrial Analog Sites

In our search for biosignatures of primitive organisms, we turn to terrestrial analog sites such as hot springs or hydrothermal vents in the deep ocean, but also hot and cold deserts and subsurface environments. Of high astrobiological relevance is the Lost City hydrothermal vent field (North Atlantic Ocean), where active subsurface serpentinization reactions result in the growth of carbonate and brucite chimneys several meters into the water column. Here, microbes with ancient metabolisms prevail, such as methanogens, methanotrophs, and acetogenic bacteria (Brazelton et al. 2006). Similarly, hot springs have received considerable attention owing to the presence of hyperthermophilic archaea and bacteria that are deeply rooted in the tree of life. These systems allow the study of sweeping community changes and associated variations in biosignatures over small spatial scales due to their strong geochemical and physical gradients. In hot spring outflow channels, temperatures increase from 50 °C to over 80 °C within only several meters and are accompanied by drastic fluid chemistry changes from an oxidizing environment to a strongly reducing one. In hydrothermal vent chimneys, such changes in temperature and fluid chemistry are observed within only centimeters.

BIOMARKERS OF EXTREMOPHILIC LIFE

Organisms adapted to extreme conditions in pH, temperature, and pressure often have very specialized and diagnostic membrane lipids. These lipid modifications are critical for cellular survival as they ensure to maintain the optimal membrane fluidity. Membranes that become too rigid or too fluid can disrupt the active solute transport, functioning of membrane proteins, and passive permeability of hydrophobic molecules. Many extremophiles belong to the domain of archaea; these microorganisms have membrane lipids that are inherently different to those of bacteria and eukarya by having exclusively isoprenoid ether lipids instead of ester-bond fatty acids (FIG. 4). Because ether lipids are chemically more robust than ester lipids, this trait was suggested to be an advantage for better adapting to extreme conditions (Valentine 2007). There are also some bacteria that can synthesize ether lipids; these include soil bacteria and bacteria that live in hot springs or at methane and hydrocarbon seeps (Naeher et al. 2022 this issue). Many of these ether–lipid-synthesizing bacteria have not yet been identified despite extensive studies. In the following, we describe some of the prominent structural and isotopic microbial membrane lipid modifications as responses to environmental stress.

Homeoviscous Adaptation

Temperature stress: As a response to increasing or decreasing temperature, bacteria can modify the unsaturation level (usually observed as the presence of double bonds), chain length, or branching level of their membrane lipid fatty acids in order to maintain optimal membrane fluidity (FIG. 4) (Zhang and Rock 2008; Naeher et al. 2022 this

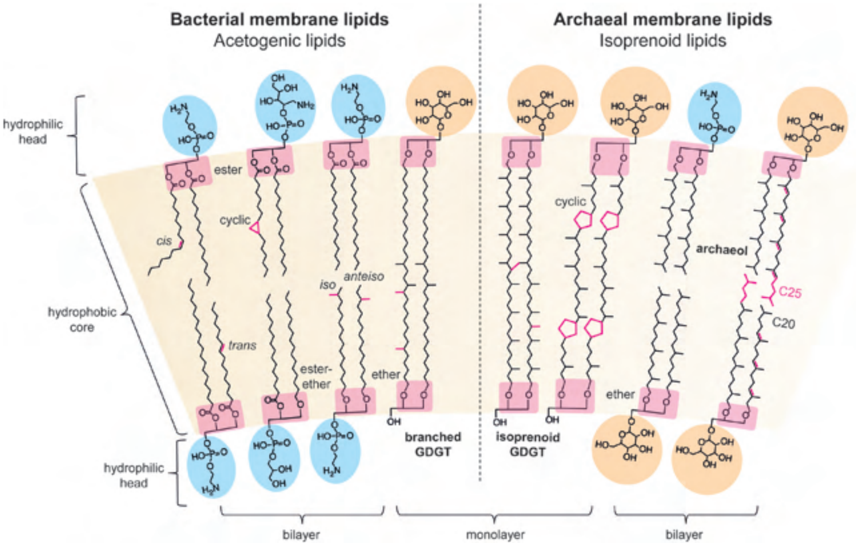

FIGURE 4 Schematic diagram of a bacterial and archaeal cellular membrane showing select lipid modifications encountered in extremophilic microorganisms. Circles signify the type of hydrophilic polar headgroups: phospholipids (oval); glycolipids (round). Ester and ether bonds are marked by a square, locations of modifications in the hydrophobic cores in response to changing environmental conditions are highlighted in bold (see text for details). GDGT = glycerol dialkyl glycerol tetraether.

issue). In archaea, typical membrane lipid modifications in response to temperature include modifying the ring abundance, changing the number of methylations, or inserting a covalent bond between the two isoprenoidal chains of the ether lipids to form so-called H-shaped tetraethers (FIG. 4) (Schouten et al. 2013). In addition, archaea can exchange phosphatidic with glycosidic headgroups when temperatures increase, making the cell membrane more rigid due to the formation of hydrogen bonds.

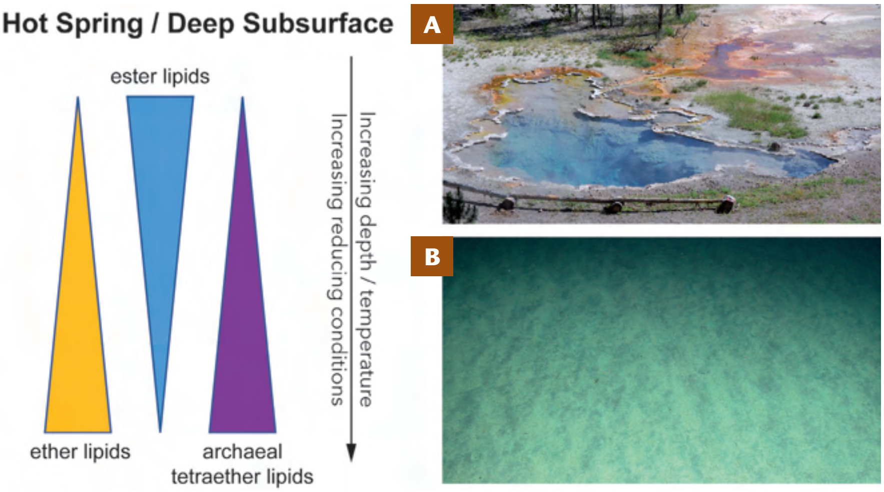

FIGURE 5 Prominent membrane lipid modifications observed in hydrothermal systems and deep subsurface environments. (**A**) Picture of "Octopus" hot spring in Yellowstone National Park (Wyoming, USA). PHOTO: F. SCHUBOTZ. (**B**) Picture of the seafloor representing the sedimented deep subsurface. PHOTO: ROV QUEST 4000, MARUM.

pH stress: Modifying membranes to include cyclopropane fatty acids in bacteria have been observed in response to acid stress, but also many environmental stressors, like exposure to oxidations, starvation, desiccation, and large temperature fluctuations (Zhang and Rock 2008). It is therefore assumed that the insertion of rings enhances the chemical and physical stability of membranes, while limiting their permeability to unwanted compounds. Membranes of acidophilic archaea are dominated by tetraether lipids (GDGTs) with little or no detectable archaeol contributions (Schouten et al. 2013).

Pressure stress: The insertion of *cis* fatty acids makes the membranes bulkier and increases permeability due to the "kink" in the acyl chain. In piezophilic bacteria, they prevent a compaction of the cell membrane due to increasing ambient pressure (Zhang and Rock 2008).

Salinity stress: A unique feature of many halophilic archaea is the synthesis of extended isoprenoid carbon chains that have one additional isoprene unit forming either one or two C_{25} isoprenoid chains in the diether lipid archaeol (FIG. 4). The unsaturation level in diether lipids also increases with increasing salinity, possibly as a mechanism to counteract the salt-induced decrease in membrane fluidity by reducing membrane permeability to ions (Dawson et al. 2012).

Molecular Adaptations Along Strong Geochemical Gradients

Common features of microbial membrane adaptations observed at hot springs, the oceanic lithosphere, and in deeply buried sediments include a general transition from ester lipids to ether lipids (FIG. 5). Investigations of lipid modifications along hot spring outflow channels have revealed a number of bacterial adaptations that go along with changes in community composition from mesophilic to thermophilic organisms. These include the increased synthesis of *iso* and *anteiso* branched fatty acids with C_{15} up to C_{20} carbon chain lengths and with a dominance of *iso* fatty acids due to their biophysical property of decreasing membrane fluidity. A notable increase in fatty acid chain length up to C_{20} and C_{22} (including cyclic fatty acids) as well as a gradual increase in bacterial diether lipid production was observed (Schubotz et al. 2013). An even greater provenance of bacterial diether lipids was observed in the carbonate chimneys of the Lost City hydrothermal vent field (Bradley et al. 2009). Evidence for exceptionally good preservation of these ether lipid signatures comes from the analysis of over 100-Ma-old mantle rocks that have hosted subseafloor serpentinization systems similar to Lost City. Here, both archaeal diether and tetraether lipids as well as the diagnostic bacterial diether lipids were found to be preserved in brucite and calcite veins (Klein et al. 2015). Analogous to this ancient lithospheric subseafloor environment, the deep sedimentary biosphere has revealed a comparable dominance of ether lipids. Here, intact archaeal tetraether membrane lipids are most prominent, but it is currently disputed whether this represents an increase in the importance of archaea or simply is a result of the preferential preservation of archaeal lipids. Nevertheless, the switch from ester to ether lipids can be observed with increasing depth and reducing conditions, as also noted for bacterial lipids (Evans et al. 2017).

Isotopic Signals of Extremophiles

While biological activity typically results in depletion of heavy ^{13}C during biomass build-up, the $^{13}C/^{12}C$ ratios of microbial lipids and biomass found at hot springs and deep-sea hydrothermal systems exhibit surprising enrichments in the heavy isotope (Bradley et al. 2009; Schubotz et al. 2013; Reeves et al. 2014). At these sites, many of the detected lipids have higher ^{13}C contents than bulk microbial biomass and even several per mil higher than inorganic carbon (FIG. 6). There is only one metabolic pathway that could explain such high values, which is the reversed tricarboxylic acid cycle, an assumed ancient pathway to fix inorganic carbon present within many deeply rooting bacteria found in these environments (Schubotz et al. 2013; Reeves et al. 2014). In this pathway, enzymes involved in synthesizing lipids run in the opposite direction from the Calvin cycle, resulting in a reversed sequence of stable carbon isotopic fractionation effects on the ^{13}C contents of biomolecules, with lipids being enriched in ^{13}C compared to biomass by up to 16‰ (van der Meer et al. 1998). When moving further away from hotter temperatures, the $^{13}C/^{12}C$ ratios of lipids decrease (become less ^{13}C enriched), indicative of a change in the carbon fixation pathway to mainly the Calvin–Benson–Bassham cycle. The Calvin–Benson–Bassham cycle is the predominant carbon fixation pathway in cyanobacteria and other phototrophs as well as many other non-photosynthetic autotrophic bacteria, which are known to inhabit the cooler regions of hot springs and hydrothermal vents (Schubotz et al. 2013; Reeves et al. 2014). Overall, many of the detected lipids exhibit a wide range of isotopic compositions, indicating that the majority of hot spring organisms have evolved towards

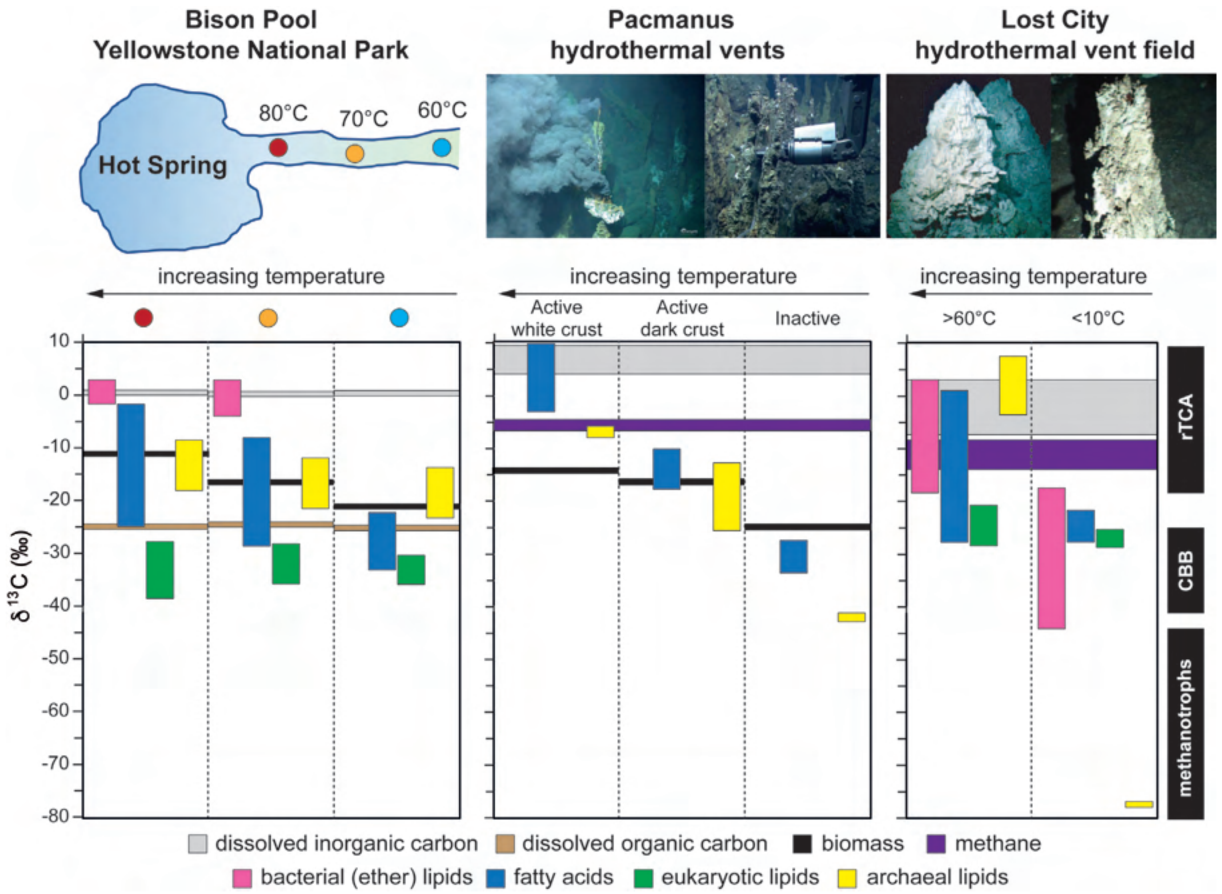

FIGURE 6 Changing microbial metabolisms assigned based on lipid carbon isotopes at hot springs and deep-sea vents following changes in temperature and strong geochemical and physical gradients (Bradley et al. 2009; Schubotz et al. 2013; Reeves et al. 2014). In black bars to the right are isotopic ranges expected for different autotrophic pathways of lipid synthesis: rTCA = via the reversed tricarboxylic acid pathway; CBB = via the Calvin–Benson–Bassham cycle; and methanotrophs = via methanotrophic activity.

an opportunistic lifestyle where they can either exploit organic or inorganic carbon sources for biomass build-up (Schubotz et al. 2013).

Archaeal lipids similarly seem to represent a mixed source with an increase in heterotrophic activity at colder temperatures, while the acquisition of inorganic carbon seems to dominate at hotter temperatures (FIG. 6). At the Lost City hydrothermal vent site, $^{13}C/^{12}C$ ratios of lipids depleted in ^{13}C with values down to −80‰ are assigned to methane-metabolizing archaea. To explain the extremely strong carbon isotopic enrichments in archaeal lipids, which are not known to utilize the reversed tricarboxylic acid cycle, Bradley et al. (2009) proposed carbon limitation induced by large-scale carbonate precipitation. This process would result in little isotopic fractionation because all available inorganic carbon is consumed without discrimination of the heavy isotope. Whatever the cause for the isotopic enrichment observed in many organisms inhabiting hydrothermal and ultramafic systems, an important consequence of this finding is that high $^{13}C/^{12}C$ ratios do not directly dispel the possibility of a biological origin of the organic matter.

PRESERVATION AND CONTAMINATION CHALLENGES

Our success of finding any traces of past or present extraterrestrial life will depend partly on whether we have identified the right habitable locations and most importantly that we have not inoculated other planets and moons with microbial life from Earth. To assess the risk of terrestrial contamination, we need to characterize well potential contamination signals and be able to distinguish them from indigenous signals.

For the organic evidence of life to be useful it must survive from the time of its formation to the time of its detection, which requires good preservation. Parameters that influence organic matter preservation include temperature, overburden pressure, radiation, mineralogy, oxidizing conditions, and dryness (Summons et al. 2008). Optimal preservation conditions may be found on mineral matrices that are suitable to entomb fossilized material or even whole cells. On Mars, the focus has turned to mudstones rich in silica and iron-bearing clay minerals, but evaporite rocks are also considered (McMahon et al. 2018). Recent findings of aromatic, aliphatic, and S- and Cl-bearing organics in pyrolysis products of ~3.5-Ga mudstones at Gale Crater by the *Curiosity* rover give reasonable hope for organic matter, from any source, to be preserved at the right locations (Eigenbrode et al. 2018). Still, we know too little regarding the long-term preservation of lipid biomarkers (and other organic material) in different mineral matrices under varying types of atmospheric conditions. Some extraterrestrial environments of astrobiological interest are very old and laboratory simulation experiments have revealed how certain mineralogy can combine over time, thus providing preservation challenges (cf. Tan and Sephton 2021). Quantitative experiments on the preservation potential of organic material in iron-rich deposits that are common on Mars revealed that long-term burial on amorphous ferrihydrite actually results in the desorption of organic matter (Tan and Sephton 2021). These neutral-pH, iron-rich deposits should therefore not be favored as candidates for optimal preservation of organic material. On the other hand, entombment of organic material in brucite and calcite veins of ultramafic mantle rock has shown to provide favorable preservation conditions and has allowed the detection of intact membrane lipids in material that is well over 100 million years old (Klein et al. 2015).

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Advancing Analytical Frontiers in Molecular Organic Biomarker Research Through Spatial and Mass Resolution

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Analytical developments have been crucial for the advancement of molecular biomarker research in the Earth sciences. In this chapter, we focus on two areas where recent technological developments have profoundly impacted the use and relevance of molecular organic biomarkers: (1) the increase in spatial resolution heralded by imaging techniques, which results in biomarker-based paleoenvironmental reconstruction with unprecedented temporal resolution; and (2) the accurate, simultaneous characterization of a wide range of compounds in complex matrices enabled by ultra-high-resolution mass spectrometry.

Keywords: FT-ICR MS; hyperspectral imaging; Fourier transform; mass spectrometry imaging; molecular stratigraphy; sedimentary pigments

INCREASING SPATIAL RESOLUTION IN MOLECULAR BIOMARKER ANALYSIS

Conventional biomarker analysis relies on the extraction of targeted organic compounds from samples that are typically cubic-centimeter-sized. Information stored within this sample volume is averaged, minimizing variability. However, bacterial cell volumes are generally less than 1 μm^3, which implies that a 1-cm^3-sized sample could average the information stored in more than one trillion (10^{12}) cells. The effect of such averaging is evident when attempting to reconstruct paleoenvironmental conditions from sedimentary archives, where spatial resolution translates into temporal resolution. Typical sedimentation rates in the marine realm are a few micrometers per year, while rates as high as a millimeter per year are restricted to high-productivity areas and lacustrine systems. A sample spanning one centimeter of depth can thus contain the information deposited over decades, centuries, or much more time. Improved spatial resolution for physically undisturbed biomarker records is therefore required to assess abrupt or short-term environmental changes and high-frequency climate variability.

Subannual to decadal climate reconstructions are especially relevant, given that the durations of extreme events (e.g., heat waves, cold spells, droughts, floods) range in time scales from days to months. High time resolution is also needed to study seasonal cycles or high-frequency climate fluctuations such as the El Niño Southern Oscillation. These phenomena take place at human time scales and are relevant from societal and ecosystem perspectives. Fortunately, certain marine and lacustrine sedimentary archives capture this variability: for instance, varved sediments contain at least two distinct micro- to millimeter-thick layers deposited every single year and thus offer an archive with subannual resolution (Zolitschka et al. 2015; Schimmelmann et al. 2016).

Conventional, wet-chemical approaches to extracting molecular biomarkers from sediments and rocks have sought to maximize spatial resolution, and thereby temporal resolution, by increasing the sampling effort (more and smaller sample sizes), but are ultimately limited to the centimeter- or millimeter-scale (e.g., Kennedy and Brassell 1992). However, it has recently become possible to approach these materials using techniques that obtain molecular information directly from intact sediment samples, without previous sub-sampling or extraction. These techniques not only provide unmatched spatial resolution in the micrometer-range, but also the possibility to explore the two-dimensional spatial distribution of characteristic biomarkers in a sample. Here, we focus on two spatially resolved techniques that are based on spectrophotometric and mass spectrometric biomarker detection.

Hyperspectral Imaging to Detect and Quantify Sedimentary Organic Pigments at Micrometer-scale Resolution

Hyperspectral imaging (HSI) is a widely used method in remote sensing and other fields that has recently been developed for biogeochemical analysis of sediment cores. The technique relies on the interpretation of spectral profiles of light reflected from the target sample in the visible to near-infrared (Vis-NIR) range (400–2,500 nm). Here, we focus on the use of HSI to measure photosynthetic pigments in sediment cores at extremely high spatial (micrometer-scale) and temporal (subannual) resolution.

The principles and development of HSI core scanning are based on simpler methods of point-based reflectance spectroscopy. Rein and Sirocko (2002) were the first to show that reflectance spectroscopy scanning of fresh sediment

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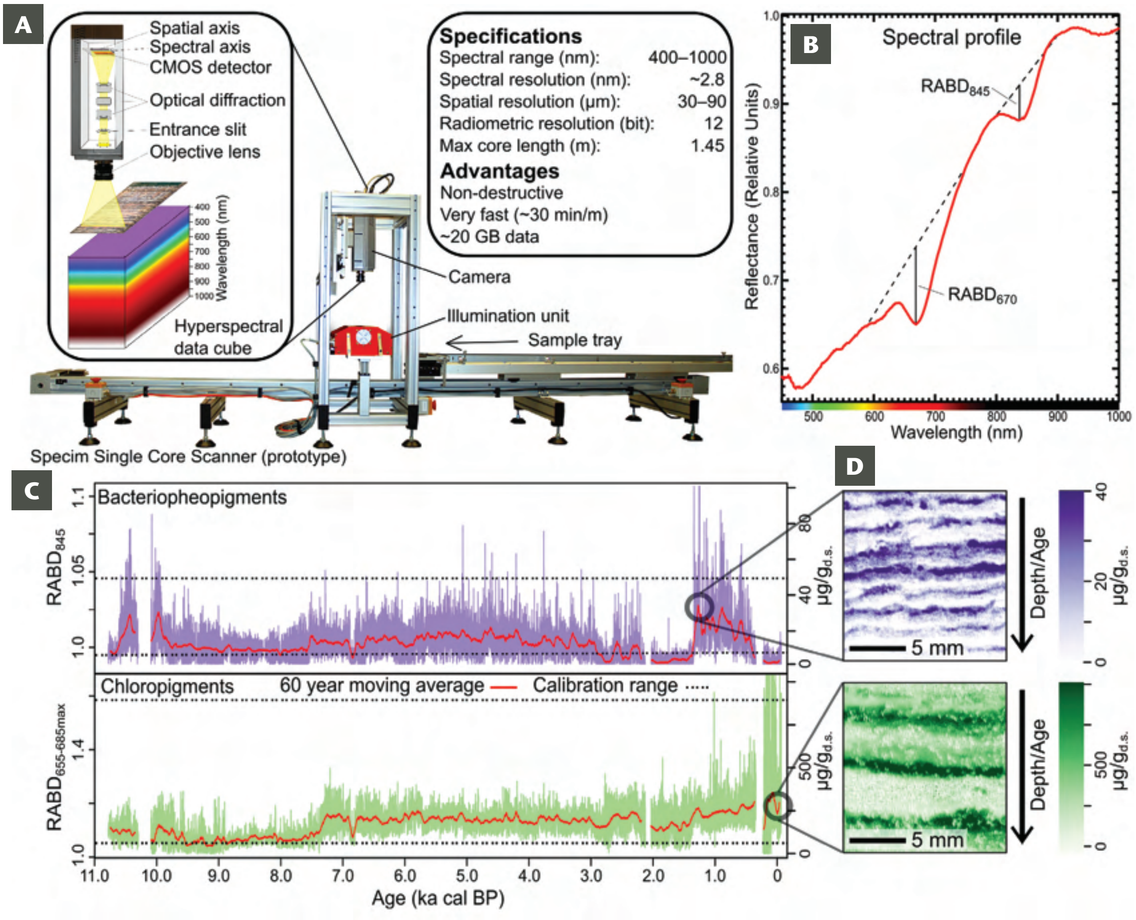

FIGURE 1 (**A**) Specim Single Core Scanner and technical specifications. IMAGE ADAPTED FROM BUTZ ET AL. (2015). (**B**) Example spectral profile showing pigment absorption troughs and relative absorption band depth index measurement principle. (**C**) Example hyperspectral imaging (HSI) pigment data from Lake Żabińskie Poland (Zander et al. 2021a) showing a 10,800-year-long record of bacteriopheopigments and chloropigments used to reconstruct aquatic anoxia and primary productivity. (**D**) Close-up of spatial distribution of pigments showing seasonal pigment variability in annually laminated sediments. Note: $g_{d.s.}$ = grams dry sediment.

cores could be used to generate relatively high-resolution (2 mm), semi-quantitative measurements of pigments with much less time and cost compared to conventional wet-chemical techniques (e.g., high-performance liquid chromatography, HPLC). The measurement principle relies on the fact that groups of pigment compounds absorb light in specific wavelengths, and the amount of that absorption, quantified by a relative absorption band depth (RABD) index, is proportional to pigment concentrations in the sediments. For many years, the hand-held Gretag Spectrolino or Minolta 2600d spectrophotometers were the state-of-the-art instruments for reflectance spectroscopy core-scanning. Pigment records from these devices were used to reconstruct aquatic productivity in lake and marine sediments, which could be related to oceanographic, climatic, and ecological conditions in studies spanning hundreds of years to over 10,000 years. However, the spatial (2–8 mm) and spectral resolutions (10 nm) of these instruments remained limited.

Hyperspectral imaging builds upon the principles of reflectance spectroscopy by connecting an imaging lens with a spectrograph. Hyperspectral images of sediment cores are acquired using a 'pushbroom' method, where the core passes under the hyperspectral camera and light source, and rows of pixels are acquired and stacked to form a complete image of the core surface (FIG. 1). Each pixel within the hyperspectral image contains an individual spectral profile of light reflected from the sediment surface.

Hyperspectral imaging was first applied to sediment cores by Butz et al. (2015), who used a prototype of the Specim Single Core Scanner (FIG. 1). Images are acquired in the Vis-NIR wavelength range (400–1,000 nm) with a spectral resolution of 2.8 nm and a scanning resolution of 30–90 µm (pixel size). Scanning a 1-m-long split core takes ~30 minutes. The following workflow is used to quantify pigment concentrations from HSI data. First, raw spectral data are normalized to standardized units based on dark (camera shutter closed) and white ($BaSO_4$ plate) references. Next, spectral endmembers (the spectral profiles that are most distinct) are identified to understand the variation in the spectral data within a sample and to identify spectral features suitable for quantification (i.e., pigment absorption troughs). RABD indices are then calculated for each individual pixel, creating spatial distribution maps of pigments within a core. Down-core profiles of pigment abundance are typically obtained by taking row averages (perpendicular to depth) of RABD values across a representative 2-mm-wide subset of the image data. The RABD indices can be calibrated to pigment concentrations measured using chemical extraction techniques and HPLC or spectrophotometry, with typical errors less than ~15%. Concentrations of pigments as low as 5 µg/g dry sediment are detectable in fresh sediment cores. This method enables measurements of pigment concentrations in sediment records that are tens of meters long (ca. 10–20,000 years) at 60–90 µm resolution in a few weeks.

To date, HSI has been shown to effectively measure distributions and concentrations of bacteriopheophytin-*a* (a derivative of bacteriochlorophyll-*a*) and total chloropigments (chlorophyll-*a* and degradation products). Bacteriochlorophyll-*a* is produced by anoxygenic phototrophic bacteria, and therefore is a biomarker for anoxia in aquatic systems (Butz et al. 2015). Chlorophyll-*a* is ubiquitous in photosynthetic organisms and is often used to reconstruct total algal production. HSI tracks all degradation products of chlorophyll-*a* that remain colored, which means that HSI-based reconstructions of algal production are less affected by pigment degradation than studies based only on chlorophyll-*a*. Detection of other pigment groups in sediments, including carotenoids, phycocyanin, and other bacterial chloropigments, remains possible but has not yet been conclusively demonstrated.

The primary advantages of HSI are rapid data acquisition and extremely high spatial resolution that cannot be achieved using conventional methods of biomarker analysis in sediments. In varved sediments, it is possible to resolve the seasonal cycle of pigment production by using HSI (Fig. 1). However, interpretations based on spectral data should be validated with conventional techniques. Spectral signatures of pigments are non-specific, thus pigments that absorb light in the same spectral range cannot be differentiated using this technique (e.g., chlorophyll-*a* and -*b*). In addition to providing calibration and validation of RABD indices, combining HSI with HPLC techniques is advantageous to obtain more detailed information about photosynthetic communities and pigment degradation processes. Other high-resolution core-scanning techniques, such as micro-X-ray fluorescence (µXRF) scanning, provide the opportunity for paleoenvironmental studies utilizing subannual measurements of both inorganic and organic proxies (Zander et al. 2021b).

Hyperspectral imaging–inferred pigment records from Poland, Switzerland, and Greece have documented how natural and human-caused changes to catchment land cover have affected lake productivity and redox conditions since the Late Glacial (Fig. 1). For example, at Lake Moossee, Switzerland, changes in pigment production were linked to climatic changes, and cycles of Neolithic/Bronze Age deforestation and afforestation related to early human activities at the site (Makri et al. 2020).

More advanced numerical and computing methods may improve the quantification of pigments or other substances in sediments based on HSI data. In a recent study, random forest regression (a machine learning technique for regression and classification) was applied to HSI data to infer grain size distributions in six Canadian lakes (Ghanbari et al. 2020). These types of techniques also could be used to improve the analysis of organic sedimentary components using HSI. HSI and other high-resolution spectroscopic techniques are expected to yield new insights in several scientific disciplines, particularly for questions that can only be answered with ultra-high spatial resolution data.

Micrometer-scale Resolution Images of Biomarker Distribution and Ultra-high-resolution Molecular Stratigraphy via Mass Spectrometry Imaging

Most organic compounds are not detectable using photometric techniques. In contrast, mass spectrometry can detect and quantify an immense diversity of ionizable molecular species. Spatially resolved mass spectrometric analysis is now feasible with ionization probes that scan across a sample in a predefined pattern, including focused solvent sprays, lasers, or ion beams. These probes generate an ion cloud at each nanometer- to micrometer-sized raster spot that is transferred to the mass analyzer, thus obtaining a spatially referenced collection of thousands of complete mass spectra for every square centimeter. In each spectrum, single molecular species can be identified and their relative abundances quantified. By documenting the distribution of single compounds, compound ratios, or more complex molecular signatures, an image of their spatial distribution is obtained.

This approach, termed mass spectrometry imaging (MSI), is firmly established in biomedical and microbiological research (e.g., Watrous and Dorrestein 2011). In the Earth sciences, however, its implementation has been slower, probably because of the complexity encountered in samples that combine organic material and minerals, and because of the low polarity and concentration of targeted compounds. Pioneering work with time-of-flight secondary ion mass spectrometry (ToF-SIMS) detected lipid biomarkers in modern and fossilized marine microbial mats (e.g., Thiel et al. 2007). These developments, as well as the use of nanospray desorption electrospray ionization (Lanekoff et al. 2013), evidenced the possibility to reveal the spatial distributions of geologically relevant compounds in environmental samples. Compared to these techniques, matrix-assisted laser desorption/ionization (MALDI) offers some additional, crucial advantages. First, it provides the opportunity to analyze relatively large, centimeter-sized sample surfaces, as opposed to the micrometer-sized areas typical for ToF-SIMS. In addition, MALDI is a soft ionization technique that prevents the fragmentation of labile compounds upon ionization and allows the detection of the intact biomarker molecules. When coupled with ultra-high-resolution mass spectrometry, such as Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS; see below), excellent mass resolution and sensitivity are attainable. These properties make MALDI-based MSI ideally suited for the exploration of sedimentary archives, as demonstrated in the early publication by Wörmer et al. (2014).

Following this initial development, a dedicated facility at the University of Bremen has been responsible for major advances in MSI of sedimentary molecular proxies, starting with the development of an optimized workflow for sample preparation, data processing, analysis, and visualization (Alfken et al. 2019, 2020; Wörmer et al. 2019). Given the need to maintain the original sediment structure, samples are stabilized by embedding, for example into aqueous solutions of gelatin and carboxymethyl cellulose (Fig. 2, left). After solidification at −20 °C, embedded pieces are sectioned into 60–100 µm thin slices on a cryomicrotome. Each slice has an approximate area of 5 × 1.5 cm and is suitable for MSI and complementary elemental mapping by µXRF (Fig. 2, middle). High-quality images of these slices are made to guide MSI and to record sediment color as an additional parameter. Solid rock archives can be cut into a suitable size, with a maximal thickness of a few millimeters, and analyzed, while the use of thin sections remains to be explored.

Measurement of molecular biomarkers in sedimentary archives typically does not require application of an additional artificial matrix, and the slices can be directly analyzed after completely drying in a vacuum chamber. However, signal enhancement due to matrix application is observed in some cases. Besides the use of typical MALDI matrices (e.g., 2,5-dihydroxybenzoic acid), unconventional matrices such as fullerite or silver may be useful in the detection of nonpolar biomarkers (Wörmer et al. 2019). Mass spectrometry imaging requires the definition of measurement area and spatial resolution and

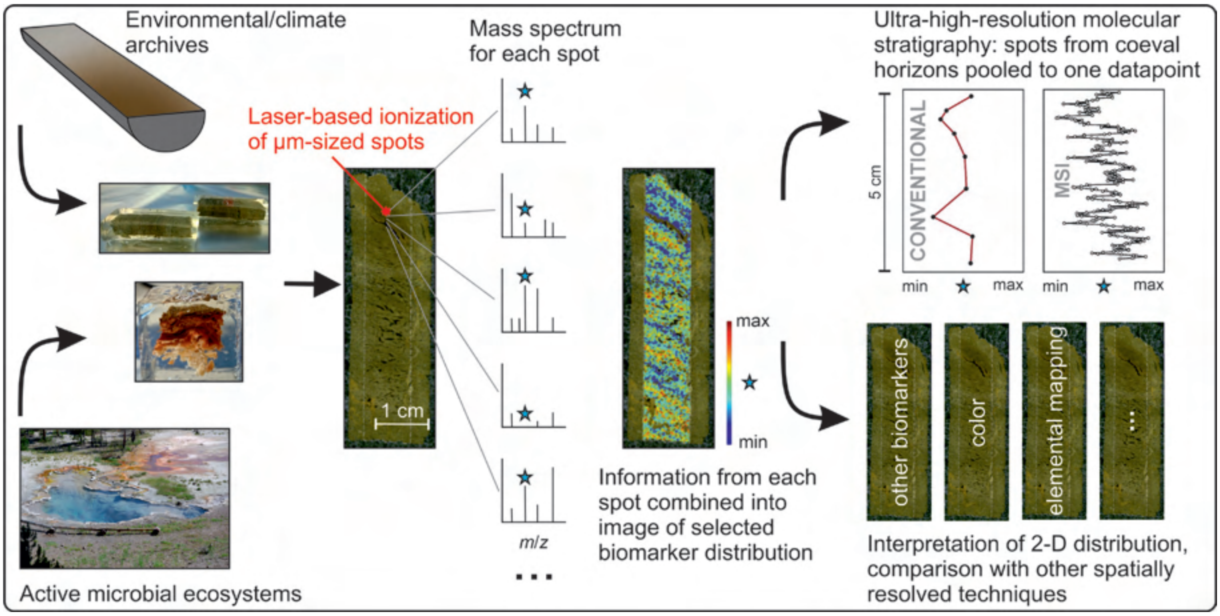

FIGURE 2 Summary of analytical process and applicability of MALDI-based molecular biomarker mass spectrometry imaging (MSI) in the Earth sciences. (LEFT) Sediment samples are stabilized by embedding, for example into aqueous solutions of gelatin and carboxymethyl cellulose. The samples are then sectioned into 60–100 µm thin slices on a cryomicrotome. (CENTER) Spatially resolved biomarker distributions can be obtained from the surface of these slices. (RIGHT) In paleoenvironmental archives, the micrometer-scale raster allows for ultra-high-resolution molecular stratigraphy. The interpretation of the 2-D biomarker distribution, in combination with other imaging techniques, can inform on characteristic spatial patterns in a diversity of sample types. IMAGE CREDITS: (LOWER LEFT) PHOTO OF OCTOPUS SPRING (YELLOWSTONE NATIONAL PARK, WY, USA) COURTESY OF R. SUMMONS (MIT, USA); IMAGES OF EMBEDDED SEDIMENT, SEDIMENT SLICES, AND MAP OF BIOMARKER DISTRIBUTION ARE COURTESY OF S. ALFKEN (UNIV. BREMEN, GERMANY).

tuning of laser power and ion optics for each sample and analyte to maximize signal intensity. A spatial resolution of 100–200 µm is recommended for sedimentary archives, while active microbial ecosystems can be analyzed with 10-fold higher spatial resolution (10–20 µm). To increase sensitivity for individual compounds, analyses are carried out in restricted mass-to-charge ratio (m/z) windows, ideally spanning less than 100 units. Given the minute amounts ionized from each micrometer-sized spot, samples with concentrations of the target compounds in the range of µg per g dry weight are ideal. Alkenones, archaeal glycerol ether lipids, sterols, fatty acids, and pigments have been detected in sediments by MALDI-MS and enable reconstructions of sea surface temperature, redox conditions, or changes in terrestrial vegetation and aquatic primary productivity. However, these compounds represent only a minor fraction of the molecular signatures revealed by MSI of sediments and other environmental samples.

The images of molecular biomarker distribution obtained by MSI can be interrogated by averaging them across horizontal layers and evaluating them against a single dimension (depth, age) or by exploiting their two-dimensional nature (FIG. 2, RIGHT). In the first case, biomarker or proxy information from a micrometer-sized coeval horizon is pooled, providing a data point that can be assigned to a certain depth (age). This approach is most consistent with conventional molecular stratigraphy, but temporal resolution is improved by several orders of magnitude. We therefore refer to it as ultra-high-resolution molecular stratigraphy. This technique relies on properly referencing the data obtained by MSI to the original core depth (and thus age), and benefits from image processing: in laminated sediments, non-horizontal sediment deposition can be corrected and data points corresponding to the same horizon aligned (Alfken et al. 2020). Mass spectrometry imaging records from approximately the last century can be compared to monthly or seasonal records of instrumental data describing the water column (for example sea surface temperature, nutrient concentration, redox conditions) or to historical climate data to understand how these conditions are recorded in the sedimentary proxy signal (Alfken et al. 2020). In older records, and when compared with other high-resolution archives (e.g., ice cores), MSI can inform on changes in high-frequency climate oscillations, on short-lived environmental disruptions, or on leads and lags in the expression of abrupt climate change events and the forcing factors behind them (Obreht et al. 2020).

The second approach to MSI measurements explores both spatial dimensions of the dataset. When combined with complementary measurements of the same sample surface, each micrometer-sized spot is described by information such as sediment color, elemental composition, and a suite of molecular biomarker or proxy signatures. In sedimentary archives, this provides a means to better understand biomarker transfer and preservation in the seafloor, but also to deconvolute the proxy signal according to other sedimentary parameters. For example, in varved sediments seasonal changes can be evaluated by binning molecular sea surface temperature proxies according to sediment color. In active microbial systems, fine spatial structure can be assessed to document variations in the abundances of molecular biomarkers along microscale environmental gradients (Wörmer et al. 2020). Moving forward, it might be possible to identify potential new biomarkers by non-targeted approaches. Thereby, MSI data are searched for compounds with distinct spatial patterns that correlate to other spatial clues in the sample. Such clues include distinctively shaped or colored regions, or regions with specific elemental compositions, and could indicate a particular depositional environment or specific microbial communities and biogeochemical processes.

Mass spectrometry imaging can be applied to a variety of environments, such as marine and lacustrine sediments, soils, rocks, or microbial mats. It provides an extremely rich data set, with typically more than 10,000 spatially referenced mass spectra for each 5-cm piece of sample,

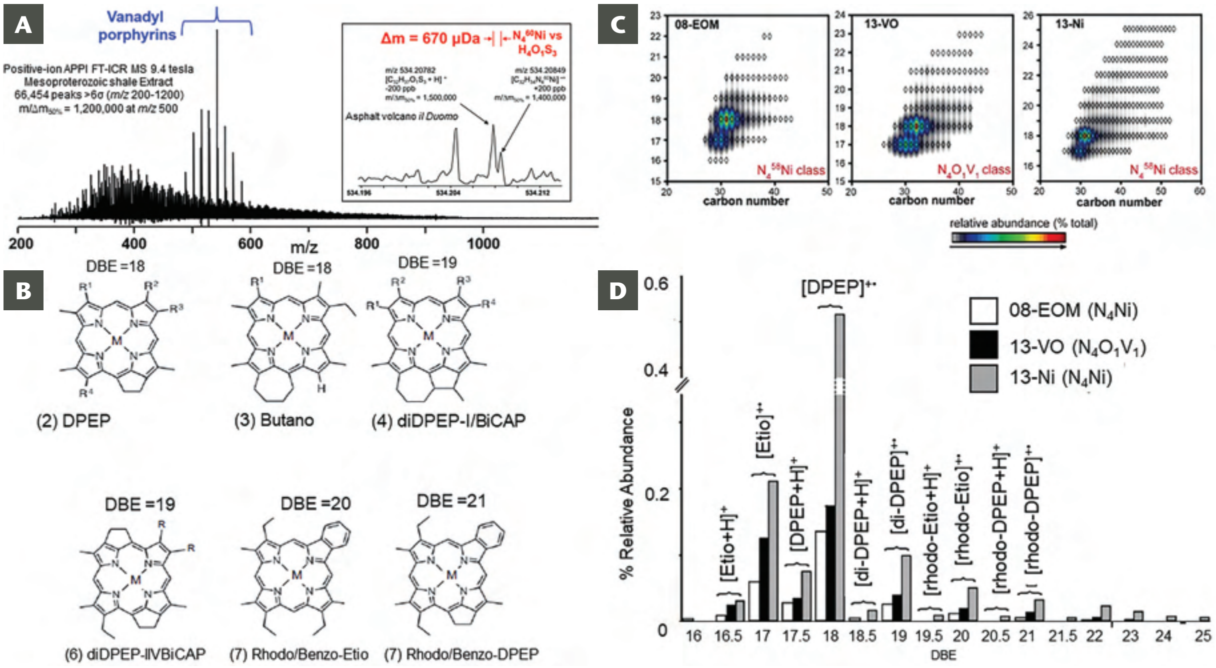

FIGURE 3 (**A**) Broadband positive-ion atmospheric pressure photoionization (APPI) 9.4 tesla FT-ICR mass spectrum from a Mesoproterozoic shale extract from the Taoudeni Basin (western Africa) that detects more than 66,000 unique elemental compositions across a molecular weight range from *m/z* 200 to 1200 with achieved mass resolving power ($m/\Delta m_{50\%}$) of 1,200,000 at *m/z* 500 (Gueneli et al. 2018). (**INSET**) A mass-scale zoom of an Il Duomo asphalt volcano (Santa Barbara, CA, USA) sample illustrating the ultra-high resolving power of two species that differ in mass by roughly the mass of an electron (McKenna et al. 2014). (**B**) Some structures of the nickel and vanadyl porphyrins identified by Fourier-transform ion cyclotron resonance mass spectrometry (FT-ICR MS) that extended the geological record of photosynthesis on Earth by 600 million years. The structures are arranged by the number of double-bond equivalents (DBE), defined as the number of aromatic rings plus the number of double chemical bonds in each molecule. (**C**) Identification of two classes of Ni- and VO-porphyrins by FT-ICR MS, plotting relative abundance versus DBE and carbon number. (**D**) The structure of C_{30}–C_{32} porphyrins identified supports phototrophs as the dominant photosynthesizing organisms on Earth 1.1 billion years ago. Identified porphyrins likely derived from simpler cyanobacteria versus phototrophic sulfur bacteria.

each spectrum containing the signatures of hundreds or thousands of compounds. We are only starting to understand how challenging and rewarding it is to simultaneously access such high information density at both the spatial and molecular level.

ULTRA-HIGH MASS RESOLUTION: FT-ICR MS

The first step in identifying biomarker molecules in environmental samples by mass spectrometry is critical. The mass detector must be capable of separating targeted molecules from the tens of thousands of other compounds present in the sample (e.g., background species, unintended contaminants, or components of complex mixtures that are intentionally analyzed without purification). Conventionally, identification of biomarkers in geochemical samples requires a mass resolution sufficient to separate species that differ in mass by roughly the mass of an electron (0.0005 u); given that many common biomarkers have molecular weights in the range ~200–500 u. This means the mass resolving power required to separate peaks of equal height is on the order of hundreds of thousands to millions (FIG. 3A, INSET). Resolution is often expressed as $m/\Delta m$, where m is the ion mass and Δm is the smallest difference in mass that can be discriminated. The mass resolutions achieved by routine detectors in mass spectrometry (e.g., quadrupoles and magnetic sectors) range from hundreds to a few thousand—clearly insufficient for biomarker identification.

The only mass analyzer capable of routinely achieving mass resolutions >1,000,000 across a wide molecular weight range (~150–1500 Da) is FT-ICR MS. These devices trap ions in cylindrical detection cells, confining them with intense magnetic fields generated by superconducting magnets that force ions into regular orbits with periods inversely proportional to *m/z*. Each ion 'packet' with a given *m/z* orbits with a single frequency (cyclotron frequency) detected as induced current as the ion packet passes near detection electrodes. Although the time-dependent induction current can be complex when multiple ion packets (tens of thousands) of different *m/z* are present, a Fourier transform analysis of the record of that current (the 'transient') yields the frequency of motion of each detected ion packet. These frequencies are in the radio range (~10^6 Hz) and can be measured with exquisite precision, down to parts per billion. Because frequency is a simple function of *m/z*, this translates to similarly exquisite mass resolution. Finally, it should be noted that a newer generation of mass spectrometers, Orbitraps, uses similar principles to FT-ICR MS, but traps ions within small, egg-shaped electrostatic traps, at reduced maximum mass resolution (<200,000). Orbitraps are challenged in resolution for complex mixtures where many species close in mass (several electron mass units) are prevalent, as well as due to peak coalescence behavior, and are best suited to lower molecular masses (up to ~300 u) (Schittmayer and Birner-Gruenberger 2017).

Major advances in several fields, including studies of organic molecular composition of crude oil, dissolved organic matter, soil organic matter, sediment extracts, and weathered oil from natural and anthropogenic releases, have benefited from FT-ICR MS. It is particularly important that FT-ICR MS achieves high mass resolution, high mass accuracy, and high dynamic range (ratio of highest and lowest peaks in a spectrum) and can simultaneously detect both abundant and less abundant species across a wide mass range, separating species by mass alone in highly complex sample matrices. Therefore, FT-ICR MS can analyze mixtures without prior chromatographic isolation, which is a great advantage in studies of exceptionally complex natural materials. Two examples are shown in FIGURE 3A: an extract from a Mesoproterozoic shale (Taoudeni Basin in western Africa) and a sample from an asphalt volcano (Santa Barbara, California, USA) (McKenna et al. 2014; Gueneli et al. 2018). First, all species must be resolved from one another and assigned elemental compositions (FIG. 3A). Next, elemental compositions can be used to calculate the number of rings plus double bond equivalents, (calculated from the elemental composition, DBE = $C - h/2 + n/2 + 1$, where C = carbon, h = hydrogen, and n = nitrogen). FIGURE 3B shows the DBE values and representative core structures for vanadyl porphyrins. Finally, compositional images of DBE versus carbon number (FIG. 3C) show the three dominant vanadyl porphyrin classes detected, and FIGURE 3D shows the relative abundance for each porphyrin class (DBE value).

A major complication of any mass spectrometry-based application to biomarker research is that the potential target molecules vary greatly in molecular structure and chemical properties. Although FT-ICR MS can separate these species in mass space, they must first be transferred to the gas phase through ionization for any mass spectral technique. One single, soft ionization technique cannot efficiently ionize all species present in geochemical samples because of the immense polydispersity and polyfunctionality in composition. For example, atmospheric pressure chemical ionization (APCI) or atmospheric pressure photoionization (APPI) are applied to oil samples to selectively ionize non-polar and aromatic compounds, whereas electrospray ionization (ESI) targets acids and bases (Qi et al. 2020). Multiple ionization techniques are often applied to selectively target specific chemical and structural functionalities and capture the widest compositional information, resulting in multiple mass spectral analyses for a single sample. Qi et al. (2020) assessed the selectivity of three ionization techniques (APPI, APCI, and ESI) and vastly increased the number of identified novel biomarkers in lignin by compiling the species identified from three separate mass spectral analyses.

These advances in mass spectral instrumentation and ionization techniques have been led by petroleum research focused on more comprehensive characterization of global energy reserves. Such advances have expanded the application of FT-ICR MS to important petrochemical, environmental, and geochemical systems and have identified new biomarkers at the level of elemental composition assignment (Kim et al. 2022). In the following paragraphs, we highlight a few selected applications of FT-ICR MS for detection of biomarker species in geochemical systems and recognize many other important research areas (e.g., marine and terrestrial organic matter).

Petroporphyrins

Applications to target porphyrins for demetallation strategies have largely utilized APPI FT-ICR MS in a host of geochemical systems, including 1.1-Ga-old sediments from the Taoudeni Basin (Gueneli et al. 2018), natural petroleum seeps (McKenna et al. 2014), bitumen (McKenna et al. 2009), and tar balls (Lima et al. 2020). A new high-mass-resolution tool for routine analysis of complex metalloporphyrin distributions in geological sample extracts couples HPLC to an Orbitrap mass spectrometer detector, and simultaneously quantitates Cu, Ni, VO, Zn, and Mn porphyrins (Woltering et al. 2016).

Lipids

Radović et al. (2016) identified a complete series of core glycerol dibiphytanyl glycerol tetraethers (glycerol dialkyl glycerol tetraethers (GDGTs) with 0 to 8 alicyclic rings), including the complete resolution of GDGT-4 and the unexpected detection of GDGTs with more than five rings, in sediments from mesophilic marine environments. These capabilities establish geochemical relationships between archaeal ether lipids, overcome the limited ability of chromatography to resolve sample polydispersity, and leverage the mass resolving power of FT-ICR MS.

Hydrocarbon Biomarkers

In a combined technique approach, FT-ICR MS analysis of an unusually blue crude oil causing deposition issues in an offshore production platform in the Gulf of Mexico identified perylene as the source of the oil's blue color (Juyal et al. 2011). Negative-ion ESI FT-ICR MS identified an enrichment of C_{27}–C_{32} hopanoic acids (DBE of 5–9) in the field deposit. Collectively, FT-ICR MS, GC–MS, and accelerator mass spectrometry results suggest that the oil originates from the hydrothermal alteration of algal and bacterial detritus and that the oil is the youngest known hydrothermal petroleum.

Polar Biomarkers

New parameters based on oxygen classes ($O_{>2}$) detected by an ESI ion source coupled with FT-ICR MS are reported as new paleoenvironmental proxies of terrestrial organic matter input in oxic waters, whereas S_1O_x compounds indicate a sulfidic depositional environment (Orrego-Ruiz et al. 2020). Organic compounds extracted from deep fracture waters in billion-year-old rocks in South Africa characterized by negative-ion ESI FT-ICR MS correspond to microbial metabolites and indicate geomicrobiological reports of chemolithoautotrophic microbial ecosystems functioning in isolation from photosynthetic primary production (Kieft et al. 2018).

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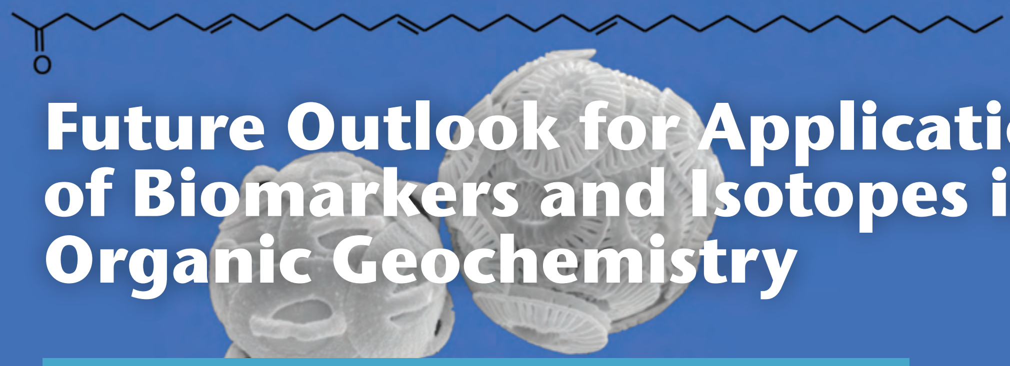

Future Outlook for Applications of Biomarkers and Isotopes in Organic Geochemistry

Structure of a long-chain alkenone found in haptophytes such as *Gephyrocapsa oceanica and Emiliania huxleyi* (coccoliths pictured). PHOTO: CSIRO.

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Organic geochemistry continues to make important contributions to our understanding of how the biogeochemistry of our planet and its environment has changed over time and of the role of human impacts today. This article provides a brief overview of the field and a perspective on how it might develop in the near future. Particular emphasis is placed on biomarkers (compounds with a distinctive chemical structure that can be related to specific organisms) and stable isotopes of carbon, hydrogen, and nitrogen, as these are major tools used by organic geochemists. Many geochemical studies involve a mixture of disciplines and so this article also focuses on how this research area can complement work in other fields.

KEYWORDS: biomarkers, Earth's history, lipids, isotopes, paleoenvironment, petroleum

INTRODUCTION

Organic geochemistry can be said to have begun with Treibs' recognition in 1936 of petroporphyrins (macromolecules derived by loss of phytol from chlorophyll and substitution of Mg with V and Ni) as unquestionable biological signatures in ancient shales. Subsequent research in the 1960s further developed the theme that specific organic compounds (termed biological markers or simply biomarkers) that can be linked to a specific biological source can provide information about the nature of early life even when recognizable fossils are absent, as well as the idea that petroleum is composed of thermally altered biological remains (Brocks and Summons 2003; Naeher et al. 2022 this issue).

Organic matter in sediments represents a large reservoir of reactive carbon-based compounds on Earth and is thus a key component in both local and global carbon cycles and in a wide range of ecological functions. Organic geochemistry encompasses studies of the sources and fates of organic matter in geological materials including sediments, coal, peat, oil, and gas. The techniques of this field have been extended to studies of aquatic environments and food web relationships using "signature" lipids (another term for biomarkers) and stable isotopes. Similar approaches have been applied to extraterrestrial samples. Organic geochemists also play an important role in studying the bioavailability, mobility, and distribution of chemical pollutants in the environment.

BIOMARKER PROXIES FOR PALEOENVIRONMENTAL ASSESSMENT

By far the most successful aspect of organic geochemical studies has been the development of proxies based on abundances of specific biomarkers that can provide information about a particular environmental characteristic in ancient sedimentary settings (e.g., biodiversity, organic matter sources, biodegradation, temperature, salinity, redox state, nutrient status, CO_2 concentration, sea-ice extent). These applications require a good understanding of the source-specificity of the biomarker, which, in turn, relies on comprehensive lipid analysis of organisms of geochemical interest (e.g., Brocks and Summons 2003; Volkman 2017; Naeher et al. 2022 this issue). The effects of diagenesis and the possibility of changes to the biomarker abundance ratios due to confounding environmental factors (i.e., other than those a given proxy is intended to measure) need to be considered. Laboratory culture experiments are a vital means for studying such effects, and the field would benefit from further studies, but they must be set up with environmentally relevant conditions. Such studies can help confirm new findings about biosynthetic pathways derived from molecular biology and identify those taxa that have the ability to make particular lipids (Summons et al. 2021; Villanueva and Coolen 2022 this issue).

Biomarker proxies for environmental variables are typically formulated either as proxy = [A]/[B] or proxy = [A]/([A] + [B]) where [A] and [B] are measures of the concentrations of biomarkers A and B. Note that A and B may include several biomarkers. Concentrations may be determined from peak areas in gas chromatograms, or in the total ion current, or mass fragmentograms in gas chromatography–mass spectrometry (GC–MS) or high-performance liquid chromatography–mass spectrometry (HPLC–MS) analyses. Whether absolute or relative concentrations are used must be clearly specified. Double-blind calibration studies to validate the analytical methods used by various laboratories have effectively improved confidence in these proxies (e.g., Schouten et al. 2013).

More effort needs to be made to ensure that the proxy is formulated in such a way that it is meaningful in terms of known cellular or organismal biosynthetic responses (e.g., change with temperature in the degree of unsaturation of lipids in membranes). Unfortunately, the scientific underpinning for some proxies has been rather weak and based solely on correlations in a particular geographic region, which may not translate well to other environmental settings. Some proxy definitions seem unnecessarily complex, as illustrated by the original formulation of the alkenone paleotemperature proxy (see below), while others involve measurements of a large number of compounds,

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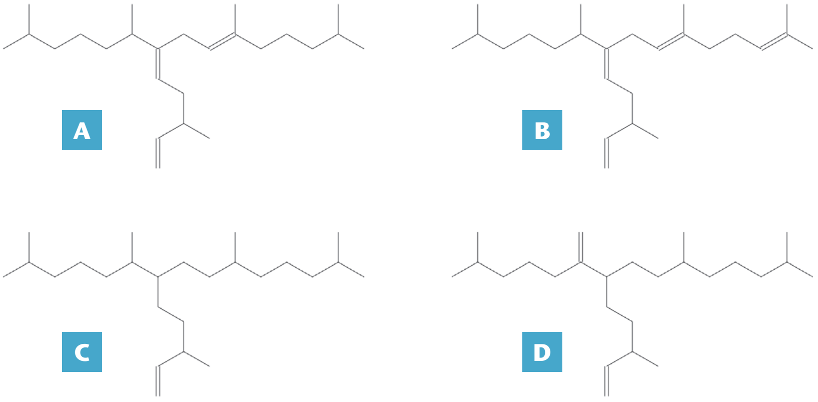

FIGURE 1 Highly branched isoprenoid (HBI) alkenes are found in several diatom genera and occur in various chain lengths (C_{20}, C_{25}, and C_{30}) and with up to five double bonds. Structures (**A**) and (**B**) are common in open marine species, but structures (**C**) and (**D**) are only found in diatoms from sea-ice environments. These latter groups have distinctive enriched $\delta^{13}C$ values and when present in sediments can be used as biomarkers for the presence of sea-ice extent when the sediment was deposited.

such as those involving the tetraether lipids known as glycerol dialkyl glycerol tetraethers (GDGTs). The identification of multiple biomarker proxies to measure a specific environmental parameter is of particular value, and the emergence of differences can provide additional insights about the environment. The following four examples (hydrocarbons, alkenones, alkyl diols, and tetraether lipids) were chosen to demonstrate these themes and opportunities, but many more compound classes could have been highlighted (e.g., fatty acids, sterols, triterpenoids, carotenoids, porphyrins, amino acids, etc.). The scope of applications is indeed vast.

Hydrocarbons as Proxies for Organic Matter Sources

Hydrocarbons exist in a variety of structural forms, from simple straight-chain *n*-alkanes, to branched alkanes, isoprenoid alkanes, cyclic alkanes including steranes, hopanes and tricyclic alkanes, alkenes (hydrocarbons with double bonds), and aromatic hydrocarbons. *n*-Alkanes were among the first compound classes used to identify sources of organic matter in sediments, given that the *n*-alkanes of vascular plant waxes show a strong predominance of odd-chain carbon numbers, typically in the range C_{25}–C_{35} (Naeher et al. 2022 this issue). In contrast, microalgae rarely contain high abundances of *n*-alkanes, and these tend be dominated by odd-number, short-chains such as *n*-C_{17}. Thus, algal contributions to sedimentary organic matter can be severely underestimated if studies are restricted only to *n*-alkanes. A few microalgal species make distinctive hydrocarbons, such as the unique highly branched isoprenoid alkenes found in certain diatoms. The structures of some such compounds are shown in FIGURE 1. This class of biomarker has a geological record extending back about 100 million years and thus provides an unambiguous record identifying when this biosynthetic pathway first emerged. Studies determining when specific biomarkers first entered the geological record (e.g., Briggs and Summons 2014) will remain a very fertile area for research.

Alkenones as Paleotemperature and Paleo pCO₂ Proxies

Alkenones remain one of the most widely studied groups of biomarkers, following the development of the alkenone-based " $U^{K'}_{37}$ " paleotemperature proxy. The study of alkenones provides a classic illustration of how many organic geochemical studies have developed.

Alkenones are unusual long-chain C_{37}–C_{41} methyl and ethyl ketones with 2, 3, or 4 double bonds with *trans* geometry rather than the *cis* form found in most biologically formed alkyl lipids. Alkenones were first identified in the haptophyte microalga *Emiliania huxleyi* (Volkman et al. 1980), but only after analytical methods had been improved (GC temperatures were too low to elute them from the glass capillary GC columns used at the time). Subsequent research at Bristol University (UK) led to the development of the first paleotemperature biomarker proxy based on a relatively complex statement of proportions of alkenones that was later refined to the simpler expression $U^{K'}_{37}$, which is in common use today:

$$U^{K'}_{37} = ([C_{37:2}]/([C_{37:2}] + [C_{37:3}])$$

More than 40 years after their first identification, new alkenones are still being identified, and environmental factors other than temperature have been shown to have some (usually small) effect on the proportions of alkenones in environmental samples. Alkenones have also found application as proxies for atmospheric pCO_2, with results that are generally similar to those derived from phytol-based proxies (e.g., Witkowski et al. 2020), although more work is needed to elucidate the effects of growth rate and other environmental factors.

With any biomarker proxy for environmental conditions, it is important to distinguish between biochemical changes that occur within the cell of a single species in response to those changes versus changes in the proportions of several species with different lipid compositions (which in itself may be an indirect measure of a changing environment). For example, we now recognize that different haptophyte groups have distinctive alkenone (and related alkenoate and alkene) compositions, and a careful examination of the alkenone distribution in the environment can reveal which group is present and hence whether a particular paleotemperature calibration is appropriate for that depositional setting. For example, Wang et al. (2021) identified a clade of Isochrysidales whose abundance in marine environments is significantly correlated with the presence of annual sea ice. This powerful study used both next-generation gene sequencing, laboratory culture experiments, and field measurements, thus providing a good model for future studies.

Alkyl Diols for Paleotemperature and Salinity

The C_{28}–C_{32} 1,15-alkyl diols were first identified as lipids of unknown origin in Black Sea sediments. Many years later they were identified in cultures of microalgae from the class Eustigmatophyceae. These lipids have been found in both freshwater and marine eustigmatophytes, but the proportions of individual alkyl diols differed among these species, as did the proportions of sterols. As an added complexity, certain diatoms were found to contain 1,14-diols (as opposed to the 1,15 compounds in eustigmatophytes), showing how small differences in biochemistry can lead to biomarkers that differ subtly in their chemical structures. A number of temperature proxies have been developed based on the abundances of specific diol isomers (e.g., Rampen et al. 2012; de Bar et al. 2020); moreover, hydrogen isotope contents of diols have been used as proxies for salinity (Lattaud et al. 2019).

GDGTs as Paleotemperature Proxies

Isoprenoid glycerol dialkyl glycerol tetraethers are membrane-spanning tetraether lipids found in some archaea. Together with the branched GDGTs of presumed bacterial origin, they form the basis for a range of new proxies for estimating paleotemperature, but are not readily measured by GC–MS techniques. Thus, a method combining normal-phase HPLC with positive ion atmospheric pressure chemical ionization mass spectrometry (APCI–MS) had to be developed (Hopmans et al. 2000). As with the alkenones, improved methods led to better isomer separation and the recognition that some chromatographic peaks contain co-eluting compounds, necessitating a revision to the proxy equations. Such changes are to be expected, but when a proxy definition is changed, it is vital that the associated nomenclature reflects this modification (e.g., with the use of a prime symbol) to allow proper comparisons between datasets. Further work is needed to define the specific bacterial sources of branched GDGTs and to identify how a wider range of environmental conditions could affect their distributions. Related ether lipids (e.g., H-shaped GDGTs) also continue to be found, which may lead to the development of new proxies.

APPLICATIONS OF BIOMARKER PROXIES TO GEOLOGICAL ENVIRONMENTS

Ancient Microbial Life

Illuminating the nature of ancient microbial ecosystems from the sedimentary record has been a fascinating area of research (e.g., Summons et al. 2021) and will continue to be the focus of many organic geochemical studies (see Hallman et al. 2022 this issue). This area is not without controversy, because the attribution of particular molecular structures in a rock hundreds of millions of years old to organisms living at that time is often uncertain. However, the presence of biomarkers provides clear evidence for life and can help to identify which life forms were present.

Mass Extinctions

Organic geochemical studies continue to throw new light on the factors causing the five major mass extinctions in the Phanerozoic eon (e.g., Whiteside and Grice 2016). For example, the end-Triassic mass extinction that occurred ~202 Ma is associated with a carbon isotope excursion that has long been interpreted as the result of a global-scale disruption of the carbon cycle, driving massive inputs of exogenous low-^{13}C carbon into the ocean–atmosphere system. Challenging this view, Fox et al. (2020) used the distributions of biomarkers (including steranes, gammacerane, and isorenieratane) and their compound-specific ^{13}C isotope signatures to show that the isotope excursion more likely reflects regional sea-level change that caused a transition from a marine ecosystem to a shallow, less saline environment dominated by microbial mats. The mass extinction occurred slightly later and was caused by the abrupt injection of volcanogenic CO_2, accompanied by only small changes in organic carbon isotope composition.

Petroleum Geochemistry

Oils, condensates, and gases contain complex mixtures of organic compounds and thus are a major focus for many organic geochemists. The thermal maturity of petroleum source rocks can be inferred indirectly from the physical properties of petroleum, such as density (commonly measured using the "American Petroleum Institute (API) gravity" index) and from relative abundances of selected saturated and aromatic hydrocarbons. A large number of maturity proxies and source rock "fingerprinting" techniques based on the relative abundances of specific biomarkers have been developed and used for decades to ascertain whether a particular oil is derived from a specific source rock or whether oils have the same source. A good overview of these methods is provided by Peters et al. (2004), but an updated review would be useful. By judicious use of these proxies, one can determine the likely type of source rock (lacustrine/marine; carbonate/shale etc.), depositional conditions (oxic/anoxic), and the thermal range (immature to post-mature) at which the constituents of petroleum were generated. This approach is now being extended to examine more polar heteroatomic compounds that have become amenable to study using advanced GC–MS techniques, as discussed later.

Some of the proxies in current use were developed for particular oil fields and do not necessarily translate well to different fields or to production of unconventional petroleum resources. Interpretations from proxies based on a good understanding of the underlying principles that govern their abundance (e.g., isoprenoids such as pristane and phytane, steranes derived from the sterols of eukaryotes, and hopanes from hopanoids in bacteria) are more robust. However, the origins of some compounds, such as tricyclic alkanes termed cheilanthanes, are still unknown and thus proxies based on them are on a less secure footing (such compounds are referred to as "orphan lipids"). There is a clear need here for further studies of the lipids of potential source organisms.

It has become apparent that many petroleum reservoirs contain mixed "charges" (inputs) of oil and gas generated at different times, with differing thermal maturity, and even from different source rocks. Deconvolution can be particularly challenging if one charge was generated at high thermal maturity, in which case absolute biomarker contents will be low and the biomarker profile of the petroleum will be dominated by a less mature charge even when it is much less abundant. Future work will need to consider not just the abundance ratios of specific biomarkers, but also their absolute concentrations in the compositional end members that contribute to mixed reservoirs.

A further complication is when one oil phase is heavily biodegraded, causing losses of more susceptible biomarkers, which most often occurs during the early phase of reservoir filling when located relatively close to the surface. Biomarkers degrade at different rates, and thus the extent of biodegradation can be inferred by comparing abundances of more- versus less-susceptible hydrocarbons (e.g., *n*-alkanes and isoprenoids versus polycyclic biomarkers such as hopanes and steranes). Measures of biodegradation are available for both saturated and aromatic hydrocarbons (e.g., Volkman et al. 1984; Peters et al. 2004) and can indicate when a particular biomarker ratio that one might use to indicate source rock type or thermal maturity has been affected by biodegradation. Mismatches of inferred extent of biodegradation, detected when analyzing ratios of compounds of different structural types, provide good evidence that the petroleum reservoir has experienced multiple accumulations of oil.

Work is still needed to refine biodegradation scales and to identify highly resistant and thermally stable compounds such as the tricyclic and pentacyclic diamondoid caged hydrocarbons (adamantanes). Advanced GC–MS methodologies will no doubt extend the range of biomarkers available for geological correlations. Additional information regarding the charging of reservoirs with oil can be obtained by studying compounds occluded in asphaltenes (Snowdon et al. 2016). These complex macromolecular structures can protect compounds from degradation and thus provide a record of the earliest oil charges.

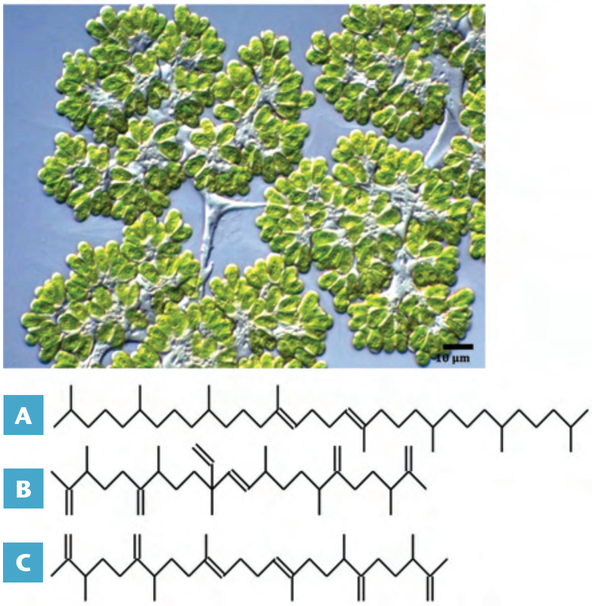

Figure 2 A colony of the hydrocarbon-rich green alga *Botryococcus braunii,* shown to be the main source of organic matter in shales such as organic-rich coorongite and torbanite. The scale bar is 10 µm. The mucilage surrounding the cells limits CO_2 transfer and so the lipids are often ^{13}C-enriched compared to other algae. *Botryococcus* strains have distinctive hydrocarbon distributions, with some containing specific hydrocarbons: (**A**) lycopadiene; (**B**) C_{34} botryococcenes; and (**C**) tetramethylsqualene. On diagenesis, these can be converted to the saturated hydrocarbons, lycopane, botryococcane, and tetramethylsqualane found in some organic-rich ancient shales and crude oils.

STABLE ISOTOPES IN ORGANIC GEOCHEMISTRY

Organic geochemists have been foremost practitioners in the use of stable carbon, hydrogen, and nitrogen isotopes of bulk organic matter and specific organic compounds to understand biogeochemical processes. Indeed, some developments such as compound-specific isotope mass spectrometry were pioneered by organic geochemists including the late Prof. John Hayes and his teams. There are at least three areas where the field will progress in the next few years: advances in compound-specific analysis (including ^{13}C, ^{14}C, ^{2}H, ^{15}N); extension to other elements such as S and O; and clumped and position-specific isotopologue research.

The ability to determine the ^{13}C or ^{2}H composition of a specific compound separated by gas chromatography has revolutionized the field. The isotope signature of bulk organic matter is simply the weighted mean of all its constituents, and we now recognize that individual compounds can have very different isotope signatures depending on how they are biosynthesized, the origin of the carbon (or hydrogen) in their structures, and the environment where the organism is found. Thus, extremely ^{13}C-depleted lipids ($d^{13}C_{VPDB}$ values of −40‰ to −80‰) are typically associated with methane-oxidizing bacteria (methanotrophs), whereas very enriched values (−8‰ to −15‰) are associated with algae growing where the CO_2 supply is restricted (such as *Tasmanites* or diatoms in sea-ice) or to organisms that can use HCO_3^- as a carbon source (such as *Botryococcus*; Fig. 2). Carbon isotope differences can be used to differentiate between lipids derived from plants that use C_3, C_4, or CAM (crassulacean acid metabolism) biosynthetic pathways. Future work will no doubt continue to refine and add to these applications.

In recent years, there have been many more studies of hydrogen isotopes in algal and plant biomarkers as a proxy for water availability and salinity, allowing one to infer the paleoenvironment at the time of deposition. The study by Weiss et al. (2020) provides a good example of how the δ^2H values in sedimentary alkenones reflect changes in salinity in the Baltic over the past 11,000 years.

Traditional stable isotope measurements typically determine the average abundance of isotopes across all molecules of the same structure by pyrolyzing them to H_2 for hydrogen isotope measurements or combusting them to CO_2 for carbon isotope measurements. The key to distinguishing between the many isotopic homologs ("isotopologues") that contribute to each compound's molecule-average isotopic composition is to measure the intact molecule using high-resolution mass spectrometry. This is analytically challenging work and has required the development of specialized techniques and mass spectrometers (Fig. 3). The ability to distinguish between $^{13}CH_3{}^2H$ and $^{12}CH_2{}^2H_2$ in clumped isotope analysis of methane can help to decipher its source (microbial vs. petrogenic) or thermal history (geothermometry). Great progress is also being made in position-specific isotopologue analysis and its scope is expanding dramatically (Gilbert 2021). Practically any molecule that can be vaporized at modest temperature is now amenable to study. Orbitrap methods are now also being used on non-volatile, polar compounds. The work is not just restricted to carbon, but can be extended to study substitutions in the isotopes of H, O, N, and S. Of particular interest is that both equilibrium and kinetic processes are involved in determining the isotope distributions, which opens up a wide range of applications from modern biochemistry to atmospheric and marine chemistry to deep, hot geochemistry.

COMING ADVANCES IN TECHNOLOGY AND METHODS

Organic geochemists have been quick to exploit technological advances that enable the detection of trace amounts of organic compounds in geological samples. This is hardly surprising, because the mixtures that organic geochemists deal with are typically highly complex. The development of more thermostable capillary phases has now made it possible to identify hydrocarbons up to C_{80} in oils and complex triacylglycerols in seawater. Two-dimensional gas chromatography (GC × GC), in which two capillary columns of different polarity are coupled, provides even more resolving power (Fig. 4). An even broader range of compounds can be studied using HPLC interfaced with different MS systems. New MS–MS techniques (where specific ions are isolated, subject to collisional fragmentation, and then analyzed) also have been valuable to deconvolute complex biomarker distributions, such as steranes and hopanes in oils. Fourier transform ion cyclotron resonance mass spectrometry (FT-ICR MS), with its unsurpassed mass resolving power and mass measurement accuracy, is considered nearly indispensable when nitrogen-, oxygen-, or sulfur-containing biomarker compounds are examined. Any new developments in these analytical techniques, such as FT-MS for isotopologue measurements, will be quickly exploited.

Another area showing great promise is the field of lipidomics, which is already important in the biosciences (e.g., Bale et al. 2021). Lipidomics is defined as "the large-scale study of structure, function, pathways and networks of the complete set of lipids (the lipidome) in a biological system (i.e., a cell or organism), as well as their interactions with other cellular components" (Law and Zhang 2019). By combining advances in HPLC techniques for lipid separation with advances in mass spectrometry for compound

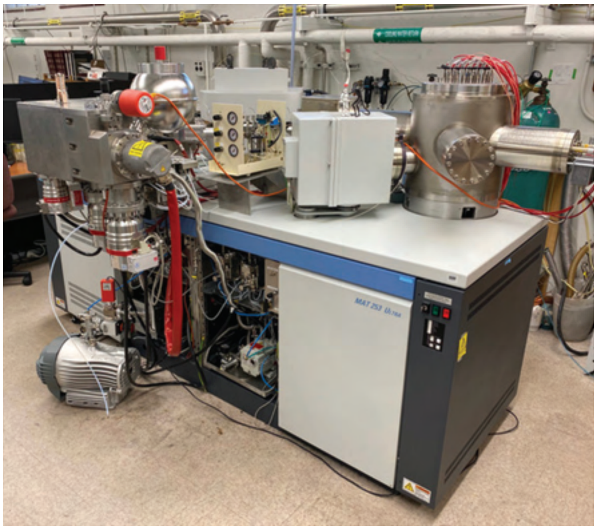

Figure 3 Continued use of advanced analytical equipment has been a key factor in the development of organic geochemistry. Shown here is the prototype MAT 253 Ultra mass spectrometer used for clumped isotopologue measurements in Dr. John Eiler's laboratory. Photo courtesy of Dr. Alex Sessions of Caltech, USA.

identification it is now possible to identify and quantify hundreds of lipids in a sample with improved sensitivity and isomer differentiation.

Pyrolysis systems, both open (i.e., continuously purged of product gases) and closed (where product gases accumulate), have been widely used by organic geochemists to study the structures of macromolecular organic matter and kerogens by breaking them into smaller, more easily identified components. While such systems cannot completely reproduce the thermal breakdown and maturation of sedimentary organic matter over geological time (in pyrolysis experiments, temperatures higher than natural maturation substitute for longer natural times), literally thousands of papers describe their use. These techniques continue to evolve with instrumentation now available to carry out pyrolysis in a stepwise fashion and thereby liberate compounds that are linked to macromolecular organic matter by bonds of different strengths (e.g., C–C, C–S, C–O, C–N), thus generating a more detailed picture of the structure of the latter. A recent example shows how ether-bonded carbon chains are a major structural feature of the polymeric algaenan of the eustigmatophyte *Nannochloropsis*, providing further evidence of the importance of algaenans as sources of preserved organic matter in some ancient sediments (e.g., Zhang and Volkman 2017).

Advances in "Big Data" and Statistical Approaches

In early studies of organic geochemistry, the number of samples analyzed was very small and statistical analysis of the data was often lacking. However, the increasing use of GC × GC–MS techniques (Fig. 4), automated extraction systems allowing analysis of large number of samples, and techniques such as MS-imaging of sediments all produce large datasets. Application of advanced data-handling techniques, such as principal component analysis, hierarchical cluster analysis, chemometrics, machine learning, and bioinformatics, are providing new geochemical insights beyond those that can be obtained using simple abundance ratios of compounds. Nonetheless, the organic geochemist must still determine which of these relationships or groupings might be of most use to answer specific geochemical questions.

The Need for Laboratory and Field Simulation Studies and Modeling

Much organic geochemical research has relied on empirical observations of organic constituents in sediments and oils, but a good understanding of how organic matter is transformed in the water column and sediment is required to understand such data. Carefully controlled simulation experiments in the laboratory and natural environments are still needed to elucidate biogeochemical pathways and measure the rates at which reactions occur. It is also vital that the data are incorporated into mathematical models that explore the physics and biogeochemistry of how ecosystems respond to environmental changes.

With living organisms, it is important to ensure that the duration of the experimental manipulation is appropriate for the effect being studied. Microalgae and bacteria can double cell numbers in less than a day, but for macroalgae and plants, where cell turnover times are much slower, it may take several weeks to months to see a measurable effect on biochemical compositions. The responses of different lipids can also vary widely. Fatty acids, for example, can be rapidly recycled within the cell within hours but membrane lipids such as sterols are turned over much more slowly over weeks to months.

Improved Sampling to Study Small-Scale Perturbations

A constraint on many organic geochemical studies is that even samples taken every cm in a sediment core can often integrate accumulations over many years. Much of the fine details of how populations of organisms or lipid distributions vary with depth can be missed. Mass spectrometry imaging provides an answer by collecting mass spectra of organic compounds from individual micrometer-sized spots. These can be converted to high-resolution images of how biomarkers are distributed on sample surfaces, thus opening up the way to ultra-high-resolution molecular stratigraphy and the calculation of biomarker proxies at an unprecedented spatial resolution (Wörmer et al. 2019; McKenna et al. 2022 this issue).

The analysis of fluid inclusions provides another example where a focus on small parts of the rock matrix, rather than the bulk, can provide valuable insights on multiple episodes of paleo-hydrocarbon migration (Volk and George 2019). Fluid inclusions are typically micrometer-sized and occur within quartz grains. They contain paleo-fluids that

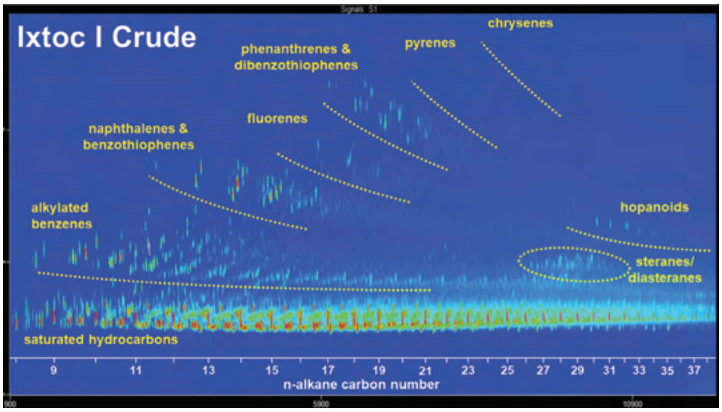

Figure 4 The study of complex mixtures of organic compounds requires advanced analytical techniques for compound separation and identification. Shown here is the separation of the complex mixture of hydrocarbons in the IXTOC-1 oil by two-dimensional gas chromatography (GC × GC). Picture courtesy of Robert Nelson and Chris Reddy of the Woods Hole Oceanographic Institution GC × GC facility, USA.

can include brine, black oil, light oil, gas condensate, as well as N_2- and CO_2-rich hydrocarbon gas. They are usually analyzed by conventional GC–MS after crushing of the sample. Analysis of hydrocarbons in fluid inclusions within reservoir rocks can often provide details of the early oil charges, even though the bulk oil may be heavily biodegraded or mixed with later charges of oil.

Interactions with Molecular Biology

The combination of genomic approaches (e.g., metatranscriptomics) with biomarker research (e.g., Becker et al. 2021) is perhaps one of the more exciting areas of interdisciplinary research applied to geochemical questions. DNA data can provide information about what organisms are present in an environment and how they have changed over time. Such data can reveal whether or not an organism thought to be the source of a particular biomarker is actually present in the environment (Villanueva and Coolen 2022 this issue). DNA breaks down rapidly in sediments, but under favorable conditions (e.g., anoxia) DNA can survive for hundreds of thousands of years (Kirkpatrick et al. 2016). This longevity is a boon for organic geochemical studies, but it must be recognized that DNA and specific lipid biomarkers can show very different degrees of diagenesis and preservation in sediments, thus any comparisons must take these factors into account.

Another important advance is the search for specific biosynthesis genes to identify whether particular organisms have the capacity to synthesize a specific biomarker. This important work will provide new data on the source-specificity of particular biomarkers and may also help identify the organisms responsible for “orphan lipids” for which sources have not yet been identified.

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Association of Applied Geochemists

DR. DAVID COOKE – AAG CAMERON-HALL COPPER MEDAL AWARD FOR 2020

The Association of Applied Geochemists is pleased to announce that the Cameron-Hall Copper Medal for 2020 is awarded to Dr. David Cooke, Director of the Centre for Ore Deposit and Earth Sciences (CODES), University of Tasmania, for his paper that appeared in GEEA volume 20 (p. 176-188):

"Recent advances in the application of mineral chemistry to exploration for porphyry copper–gold–molybdenum deposits: detecting the geochemical fingerprints and footprints of hypogene mineralization and alteration"

By David R. Cooke, Paul Agnew, Pete Hollings, Michael Baker, Zhaoshan Chang, Jamie J. Wilkinson, Ayesha Ahmed, Noel C. White, Lejun Zhang, Jennifer Thompson, J. Bruce Gemmell, Leonid Danyushevsky, and Huayong Chen.

David Cooke completed his PhD at Monash University in Melbourne, Australia in 1991. He joined the faculty of the University of Tasmania and since 1998 has led numerous team-based industry-funded research projects. He has been CODES Director since 2017.

The Cameron-Hall Copper Medal is the newest medal of the AAG, first awarded last year for the year 2019. The Association annually awards the medal to the lead author of the most outstanding scientific publication in our journal Geochemistry: Exploration, Environment, Analysis (GEEA). It is named in honour of two prominent and highly published AAG members and past editors of GEEA, Eion Cameron and Gwendy Hall. Both are the only AAG Gold and Silver Medal awardees since the Association was formed over 50 years ago. Selection of the winning paper is highly competitive. The GEEA Editorial Board first recommends four nominees from those papers published during the year. The members of the AAG Awards & Medals Committee vote on the list of recommendations, and their selection must then be approved by a majority vote of the AAG Council. More information is available on the AAG website https://www.appliedgeochemists.org/association/awards.

Formal presentation of the Cameron-Hall Copper Medal to Dr. Cooke will take place at the 29th International Applied Geochemistry Symposium (IAGS) in Chile in October 2022.

Stephen Cook
AAG Past President
Chair, Awards & Medals Committee

RECENT ARTICLES PUBLISHED IN *EXPLORE*

The following abstract is for an article that appeared in issue 190 (March 2021) of the *Explore* newsletter.

"Minor Elements – the Middle Child between Petrochemistry and Geochemistry"

Robert G. Garrett[1]

Some 30 years ago I wrote an article for *Explore* titled 'A Cry from the Heart', then four years later, 'Another Cry from the Heart', both concerned the application of statistical procedures to geochemical data. I cannot write 'Another another …', but that is what this is, and this time the cry concerns the data and how they are reported. It has been demonstrated that the reporting of minor element data in whole rock, 'Total', analyses is inadequate for geochemical studies. The frustration that this unnecessary inadequacy is the reason for this 'Cry', the 'Another another …'. The minor elements are the awkward 'middle child' between the major and trace elements. Their reporting is torn between the needs of petrochemists and geochemists. This is unnecessary. There is no reason multiple reporting styles cannot be supported, and data not castrated by reporting with insufficient non-zero significant figures. It is the hope of the author that this article will initiate a conversation between the scientists who use the data and the laboratories who provide them, so that no information is wasted.

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The following abstract is for an article that appeared in issue 191 (June 2021) of the *Explore* newsletter.

"Integration of Geochemical and Mineralogical Data: An Example from the Central Victorian Goldfields, Australia"

Dennis Arne[2]

Recent advances in Compositional Data Analysis (CODA) have provided a solution to the Harker diagram problem, where due to the fact that the data sum to a constant, e.g., 100%, the displays make no sense in terms of petrological and mineral stoichiometry knowledge. The article employs the Nockolds data set for major element average compositions of igneous plutonic rocks as the basis for a brief tutorial focusing on the Si-Al, Ca-Na and K-Ti relationships in the data. The transformation of the data pairs into symmetric coordinates permits displays of the element relationships free of the constraints of closure. As a result, Si and Al are seen to increase sympathetically from femic to felsic rocks; Na to decrease with increasing Ca from felsic to femic rocks and in the albite-oligoclase solid solution; and the inverse relationship between K and Ti to become much clearer due to the reduction of the impact of the remaining parts of the composition. The procedure also permits the estimation of correlation coefficients free from the effects of closure. R scripts are provided for the necessary computations and displays, together with the Nockolds data and examples of the use of the R functions.

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ACADEMIA–INDUSTRY TRANSITIONS: Q & A WITH GEOCHEMISTS WHO MADE THE MOVE!

Many geochemists have transitioned from academic to non-academic jobs, or vice-versa, during their careers, and sometimes back again or more than once. The EAG Communications Committee recently interviewed geochemists who made the move, to find out how they made the transition and to ask their advice for other scientists in the community who may be considering a similar change. Read their responses below and visit the EAG Blogosphere at https://blog.eag.eu.com/ to find out more and to hear from geochemists working in other industries.

Ye Zhao – Senior Product Specialist & Business Development Manager, Nu Instruments, Ametek Inc.

What is your job?

I work for Nu Instruments, AMETEK Inc., a multinational corporation manufacturing high-precision analytical instrumentation, serving the Earth, environmental, nuclear, and life sciences sectors. As a Senior Product Specialist & Asia Pacific Business Development Manager, I'm responsible for the product management, new business development, and collaborations with academia.

How did you get your job?

While doing my first post-doc, I was considering a career change to the instrumentation industry. After uploading my CV to recruitment websites, an opportunity arose as I was approached by a headhunter for an Application Scientist position at Nu Instruments. I went to North Wales for an interview and got the job. And here I am, still working for Nu 9 years later.

Did you initially plan on this career at the onset of your PhD?

It wasn't something I had planned for at the beginning. I started my PhD in hopes of becoming an academic. But as much as I enjoyed my own research topic and the guidance from my then supervisor, with time, I gradually woke up to the idea that I preferred width over depth in knowledge, which makes a career outside of academia, at the interface between science and business, something involving multi-disciplines, more appealing.

What advice do you have for PhD students who are thinking of leaving academia?

Do your research and make a list of bullet points of the pros and cons of leaving academia to help determine what's best for you. Do you know the outside world well enough to be sure this is the right step? Don't leave academia just because it asks for commitments—academia or industry, hard work will always be a key to success. You may no longer be under pressure of publishing in industry, but you will need to learn to adapt to a fast-paced work environment, be target-driven, be able to work with different people, and deliver strong results. It's a change of life style. Make sure you know what you are about to dive into. And if you still believe this is the right path for you, then create a LinkedIn account and connect to alumni in your dream industry, try and gather as much background information as you can. Go to career services at the university, as they can be quite helpful. Go to conferences in your field and talk to the exhibitors, most of them will be happy to give advice. It's a big step, so be prepared. Above all, finish your PhD, if possible. You made a commitment; complete it before moving on—it will serve you well in the long run.

Hauke Vollstaedt – Product Manager, Thermo Fisher Scientific (Bremen) GmbH

What is your job?

I am a Product Manager at Thermo Fisher Scientific and cover the Triton Thermal Ionization Mass Spectrometer (TIMS), Element High Resolution ICP-MS, and Element Glow Discharge MS. My primary responsibility is to drive, strategize, and communicate the vision for these products. This includes management of the planning, forecasting, production, launching, and marketing of products at all stages of the product life cycle.

I started at Thermo Fisher Scientific as a Product Specialist, being responsible for demonstrating our instruments to prospective customers, producing application data reports and marketing materials, presenting data at scientific conferences, and forming collaborations with customers.

How did you get your job?

A sales representative from the company pointed me towards an open position at the factory in Bremen, Germany. I simply applied for the position.

Did you initially plan on this career at the onset of your PhD?

Not at all. My initial plan was to go for a career in academia. Although I enjoyed working in academia a lot, pursuing a scientific career requires a lot of flexibility in terms of residence and uncertainty in the early stages due to short-term temporary contracts. Additionally, I was stressed by feeling required to publish and apply for funding while researching and teaching at the same time. Therefore, I made the personal decision to apply for a position in industry. In industry, I can combine career and family much better.

What advice do you have for PhD students who are thinking of leaving academia?

Try to be open to explore new things beyond what you are doing currently. The change from academia to industry helped me a lot to find out what I like and dislike in each of my positions.

While academia offers work in interesting and challenging scientific projects, as well a high degree of freedom regarding the how and on what you are working, industry can offer as ambitious jobs, team spirit, and job security due to permanent positions.

Starting a job in industry is not a definitive step to turn your back on academia, but enables you to gain competencies that are useful in both fields.

Dr. Kim Nicole Dalby – Principal Scientist, Topsoe A/S

What is your job?

My job title changed from Associate Professor to Principal Scientist four years ago, but my job remains largely the same—I use scanning electron microscopy to probe the chemical and physical properties of solids to help understand reaction pathways. Now I am part of a team, with several microscopes, who support the R&D side of the company. I also have collaborations with universities and am still able to publish science (not that I think publications should be used as a metric for a successful academic career, but that is a whole other conversation...).

How did you get your job?

This is a fun little story. I used to say I was "lucky" but after confronting my imposter syndrome, I realise that it all happened because I was qualified. I had been in academia my entire career (since 2002), and I became interested in industry later on (ca. 2010), specifically how industry and academia communicated. So when a one-year maternity-leave position in microscopy came up at a private company, I asked if I could take a sabbatical and applied and landed the position. During my sabbatical, my entire research section was fired from the university. With a couple of months to go on my one-year contract, the company offered me a full-time position. I accepted and have never looked back.

Did you initially plan on this career at the onset of your PhD?

Absolutely not. I wanted to be that old, grey-haired professor in a giant wing-back chair with leather elbow patches and a pipe. I now have the pipe, and the knowledge that you can also have a very rewarding scientific career in a private company.

What advice do you have for PhD students who are thinking of leaving academia?

It is a myth that leaving university is a one-way street. The door between industry and academia swings both ways and is more open (in my opinion) than ever before. But the transition can be messy, and I would lie if I said I didn't have days in the beginning where I felt like a failure because I didn't make it to full professor. But my cheer squad and my experience have shown that academia is like any other job and (if you are privileged enough) you should leave if it is not treating you well.

Geochemical Society

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2022 GS AWARDS

V.M. Goldschmidt Award

Marilyn L. Fogel, Professor Emerita at the University of California, Riverside (USA), received the 2022 Victor M. Goldschmidt Award. The Goldschmidt Award is the society's highest honor, presented annually for major achievements in geochemistry over a career. Dr. Fogel revolutionized the use of stable isotopes in ecology, geochemistry, and cosmochemistry. Her research ranged from stable isotope fractionation in photosynthesis, to tracking the anthropogenic impact of the colonization of Australia, to the understanding of cosmochemical processes in meteorites.

Victor Moritz Goldschmidt (1888–1947) was a chemist considered to be the founder of modern geochemistry and crystal chemistry. He developed the Goldschmidt Classification of elements and worked for many years at the University of Oslo (Norway). The society has presented a medal in his honor since 1972.

C.C. Patterson Medal

Xiangdong Li received the 2022 Clair C. Patterson Award, which recognizes an innovative breakthrough of fundamental significance in environmental geochemistry, particularly in service of society, consisting of either a single outstanding contribution or a short series of papers published within the last decade. Professor Li holds the positions of Dean of Faculty of Construction and Environment, Director of Research Institute for Sustainable Urban Development, Chair Professor of Environmental Science and Technology, and Ko Jan Ming Professor in Sustainable Urban Development at The Hong Kong Polytechnic University. He is recognized for his innovative and dynamic work in environmental biogeochemistry, including research in the fields of regional contamination, urban air PM2.5 pollution, and the origin and dissemination of antimicrobial resistance.

Clair C. Patterson (1922–1995) developed the uranium-lead dating method. Using lead and uranium isotopic data from the Canyon Diablo meteorite, he calculated an age for the Earth of 4.55 billion years. This figure was far more accurate than those that existed at the time and has remained unchanged for over 50 years. Patterson also made enormous contributions to the understanding of lead's role as an environmental contaminant and subsequent elimination from many products.

F.W. Clarke Medal

Yige Zhang, assistant professor at Texas A&M University (USA), received the 2022 F.W. Clarke Award this July. The Clarke Award recognizes an early-career scientist for a single outstanding contribution to geochemistry or cosmochemistry published either as a single paper or a series of papers on a single topic. Dr. Zhang is recognized for his contributions to the application and refinement of lipid biomarker proxies for paleotemperature and atmospheric CO_2 reconstructions, including development of the "Methane Index" and "Ring Index".

Frank Wigglesworth Clarke (1847–1931) was a chemist who determined the composition of the Earth's crust. He taught chemistry and physics at the University of Cincinnati (USA) and served in the U.S. Geological Survey for many years. He also collaborated with the Smithsonian Institution on atomic weight research. The society established the award in his name in 1972.

2022 GEOCHEMISTRY FELLOWS

In July, the Geochemical Society and European Association of Geochemistry welcomed a new group of Geochemistry Fellows. These scientists are recognized for a broad spectrum of achievements that advance geochemistry.

Marly Babinski
Universidade de São Paulo (Brazil)

Christopher J. Ballentine
University of Oxford (UK)

Simon Brassell
Indiana University (USA)

Ken Buesseler
Woods Hole Oceanographic Institution (USA)

Marie Edmonds
University of Cambridge (UK)

Stephen Foley
Macquarie University (Australia)

Gideon Henderson
University of Oxford (UK)

Jörg Hermann
University of Bern (Switzerland)

Noriko Kita
University of Wisconsin-Madison (USA)

Xiang-dong Li
Hong Kong Polytechnic University

Harue Masuda
Osaka City University (Japan)

Tamsin Mather
University of Oxford (UK)

Ann Pearson
Harvard University (USA)

Laurie Reisberg
University of Lorraine CRPG Nancy (France)

Lenny Winkel
ETH Zurich (Switzerland)

Yi-Gang Xu
Guangzhou Institute of Geochemistry (China)

Japan Association of Mineralogical Sciences

http://jams.la.coocan.jp/e_index.html

(FE, AL)-BEARING BRIDGMANITE IN A SUBDUCTING MID-OCEAN RIDGE BASALT

Akihiko Nakatsuka[1]

Studies on crystal chemistry of minerals have provided a lot of substantial knowledge of transformations, phase relations, physical properties, and dynamics in the Earth's interior. In particular, precise atomic-level knowledge of bridgmanite (simplified formula $MgSiO_3$), occupying about 80 volume percent of the Earth's lower mantle, is indispensable for a detailed understanding of the deep mantle. Because Fe and Al are important major elements in the mantle composition after Mg and Si, their incorporation effects into the bridgmanite structure (Fig. 1A) have attracted much attention because of their great influence on the lower-mantle dynamics. Bridgmanite formed from a mid-ocean ridge basalt (MORB) component of subducting slabs contains much larger amounts of Fe and Al than that formed from a pyrolytic composition (Hirose and Fei 2002). Different bridgmanite compositions can produce different incorporation mechanisms of both cations into the crystal structure between subducting slabs and the surrounding lower-mantle. This should cause heterogeneity in the physical properties and rheology of the lower mantle. Elucidating the crystal chemistry of bridgmanite that forms from the MORB composition is thus a key to solve this issue. We focused on the incorporation effects of Fe and Al into bridgmanite and investigated the crystal chemistry of its single-crystal form with both cation contents expected in MORB using a combination of X-ray diffraction structure analysis, synchrotron ^{57}Fe-Mössbauer spectroscopy, and electron probe microanalysis (Nakatsuka et al. 2021). In particular, ^{57}Fe-Mössbauer spectroscopy is a powerful probe to distinguish the valence- and spin-states of Fe, which cannot directly be observed by X-ray diffraction.

Bridgmanite single- crystals were synthesized in a bulk composition with the Fe- and Al-contents expected for bridgmanite formed from the MORB composition at 28 GPa and 1873 K, using a Kawai-type multianvil apparatus. The zero-pressure/room-temperature crystal structure was determined and refined on the basis of single-crystal X-ray diffraction intensities collected using a four-circle diffractometer with a laboratory MoKα-radiation source. Energy-domain synchrotron ^{57}Fe-Mössbauer spectroscopy at room temperature using a nuclear Bragg monochromator was conducted at the BL10XU beamline of SPring-8 (Japan).

The electron probe microanalyses of the synthesized crystals gave a chemical composition of $Mg_{0.642(7)}Fe_{0.341(6)}Si_{0.656(10)}Al_{0.356(4)}O_3$, agreeing excellently with $Mg_{0.662(3)}Fe_{0.338(3)}Si_{0.662(3)}Al_{0.338(3)}O_3$ from the structure refinement. The measured Mössbauer spectrum (Fig. 1B) gave an isomer shift of 0.40(3) mm/s and a quadrupole splitting of 0.86(4) mm/s, indicating that Fe ions exclusively occupy the eightfold (nominally 12-fold) coordinated A-site in trivalent high-spin (HS) state. In consideration of the cation ratio from the electron probe microanalyses, this shows that Al^{3+} ions exclusively occupy the sixfold coordinated B-site and there are no vacancies. These cation distributions were also confirmed from the structure refinement. We thus conclude that the charge-coupled substitution $^{A}Mg^{2+} + {}^{B}Si^{4+} \leftrightarrow {}^{A}Fe^{3+}(HS) + {}^{B}Al^{3+}$ is predominant in the incorporation of Fe and Al into our bridgmanite, where the superscripts "A" and "B" represent the occupied sites.

Some studies (Meade et al. 1995; Shim et al. 2001) suggested that bridgmanite could transform to another perovskite phase with a different symmetry before the phase transition to the post-perovskite phase, associated with the D″ seismic discontinuity. In terms of the compressibility ratio β_B/β_A (Angel et al. 2005), we conclude that this possibility cannot be ruled out and suggest that the phase transition to another perovskite phase, if present, might be found in slabs that have fallen/subducted into the lowermost mantle, where β_A and β_B are the compressibility of AO_{12} (practically AO_8) and BO_6 polyhedra, respectively. We also revealed that β_B/β_A increases depending only on the rigidity of the BO_6 octahedron by the incorporation of Fe^{3+} and Al via the charge-coupled substitution. Because such an increase in β_B/β_A can correspond to a reduction of the bulk modulus, the bulk sound velocity would decrease with increasing contents of both cations. This crystallographic approach can be effective for gaining important insights into the seismic properties within the lower mantle.

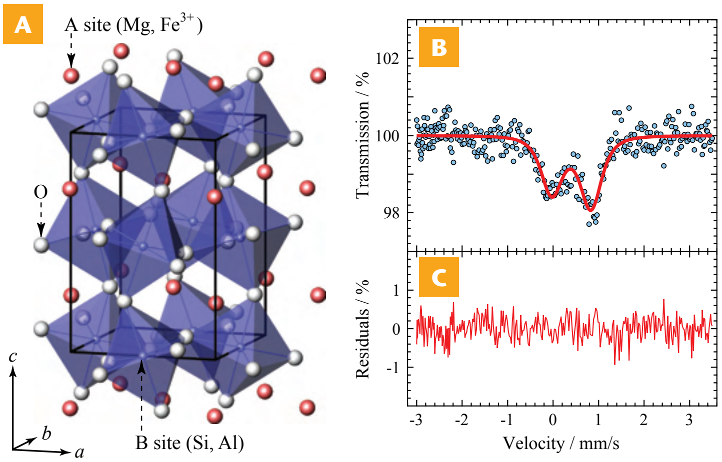

Figure 1 (**A**) Crystal structure of our (Fe^{3+}, Al)-bearing bridgmanite. The structure has the two cation sites: a larger eightfold (nominally 12-fold) coordinated A-site and a smaller sixfold coordinated B-site, consisting of a network of corner-linked BO_6 octahedra with A-site atoms located at the centers of cavities in the network and being distorted largely from the ideal cubic perovskite structure owing to the tilting of BO_6 octahedra. In the $MgSiO_3$ bridgmanite, the A and B sites are occupied only by Mg^{2+} and Si^{4+}, respectively. In our (Fe^{3+}, Al)-bearing bridgmanite, parts of Mg^{2+} and Si^{4+} are replaced with high-spin Fe^{3+} and Al^{3+}, respectively, via the charge-coupled substitution. (**B**) Mössbauer spectrum of our (Fe^{3+}, Al)-bearing bridgmanite single- crystal and (**C**) the fitting residuals. In (**B**), the pale-blue dots and red curve are the experimental data and fitting result, respectively. Taking some constraints required from the crystal structure into account, the measured Mössbauer spectrum can be interpreted as one asymmetric doublet.

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German Mineralogical Society

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FROM THE PRESIDENT


Friedhelm von Blanckenburg

Dear members of the DMG,

Have you ever thought of submitting a topical proposal to *Elements* Magazine?

With more than 1400 members, the DMG represents the fourth largest group of subscribers. It is, in part, also "our" journal. Yet in 16 years of *Elements* magazine with six issues per year, there have been only seven issues in which scientists from Germany served as guest editors.

Yes, being guest editor of an *Elements* issue does mean work. But it is incredibly rewarding work. You yourself will collect an exciting group of international scientists from your field as authors. Typically co-authors consist of individuals who would often not even write a joint "ordinary" scientific article. In fact, you may even liase with your fiercest competitor to provide a balanced view of the state of affairs in a field. This can be productive and lead to new frontiers. You will write for an audience that differs from specialists in your field. In the process, *Elements*' authors become much more proficient in communicating complex scientific content to a general audience—an ability that is rare but that we increasingly need in an era in which public science communication is in ever-increasing demand. You will also design a few beautiful colourful graphics that you and many others will use in undergraduate lectures for years to come.

With 15,000 printed copies and online access through Geoscience World, your article will likely be much more read than your papers published in specialty science journals. As a result, your name will increase in recognition—something that can be very beneficial for early-career scientists.

I was guest editor of one *Elements* issue, and I served as a Principal Editor for three years. Many articles have moved across my desk and all of them were a lot of fun to deal with. I learned much in-depth scientific content, how to write accessible text, and great collaboration with the *Elements'* staff.

So why wait? I know of many exciting topics that we work on in the DMG community. Think of the one topic that you wish to broadcast to a large audience, be that a scientific field, a method, or a field area. Seek a co-guest editor somewhere on this planet, suggest six articles and their authors, and send the proposal off to *Elements*. And then the fun work begins...

I am looking forward to holding your issue in my hands.

Yours,

Friedhelm von Blanckenburg
President of the DMG

PUBLIC OUTREACH EVENT

Family Science Sunday, GeoMinKöln 2022

The GeoMinKöln 2022 will take place in late summer this year, September 11–15 right in the center of Europe. The beautiful city of Cologne will host this conference and will be the meeting point for many Earth scientists from Germany, Europe, and the whole world, who will present their latest and most exciting research results. This conference also marks the 100th general assembly of the German Mineralogical Society that will be celebrated by several special events. One of these is the "Family Science Sunday“, 11 September, between 11 am and 3 pm. We, the Earth Science community, invite families, teachers, young and old explorers, students, and everyone who is interested to visit the conference venue for this special outreach event. Here, you will have the chance to talk to scientists and discover all the different aspects that make the Earth Sciences not only exciting, but also highly relevant for many different aspects of our daily life and for future challenges that we are facing as a society.

Example for a booth at the science market. PHOTO: L. FISCHER

This event addresses all members of the public and offers many different formats to meet the interests of visitors of all ages, backgrounds, and interests.

The core of the "Family Science Sunday" is the *science market* that will comprise a variety of exciting science booths on different Earth Science related topics such as volcanoes, the mineralogy of sand, meteorites, or mineral resources that we can find in mobile phones or even in our food. We would like to get in contact with people and give visitors the chance to walk around, watch, investigate, try and explore whatever catches their attention.

Visitors who like to watch documentaries or want to learn a bit more about a specific topic are invited to attend short presentations in lecture halls located directly next to the market. Here you can, for example, learn about how the Earth became a habitable planet, as well as the quality of Cologne's drinking water and why it is enriched in Rare Earth Elements. You can have a look on our planet from a satellite view or learn about what to expect, if you are interested in studying Earth Sciences in Germany.

Everyone who really wants to dive deeper into a topic and participate more can book a workshop. Teachers may want to get to know more about the mineralogical tool boxes (Mineralogischer Lehrkoffer "mileko") and their applications in school education. There is also the chance to learn what pigments are and what it takes to create colors of your own.

These are of course only a few examples and there will be much more to explore. With this, we want to invite all *Elements* readers to visit us in September and hope to see many of you at the "Family Science Sunday".

Bastian Mrosko on behalf of the organizers

SECTION MEETING 2022

Crystallography and Applied Mineralogy

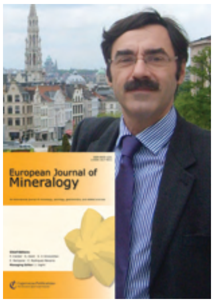
The joint meeting of the DMG sections Applied Mineralogy and Crystallography was held online on March 3rd. Presentations were given to the topics *recycling*, *mining*, and *new materials* followed by a lively discussion. The participants also discussed future activities of the sections. We all hope that face-to-face meetings will resume soon and look forward to the next joint workshop, which will be held on 8–10 March in 2023.

Uta Helbig (Nürnberg)

EDITORIAL

Back to basics on scientific publishing

The first scientific journals date back to the 17th century, when the French *Journal des sçavans* and the English *Philosophical Transactions of the Royal Society* first began systematically publishing research results[1]. After more than three centuries, I would like us to reflect on the fundamental function for writing scientific papers and publishing. Scientists publish papers in specialized international journals essentially for two reasons: i) to test their results and ideas within the community, and ii) to allow the community to (re)use these results to progress in their own research:



- The review process by the peers is an important step in the testing process for authors, even if it is not always seen as such. It provides essential validation and feedback to the authors at a stage prior to publication of their work.
- The editorial process is also key to ensure that the publication correctly and completely conveys the information to the community.

The continuous exchange of knowledge and feedback within the communities is fundamental for research advancements. Overall, research is a mix of a community and an individual adventure. A good equilibrium between these two dimensions is required to make new discoveries.

Some of us may feel that these two objectives are no longer the main motivation for publications. The search to gain visibility in order to attract more funding, enhance one's career, and to become more influential are more and more present, risking to shifting significantly the equilibrium toward the individual dimension of research.

At the European Journal of Mineralogy (EJM), we remain loyal to the two main basic reasons for scientific publication. As editors, our decisions are taken without judging how influential a paper could become. If a manuscript is scientifically original and of high quality, we try to provide the most complete possible review to the authors. We encourage a publication culture that ensures that the data and ideas are understandably transferred to the scientific community. The team at our journal works hard to defend the fundamental function of scientific publications. Editors, publishers, and authors should never forget the final objective of scientific publications and our role within the community.

J. Ingrin
Managing Editor of EJM

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[1] Kronick DA (1976) A History of Scientific and Technical Periodicals: The Origins and Development of the Scientific and Technical Press 1665–1790. (Second Edition) Scarecrow Press, 336 pp.

KLAUS KEIL (1934–2022)

A special issue of the international journal *Geochemistry* was dedicated to Klaus Keil on the occasion of his 85th birthday.

On February 26, 2022 Klaus Keil passed away. Professor Keil was an outstanding petrologist, who worked on extraterrestrial samples. He was a pioneer in the application of the electron microprobe to meteorites. Together with Kurt Fredriksson, he was the first to quantitatively determine the compositions of minerals in meteorites, and their carefully performed analyses are still valid today. Klaus later became interested in the strongly reduced enstatite chondrites. Using the electron microscope, he and his co-workers detected a series of new minerals in these meteorites such as sinoite, ninigerite, heidite, and others. A sulfide carries his name, keilite (Fe,Mg,Mn,Ca,Cr)S.

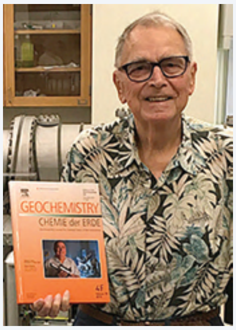


PHOTO: HAWAI'I INSTITUTE OF GEOPHYSICS AND PLANETOLOGY

Klaus Keil was born in Hamburg in 1934. He grew up in Jena, where he studied mineralogy and chemistry at the local Friedrich Schiller University. Early on, Fritz Heide, one of his teachers, got him interested in meteorites and convinced him to begin a dissertation in meteoritics. Hans Suess, working in La Jolla at the time, learned about the work Klaus was doing in Jena and tried to convince him to come to La Jolla. As a result, Klaus left East Germany, shortly before the Berlin Wall was built. He first travelled to the Max-Planck-Institute for Chemistry in Mainz, where he completed the research for his dissertation and was awarded his doctoral degree. He then moved to La Jolla and later took positions at the NASA Ames Research Center at Moffett Field. In 1968, he was appointed director of the Institute for Meteoritics and Professor of Geology and Geophysics at the University of New Mexico. In 1990, he became Director of the Planetary Geosciences Division at the Hawaiʻi Institute of Geophysics and Planetology. He retired from university in 2012, but remained active doing research.

After becoming director of the Institute for Meteoritics in Albuquerque in 1968, Klaus established one of the most influential research groups in cosmochemistry with Marty Prinz, Jeff Taylor, Ed Scott, Hort Newsom, Adrian Brearley, Rhian Jones, and others. During the Apollo program, Klaus and his group participated in the study of lunar rocks. Their focus was on highland rocks. Klaus created the acronym ANT-series for a variety of interrelated rock types such as anorthosite, norite, and troctolite. He was Principal Investigator for studies of lunar rocks for many years and was also very active as a member of several NASA advisory boards and committees.

At the same time Klaus's research group also performed ground-breaking research on meteorites. The meteorite work continued in Hawaiʻi, where Klaus established a very successful new meteorite research group, including researchers from his Albuquerque time. At the Hawaiʻi institute, Klaus and the volcanologist Lionel Wilson developed a concept for the early history of planetesimals. They postulated formation, ascent, and loss of early gas-saturated partial melts in small planetesimals, in order to explain the residual character of many differentiated meteorites.

In 1988, Klaus was awarded the *Leonard Medal* of the Meteoritical Society and in 2014 he was recipient of the *Abraham Gottlob Werner Medal in Silver*, the highest scientific award of the German Mineralogical Society (DMG). In 2019, a special issue of the international journal *Geochemistry* was dedicated to Klaus on the occasion of his 85th birthday (vol. 79, issue 4) and in 2020 he became an honorary member of the DMG.

Astrid Holzheid (Kiel), **Herbert Palme** (Frankfurt/Main)

Mineralogical Association of Canada

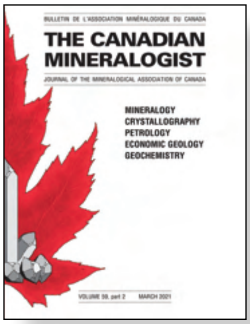
www.mineralogicalassociation.ca

THE CANADIAN MINERALOGIST

LEE GROAT STEPPING DOWN AS EDITOR OF THE CANADIAN MINERALOGIST

Dr. Lee A. Groat of the University of British Columbia (Canada) is stepping down after serving as Editor of *The Canadian Mineralogist* since 2012. The association owes a great debt of gratitude to Professor Groat. He successfully steered the journal through some trying times and maintained the high quality and international reputation of the journal throughout his tenure, while still maintaining a burgeoning research group at the University of British Columbia.

Professor **Ron Peterson**, from Queens University (Canada) served as technical editor with Lee for *The Canadian Mineralogist*. Dr. Peterson is also stepping down and is likewise thanked for his tireless efforts on our journal during his tenure of over a decade.



BULLETIN DE L'ASSOCIATION MINÉRALOGIQUE DU CANADA

THE CANADIAN MINERALOGIST

JOURNAL OF THE MINERALOGICAL ASSOCIATION OF CANADA

MINERALOGY
CRYSTALLOGRAPHY
PETROLOGY
ECONOMIC GEOLOGY
GEOCHEMISTRY

VOLUME 59, part 2 MARCH 2021

NEW EDITORS FOR THE CANADIAN MINERALOGIST

The **Mineralogical Association of Canada** is pleased to announce the appointment of two leaders in the mineralogical and petrological sciences to serve as editors for *The Canadian Mineralogist* on a three-year appointment.

Dr. Andrew ('Andy') M. McDonald

Andy is an applied mineralogist in the Harquail School of Earth Sciences at Laurentian University (Canada). His background is firmly planted in the crystal chemistry of minerals, which he uses to solve geologically relevant problems, specifically those in the areas of high field strength element (Ti, Zr, Nb) mineralogy, platinum-group minerals, and sulfides from magmatic ore deposits. He obtained a B.Sc. (Hons.) from the University of Toronto (Canada) (1987) and graduate degrees from Carleton University, Canada (M.Sc. 1989, Ph.D. 1992). He joined the faculty at Laurentian in 1992 and holds the rank of full professor there. He volunteered with International Centre for Diffraction Data for nearly two decades, served as Associate Editor of the *American Mineralogist* (2010–2013) and has held IMA-related positions, including as the Vice-Chair, COM (2010–2013), and the former IMA Commission on the Classification of Minerals (1996–2002). Within the MAC framework, he served as Secretary (2000–2006), has been a member of the Executive Council (2014–2022), served as Associate Editor of *The Canadian Mineralogist* (2006–2009), along with being a guest editor for both the special volume on The Mineralogy and Beneficiation of PGM-Cu-Ni ores (vol. 49, no. 6) and the recently published thematic issue dedicated to Prof. A. J. Naldrett (vol. 59, no. 6). His students and he have been awarded the Hawley medal three times (2015, 2018, 2019). He organized a Berry Summer School on Optical Mineralogy with Prof. Jim Nicolls (2014), was Vice-Chair for the Sudbury 1999 GACMAC meeting, and will be serving on the LOC for the Sudbury 2023 GACMAC meeting.

Andy welcomes the opportunity to continue the legacy of high-quality research being published in *The Canadian Mineralogist* and to build upon its established commitment to supporting a strong forum for research in a broad range of areas.

Dr. Stephen ('Steve') A. Prevec

Steve is a geochemist and petrologist in the Department of Geology at Rhodes University in South Africa. His research is rooted in the application of petrography, geochemistry, and radioisotope geochemistry to understanding the genesis of (mostly mafic) igneous rocks and their ores, and in igneous rocks associated with large terrestrial impact craters. He obtained his B.Sc. (Hons) from McMaster University (Canada) in 1985, followed by an M.Sc. at the same institution and a Ph.D. from the University of Alberta, Canada (1987-1990, although he only collected the degree in 1993). He was employed in the geochronology unit of the Geological Survey of Canada (Ottawa; 1991–1992), and conducted post-doctoral research at GEOTOP (UQAM, Montréal) from 1992–1994 and at Laurentian University (1994–1998). In 1998, he took up an appointment at the University of the Witwatersrand in Johannesburg, South Africa, moving in 2004 to Rhodes University, where he is currently an Associate Professor and a full-time lecturer and researcher. He served as Head of Department from 2008 to 2016. Steve has been a member of the GAC since 1984, and of the Geological Society of South Africa (GSSA) since 2003, in which he currently serves as a Fellow and Council Member. He served as editor of the quarterly magazine of the GSSA from 2003 to 2011, and was awarded the society's Honours Award in 2010 for this service. He is currently the managing and production (i.e., sole) editor of the quarterly magazine of the Mineralogical Society of South Africa (since 2017). He has served as guest coeditor for a special volume of the *South African Journal of Earth Science* (a memorial issue for Prof. J. Moore in 2012), and has organized and run two national meetings of the Igneous and Metamorphic Studies Group, of which he is a founding member (2009) and Executive General Secretary.

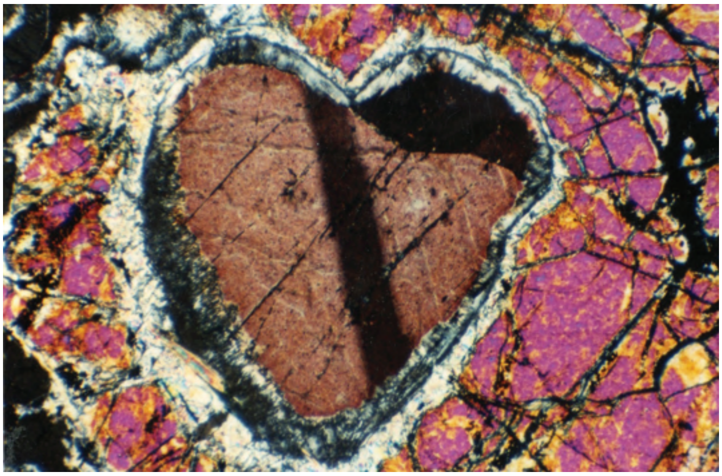
Steve is honoured by the prospect of serving the geoscience community, and particularly that of Canada, in an editorial capacity with *The Canadian Mineralogist*, where he aspires to build on the existing high standards of the journal and the society it represents. He shares his reflections below.

Mackenzie Parker, our stalwart managing editor, will continue to work with Steve and Andy to maintain the journal's premium quality set by Lee and his predecessors.

MINERALOGY: WHAT'S THE ATTRACTION?

In January this year, I was invited to become the co-editor of *The Canadian Mineralogist*, as of April. I said yes. I have been asked to explain why (more than once), and it's an interesting question. My geological career began in Canada, before following a job to South Africa, where I am now in my 25th year here in my adopted country. So what is the appeal of serving a geological community with which I am no longer physically much of an active participant in, and in a geological subdiscipline, mineralogy, which is not notionally my specialty?

In my formative years as a graduate student, I fancied myself as an isotope geochemist (or as some would say, evidently, but regrettably, an isotopist), helping to set up one of the first Sm-Nd labs in the country in the mid-1980s, with delusions of grandeur that I'd win the fabled case of Scotch offered by Stephen Moorbath for producing a reliable Hadean Rb-Sr isochron. As it turned out, I discovered that to solve the geological problems and to tell the kind of geological stories I wanted to tell, I needed to understand the rocks from their isotopes all the way back through their geochemistry to the field relationships and petrography, if not for the story, then for myself (I had not yet discovered the joys and trials of collaborative subdisciplinary team-driven research).



Interstititial plagioclase crystal, with polysynthetic twin, stained red with barium dichloride, surrounded by red-blue (2nd order) birefringent olivine, separated by a double corona of radial orthopyroxene replacing the olivine, and pargasitic amphibole replacing the feldspar. It is from the White Bear Arm Complex in the Grenville Province, Labrador, Canada.

At the root of everything is the mineralogy, and as my new coeditorial colleague, Andy McDonald, likes to observe, if you are studying rocks, then you are practicing mineralogy (he says it more poetically); the point is that you don't need to be a crystallographer, fortunately! (I don't worry, we have plenty of Associate Editors who are, as well as being "proper" mineralogists). As it has transpired, through studies of coronitic gabbros and granulites, mineralised impact melt sheets, and layered intrusions of various sizes, among other things, the really fascinating (not to mention aesthetically appealing) features were usually in the mineralogy, apart from my Ph.D. rocks, which were mostly a greenschist facies disaster of amphiboles and chlorites, forcing me to learn how to use immobile trace elements as petrogenetic tools; apologies to Pentti Eskola (the geologist, not the long jumper). Even in some of the least well-preserved of those rocks, I discovered (20 years later; persistence is key) evidence of in situ melting related to a combination of faulting and thermal metamorphism from a superheated impact melt sheet. I find that I am constantly drawn back to the mineralogy as the "ground truth", and I continue to find more and more applications of all of the stuff I was taught, and now teach, about mineral stabilities and solubilities, rheological and phase relationships, and discover constantly that there is a world full of way more interesting and useful stuff that I know not nearly enough about, and other people that do, which is very motivating.

About five years ago, I was invited to perform a similar but much less scientifically rigorous task of producing a quarterly magazine for the Mineralogical Society of South Africa (Minsa). They were similarly undeterred by my initial response of "but I'm not a mineralogist," and as a consequence, I have been exposed to aspects of the breadth of mineralogical studies across a much wider range of applications than my personal modest geological research would facilitate. The opportunity to participate in facilitating the production of a broad palate of robust and interesting mineralogically- based research and, in effect, rejoining the Canadian geological community (aside from when I pop back every year or two and relocate a few kilograms of rock from the Sudbury area to South Africa) was too attractive to pass up. As it happens, my work with Minsa had already led to reuniting with a quintessential Canadian mineralogist, Louis Cabri, and soon afterwards the circumstance arose to publish in *The Canadian Mineralogist* to honour Tony Naldrett and his work. After four months on the job with *The Canadian Mineralogist*, the work has been suitably interesting, my working colleagues very engaging, and I'm looking forward to the task ahead in maintaining a viable research journal in a challenging publishing environment. This has been a rewarding environment in which to do it.

Steve Prevec
The Canadian Mineralogist Co-Editor
Dept. of Geology, Rhodes University, South Africa

Mineralogical Society of America

web

www.minsocam.org

PRESIDENT'S LETTER

In this letter I would like to reflect on the state of mineralogy in the USA in the context of our university education system. I suspect the situation is similar in other parts of the world, however I think it wisest to focus my discussion on what I know best.

In 2021, the Mineralogical Society of America launched a baseline study examining the status of mineralogy and petrology teaching in the U.S. colleges and universities. A survey was sent to MSA members working in academic positions. Seventy-four completed surveys were returned from 73 institutions in 37 states. One of the study's principal findings is that over the past five years, fewer geoscience departments are offering separate mineralogy, petrology, and optical mineralogy courses; with nearly a third reporting the deletion of either a mineralogy or optical mineralogy class from their curriculum. For those familiar with U.S. academic institutions, this should come as no surprise. University curricula have finite sizes, often imposed by the institution, to ensure that it is feasible for a student to complete a degree in four years. As the world of science expands, there is less time in the curriculum to teach any given topic. Therefore, mineralogy and optical mineralogy get squeezed into one class or mineralogy and petrology are combined into a single earth materials class. This consolidation is to make space for topics such as Geographic Information Systems (GIS) and global climate change, which are essential in the modern world. Perhaps more worrisome is that 40 percent of respondents saw a decreasing demand for the skills taught in mineralogy and petrology courses, while only 20 percent saw increasing demand, and 20 percent perceived a steady demand (the remainder didn't know). Recommendations from respondents for bolstering mineralogy and petrology classes included the need to involve more research instrumentation (SEM, XRD, etc.); making more connections to society and the broader geological context; teaching more applied and transferable skills, including field work and real-world projects; and making classes more fun for students.

For me, this topic is personal, as I have taught mineralogy for many years. I have spent quite a lot of time pondering which topics are most important to teach, and which I can skip over in the interest of not completely snowing my students. At one point, I was willing to stake my career on the importance of teaching stereonets and the phase rule, but more recently, have abandoned both in favor of more intuitive approaches. Some years ago, I had to adjust my course to the loss of an optical mineralogy course, which required more tough decisions regarding the contents of the lecture as well as the lab. Much to my consternation, X-ray diffraction landed on the chopping block. Having taught remotely during the pandemic and recorded all my lectures, I now teach in 'flipped mode', which gives me an even clearer picture of what sticks in my students' brains and what slips quickly away. I tell my students repeatedly that the skills they learn in mineralogy are very important and that their mineralogical knowledge will be the foundation of their understanding of rocks. However, as I look into their entirely baffled faces as we work through the beauty and intricacy of Si/Al ordering in feldspars, I sense that what I am teaching is still not well aligned with their needs or even my own priorities. There is a lot of inertia that comes from teaching what is in the book, teaching what I was taught, and teaching what is most intriguing to me.

One of the things I have learned over the years is that if you want students to learn something, it has to be front and center of your course organization. For example, at one point I realized that my students could finish mineralogy and have no clue what quartz was composed of or where you might expect to find it, but instead have randomly retained the formulas for galena, molybdenite, and hydrogarnet. Even though I lectured on associations, they would forget that calcite is not likely to show up in granite. So, I reinvented my mineralogy lab to center around associations, rather than systematic mineralogy. Because the lab covered the minerals in a specific rock type (e.g., felsic igneous rocks, mafic igneous rocks, sediments, hydrothermal deposits), the students would see the common rock-forming minerals like quartz, feldspar, and pyrite over and over again and through experience get very good at identifying them. They also had a much better feeling for how minerals fit into rocks. I was nervous about throwing away the time-honored adherence to Dana's classification of minerals, but, to be honest, how useful is that particular nugget of information compared to the relationship between rock bulk composition and which minerals occur in them?

Is it possible to envision radical reform of what is taught in mineralogy courses that would put mineralogy front and center on the list of highly relevant topics that all geoscience majors want to take? To connect mineralogy to modern scientific questions and applications, is it sufficient to just point out to students that there are connections, or should we instead build our course around those connections? Perhaps we should spend more time on zeolites and less on pyroxenes, more time on clay mineralogy and less time on muscovite and biotite. Living on a warming planet, perhaps we should use the methane clathrate phase diagram rather than the Si phase diagram to introduce phase equilibria; after all, stability between alpha and beta quartz is not likely to have nearly the impact on humanity as the destabilization of clathrates stored in permafrost. Are crystallographic forms and the wooden blocks made to teach them (nearly sacred objects to the mineralogy professor) really more important to teach than the function of cryptocrystalline materials in the weathering environment?

Changing how we teach mineralogy to put the value of understanding mineralogy front and center will take some work. As a community, we will need to convince ourselves that modifying, or even abandoning, the traditional course structure is OK. We will need to think critically about the topics that we currently teach, identify and prioritize new topics which key better into new modern scientific and societal needs, and figure out how to weave everything into coherent course structures. Finally, we will need to gather or create curriculum materials to support this new way of teaching mineralogy. I hope the new baseline study will convince people that this is an effort well worth undertaking.

Pamela Burnley
2022 MSA President

NOTES FROM CHANTILLY

- The MSA 2021 Annual Report is now available via a link on the homepage of the MSA website: www.minsocam.org. The Report details highlights in the past year, including awardees, Fellows, grantees, publications, communications, programs, and events.
- MSA 2023 membership renewals have begun. Please renew today using the link on the MSA home page (www.minsocam.org) if you have not already done so.
- Members and Fellows who are in the senior, honorary, and life categories are sent renewal notices. They need not pay dues, but are sent notices as the best way to prompt an update of membership information, particularly mail and e-mail addresses.


MINERALOGICAL SOCIETY OF AMERICA
2021 ANNUAL REPORT

CONTRIBUTIONS

Many members make a gift to MSA by including a contribution with their annual dues and/or by responding to special appeals. Depending on the wishes of the member, the money is deposited with the principal of the MSA Endowment, the J. Alexander Speer Outreach Fund, MSA Mineralogy/Petrology Fund, J. B. Thompson Fund, Edward H. Kraus Crystallographic Research Fund, F. Donald Bloss Fund, General Operating Funds, or the new Peter R. Buseck Lecture Fund. These Funds are used to support MSA's research grants in crystallography, mineralogy, and petrology; the MSA Undergraduate Prizes; the Mineralogical Society of America Award; the Distinguished Public Service Award; the Dana Medal; the Roebling Medal; the website; and the Distinguished Lecturer program. If you have not done so previously, please consider making a tax deductable gift at the next opportunity.

REVIEWS IN MINERALOGY AND GEOCHEMISTRY (RIMG): VOLUMES 87 AND 88

MSA is pleased to announce the 2022 publication of two new *Reviews in Mineralogy & Geochemistry* volumes: Volume 87: *Geological Melts* (D.B. Dingwell, G.S. Henderson, and D.R. Neuville, Editors) and the open access Volume 88: *Diamond: Genesis, Mineralogy & Geochemistry* (K. Smit, S. Shirey, G. Pearson, T. Stachel, F. Nestola, and T. Moses, Editors). More information on Volumes 87 and 88 is on the MSA website under the Publications tab.


REVIEWS in MINERALOGY & GEOCHEMISTRY
Volume 88
DIAMOND:
NESIS, MINERALOGY
ND GEOCHEMISTRY
EDITORS:
Karen Smit, Steve Shirey, Graham Pearson,
mas Stachel, Fabrizio Nestola & Thomas Moses
MINERALOGICAL SOCIETY OF AMERICA
GEOCHEMICAL SOCIETY

REVIEWS in MINERALOGY & GEOCHEMISTRY
Volume 87
GEOLOGICAL MELTS
EDITORS:
D.R. Neuville, G.S. Henderson, D.B Dingwell
MINERALOGICAL SOCIETY OF AMERICA
GEOCHEMICAL SOCIETY

RiMG is a series of multi-authored, soft-bound volumes containing concise reviews of the literature and advances in theoretical and/or applied mineralogy, crystallography, petrology, and geochemistry. The series is jointly published by the Mineralogical Society of America (MSA) and the Geochemical Society. Volumes are available both in hard copy and online via the MSA website: www.minsocam.org/publications.html

25- AND 50-YEAR MSA MEMBERS

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Shoichi Kobayashi	Carl A. Francis
Eugen Libowitzky	Byrce Ronald Frost
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	Floyd N. Hodges
	Frank E. Huggins
	Anthony R. Kampf
	Richard H. Langley
	Ho-Kwang Mao
	Walter V. Maresch
	Georgia Pe-piper
	Frank S. Spear

EVENTS

MSA will be hosting a virtual Short Course on Diamonds on October 26 and 27, 2022. The course is designed to accompany *Reviews in Mineralogy and Geochemistry* Volume 88: *Diamond: Genesis, Mineralogy & Geochemistry* (2022). For more information, visit the MSA website at www.minsocam.org.

DID YOU KNOW?

MSA membership comes with a number of benefits for a low annual fee. In addition to being part of a thriving scientific community, members receive discounts on MSA publications, Short Course and joint meeting registration fees, and subscriptions to a variety of geoscience journals. They receive copies of *Elements* magazine six times yearly, and online access to the journal *American Mineralogist.* Members also have access to the online member directory and receive free online color and e-prints for articles published in *American Mineralogist*. Join or renew today!

Meteoritical Society

http://meteoriticalsociety.org

THANKS TO OUR SOCIETY'S COMMITTEE MEMBERS

The Meteoritical Society would like to extend its sincere thanks to all those members who are serving on society committees this year. We have listed their names below, with the names of the committee chairs in bold. Without the generous help of these members, the Met Soc could not function. We greatly appreciate their help!

Officers and Council

Elected Officers and Councilors of the Society

Brigitte Zanda	**President**
Nancy Chabot	**Vice President**
Meenakshi Wadhwa	**Past President**
Munir Humayun	**Secretary**
Tasha Dunn	**Treasurer**
Henner Busemann	Councilor
Sarah Crowther	Councilor
Elena Dobrica	Councilor
Denton Ebel	Councilor
Chris Herd	Councilor
Kuljeet Kaur Marhas	Councilor
Takashi Mikouchi	Councilor
Ann Nguyen	Councilor

Editorial Personnel

The editors of the Society's publications and website

Tim Jull	Editor of *Meteoritics and Planetary Sciences*
Jeff Catalano	Executive editor of *Geochemica et Cosmochemica Acta*
Cari Corrigan	Editor of Meteoritical Society contributions to *Elements*
Jim Rowe	Chair of website & Outreach Committee

Leonard Medal Committee

Nominates candidates for the Leonard Medal, Nier Prize, and election of Fellows

Hiroshi Hidaka 2022
Zita Martins (chair) 2023
Jeff Cuzzi 2024
Alexander N. Krot 2025
Larry Nittler 2026

Barringer Award Committee

Annual award for outstanding work in the field of impact cratering

Sarah T. Stewart 2022
Roger Gibson 2023
Thomas Kenkmann 2024
Ludovic Ferrière 2025

Publications Committee

Oversight for the journal *Meteoritics and Planetary Science*

Ian Lyon (chair) 2023 (2nd term)
Mikhail Zolotov 2023
Hikaru Yabuta 2022
Sandeep Sahijpal 2022
Janice Bishop 2023
Suzanne Schwenzer 2023
Ex officio member:
the Society Treasurer, Tasha Dunn

Joint Publications Committee

Oversight for the journal *Geochimica et Cosmochimica Acta*

Karim Benzarara (chair, GS) 2022
Jon Friedrich (MS) 2022
Sara Russell (MS) 2022
Caroline Peacock (GS) 2023
Conel Alexander (MS) 2024
Fang-Zhen Teng (GS) 2024

Endowment Committee

Members serve as the trustees for the Society's investment fund

Drew Barringer (co-chair, 7th term) 2022
Rhian Jones (co-chair, 2nd term) 2022
Gary Huss 2021 (2nd term)
Candace Kohl 2022
Dennis Harries (1st term) 2024
Ad hoc member: Allan Treiman
Ex officio member:
Treasurer of the Meteoritical Society, Tasha Dunn

Audit Committee

Produces an audit of the Treasurer's annual report for each fiscal year

Kevin McKeegan (chair) 2021
Denton Ebel 2021
TBD

Nomenclature Committee

Guidelines for naming meteorites; publication of *Meteoritical Bulletin*

Francis McCubbin (chair, 3rd term) 2024
Mutsumi Komatsu (2nd term) 2022
Bingkui Miao (2nd term) 2024
Devin Schrader (1st term) 2022
Cyrena Goodrich 2023
Ansgar Greshake 2023
Juliane Gross 2023
Katherine Joy 2024
TBD 2024

Pellas-Ryder Award Committee

Selection of candidates for the Pellas-Ryder Award

Nick Lang (chair) (GSA) 2022
Joseph Boesenberg (MS) 2022
Jemma Davidson (MS) 2022
Marisa Palucis (GSA) 2023
Steven B. Simon (MS) 2023
TBD (GSA) 2024

Nominating Committee

Nomination of the Society's Officers and Councilors

Ludovic Ferrière
Michaël Zolensky
Emma Bullock
Akiko Nakamura
Maria Eugenia Varela
Katherine Joy

Membership Committee

Recruit and retain members; nominate Service Award recipients

Arya Udry 2022
Asma Steinhausser 2022
Christian Koeberl 2023
Hasnaa Chennaoui 2023
Shigekazu Yoneda 2023
Beda Hofmann 2023
Ex officio member: Chair of the Endowment Committee, Rhian Jones

McKay Award Committee

Nominates candidate for best student presentation at annual meeting

Romy D. Hanna (Chair) 2022
Lydia Hallis (vice-chair) 2022

Jessberger Award Committee

Nominates outstanding mid-career female isotope geochemists for the Jessberger Award

Mario Trieloff (chair) 2023
Noriko Kita 2023 (vice chair)
Zita Martens 2023 (Leonard Medal Committee liaison)
Sara Russell 2023
Thomas Stephan 2023

Outreach ad hoc Committee

Jim Rowe (chair) 2024
Mendy Ouzillou 2023
Cari Corrigan 2023
Philippe Claeys 2023
Zoe Wilbur 2023
Steffanie Sillitoe-Kukas 2023
Ex officio member: Chair of the Endowment Committee, Rhian Jones

Ethics ad hoc Committee

Trevor Ireland (chair) 2023
Tracy Rushmer 2023
Natalia Artemieva 2023

IN MEMORIAM – PETER SIGNER

Peter Signer died on Friday, Dec. 10, 2021. After a long illness, he peacefully fell asleep at the age of 92. He was a Fellow of the Meteoritical Society since 1967. His name is memorialized in the Baur-Signer ion source in noble gas mass spectrometry and the Signer-Nier model for cosmogenic noble gases.

Following his dissertation at the University of Bern (Switzerland) on a mass spectrometric study of the ^{176}Lu decay constant with Friedrich Houtermans and a seven-year stay with Alfred O. Nier at the University of Minnesota (USA), Peter was appointed professor for Geo- and Cosmochronology at ETH Zurich (Switzerland) in 1965. He founded the Laboratory for Noble Gas Mass Spectrometry, which he led until his retirement in 1994, and which is now headed by Henner Busemann in the third generation.

In Minneapolis, Peter contributed much to a better understanding of noble gases in meteorites. In now classical works, he developed the Signer-Nier model describing cosmogenic noble gas production in iron meteorites and with Hans Suess he coined the terms “solar” and “planetary” for different noble gas components in meteorites.

In his first years at ETH, Peter proposed to capture ions from the solar wind with metal foils on space missions, an idea that was ultimately realized by his colleagues at the University of Bern as the famous solar wind experiment during the Apollo lunar missions. Under his leadership, the ETH noble gas laboratory received worldwide recognition, first of all with work on lunar samples and meteorites, studying solar, cosmogenic, and primordial noble gases. Further major activities—in close collaborations with colleagues in Earth and environmental sciences—included surface exposure dating of terrestrial samples with “cosmogenic” noble gases, as well as studies of lake dynamics with noble gases, e.g. by tritium-^{3}He dating.

Peter Signer was an enthusiastic lecturer who reminded generations of Earth Science students about the importance of the other planets for understanding Earth.

Peter is survived by his wife Gerti and their two children Ina and Reto. We mourn with them a good friend and teacher.

Rainer Wieler
ETH Zürich

ANNUAL MEETING SCHEDULE

2022	Glasgow, Scotland, 14–19 August
2023	Los Angeles, California, USA, 13–18 August
2024	Brussels, Belgium, EU, July/August (dates TBD)
2025	Perth, Australia, July (dates TBD)
2026	Frankfurt, Germany, July/August (dates TBD)

RENEW YOUR MEMBERSHIP NOW!

Don’t forget to renew your society membership! You can renew online at: https://meteoritical.org/membership/join

Sociedad Española de Mineralogía

www.semineral.es

Linares mining landscape. La Cruz foundry (Spain).

SEM 2022 ANNUAL MEETING IN BAEZA

The 39th Annual Meeting of the Spanish Mineralogical Society (SEM) will be held in Baeza (Jaén, Spain) on June 28–July 1 2022. It will be organized by the University of Jaén and coordinated by Isabel Abad and África Yebra. This year we have a special meeting as it is coorganized with the Spanish Clays Society (SEA) with which there is a long and close relationship.

The program for the SEM-SEA 2022 meeting includes the following:

A two-day workshop seminar entitled "Continental sediment metal contamination by agricultural, industrial and mining activities: mineral processes and bioavailability." This workshop will take place on June 28–29, and the speakers will include scientists and professionals of international prestige in this field. The aim of the seminar is to present and discuss new perspectives and ideas about metal contamination in sediments mediated by anthropic activities, particularly for young scientists. The second day includes a scientific excursion to the Linares Mining District (metal(loid)s transport in hydrographic networks of mining basins). The lectures will be published in volume 15 of the journal *Seminarios de la Sociedad Española de Mineralogía*.

On June 30–July 1 will take place the scientific sessions which include oral presentations and poster sessions, as well as three plenary lectures on topics of general interest. Communications in the fields of clays, mineralogy, petrology, and geochemistry may be submitted. The main objective is to hold high-quality scientific sessions that become a platform for debate, the exchange of ideas, and the establishment of new scientific collaborations. All of these scientific contributions will be published in volume 26 of *Macla*, the journal of the SEM.

For updated information, please go to www.semsea2022.es

Isabel Abad and **África Yebra**
Coordinators SEM-SEA 2022 (Universidad de Jaén)

MINERALS 2021 BEST PHD THESIS AWARD

Núria Pujol-Solà defended her Ph.D. thesis on June 30th 2021 at the University of Barcelona, Spain. Her thesis entitled "Diverse origin and processes in the formation of diamond and other exotic minerals in ophiolitic chromitites" was supervised by Dr. Joaquín A. Proenza from the University of Barcelona and Dr. Antonio García Casco from the University of Granada, Spain. She investigated the petrogenetic aspects for the formation of unusual phases in ophiolitic chromitites from Cuba and Morocco, providing the first ever report in nature of in situ nanodiamond within methane-rich olivine-hosted fluid inclusions. Her new observations and interpretations support the idea of metastable diamond growth during low-pressure serpentinization. She has now received the Minerals 2021 Best Ph.D. thesis Award that recognizes her work. (https://www.mdpi.com/journal/minerals/awards).

Société Française de Minéralogie et de Cristallographie

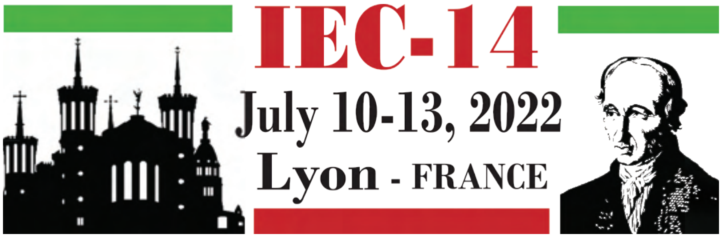
www.sfmc-fr.org

14th INTERNATIONAL ECLOGITE CONFERENCE

10-13 July 2022, Lyon, France

The 14th International Eclogite Conference (IEC-14) was held in France, where the First International Eclogite Conference was organized in 1982. After 40 years, it is high time to bring this series of conferences in the country where two centuries ago, in 1822, the mineralogist René-Just Haüy created the name "eclogite", meaning "chosen rock".

After a year of lockdown due to the Covid19 pandemic, this conference also provided an opportunity to meet again and exchange on current issues related to high-pressure metamorphism in general. More information can be found at https://iec14.sciencesconf.org/



Program Topics

- Eclogites and their geodynamic meaning
- Extreme metamorphism and mantle eclogites
- P-T-X conditions estimated from crystal-chemical, experimental, or thermodynamic petrology
- Mega-, medium-, micro-, and nano-structural data and their implications for HP rheological processes
- Geochemistry and fluid interactions
- Petrochronology and ancient eclogites
- Open session, historical perspective / prospective for future research

The Clay Minerals Society

www.clays.org

THE PRESIDENT'S CORNER

Over the years I have attended many conferences in disciplines ranging from chemistry, geochemistry, materials science, and of course clay science. Geochemistry conferences tend to be much more international, which provides us with excellent opportunities for travel and meeting international colleagues. For example, I have attended clay or geochemistry conferences in Canada, France, Germany, Italy, Japan, Switzerland, the UK, and the USA. And since 2020 most of us have attended at least one conference virtually. It will be interesting to see if virtual attendance continues to be an option for scientific conferences in the long term.

With a few exceptions, CMS annual meetings have taken place in the USA, even though members living/working in the USA comprise only about half of our current membership with the CMS. Our annual meeting has been a part of international conferences (e.g., this year's International Clay Conference), but dedicated CMS meetings tend to be held in North America. I encourage CMS members to consider organizing our annual meeting outside of the USA, to reflect our international membership.

Jeffery Greathouse, CMS President

CMS PROFESSIONAL AWARD 2022 SPOTLIGHT

Young-Shin Jun, the recipient of the 2022 Marion L. and Chrystie M. Jackson Mid-Career Scientist Award, is a professor in the Department of Energy, Environmental & Chemical Engineering at Washington University in St. Louis (USA), where she leads the Environmental NanoChemistry Laboratory (http://encl.engineering.wustl.edu/). She received her Bachelor's and Master's degrees in Environmental Science and Engineering from Ewha Womans University (South Korea), holds Master's and Ph.D. degrees in Environmental Chemistry from Harvard University, MA)USA), and conducted postdoctoral research in nanogeoscience at the University of California-Berkeley/Lawrence Berkeley National Laboratory, CA (USA). Professor Jun's group investigates many aspects of environmental chemistry and geochemistry, with a special interest in the structure and behavior of clay minerals and their surfaces. In particular, she has conducted extensive research in clay (or layered) mineral–water interactions in energy-related subsurface engineering systems, which can benefit safer CO_2 capture and sequestration, conventional and unconventional oil and gas recovery, hydrogen storage, geothermal energy, and nuclear waste disposal. She also seeks a new understanding and utilization of clay (or layered) materials for purifying drinking water and remediating contaminated water and soil. Her group has utilized powerful spectroscopic and scattering techniques at synchrotron-based X-ray facilities and surface-sensitive approaches to investigate nanoparticle nucleation and nanoscale chemical reactions. She serves on the American Chemical Society (ACS)'s organizational level Committee on Science as Chair of the Science & Technology Subcommittee. She is an editorial board member for *Geochemical Transactions*, *RSC Advances*, *Journal of Hazardous Materials*, *ACS ES&T: Engineering*, *Current Opinion in Chemical Engineering*, and *Scientific Reports*.

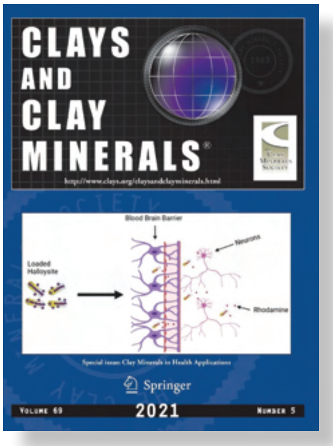
Jin-Ho Choy is the recipient of the 2022 Marilyn and Sturges W. Bailey Award. He is is currently a chair professor at Dankook University, Korea (2019–present), and an appointed professor at Tokyo Institute of Technology, Japan (2019–present). He received his B.Sc. (1970) in Chemical Engineering from Yonsei University, Korea, and Ph.D. (1979) in inorganic solid-state chemistry from Ludwig-Maximilians Universität München, Germany. He has since held numerous research positions, including postdoctoral fellow at the Inorganic Chemistry Laboratory, Oxford, England (1980), professor in the Department of Chemistry at Seoul National University, Korea (1981–2004), and distinguished professor and director of the Center for Intelligent Nano-Bio Materials (CINBM) at Ewha Womans University, Korea (2004–2019).

Professor Choy received many awards and recognitions at various stages of his research career. A National Science Award in Chemistry from the Korean Government (2003), a Distinguished Service Knight Medal from the French Government (Chevalier dans l'Ordre des Palmes Académiques) (2003), a Korean Best Scientist Award from the President of Korea (2007), a Proud Yonsei Engineer Award from Yonsei University (2012), and an Academic Award (Sungok) from Korean Ceramic Society (2015) are some of his accolades.

He is a Fellow of the Royal Society of Chemistry, UK (2008). He is also an elected Academician in the World Academy of Ceramics, Italy (2017) and the National Academy of Science in Korea (2018).

His research interests include various clay intercalation compounds with theranostic functions. He works on 2D intelligent materials with imaging and drug delivery functions for gene-, chemo-, and radiation therapies, and various nanohybrids for nanomedicine.

JOURNAL ISSUE HIGHLIGHT



The largest volume of ***Clays and Clay Minerals*** for several years, totaling 797 pages, closed out in early 2022. This is our second year of publication in conjunction with Springer Nature. Our 'reach' (i.e., the number of readers who can access our content) continues to grow; this is reflected in the increasing number of downloads.

The fifth of sixth issues in 2021 consisted of a set of papers on the topic 'Clay Minerals in Health Applications'. These papers are excellent examples of the rapid extension of how clays can be applied in various ways. Please visit the following link to read them via https://link.springer.com/journal/42860/volumes-and-issues/69-5.

CMS MEMBERSHIP RENEWAL

Don't forget to renew your membership!

Mineralogical Society of the UK and Ireland

www.minersoc.org

NEW YEAR, NEW NAME, NEW LOGO

Mineralogical Society
of the UK and Ireland

As mentioned in the previous issue of *Elements*, our name has changed: we are now the Mineralogical Society of the United Kingdom and Ireland. This represents a bit of administrative tidying up. All activity, meetings, journals, grants, etc. remain the same.

The name change came up as we were reviewing our bye-laws. Some inconsistency had crept in during many changes over the 146 years since they were first written. This has now been ironed out. While we await final confirmation (by the Charity Commission for England and Wales) of the changes to our bye-laws, specifically a change to our 'Mission' or mission statement which will now read as follows:

MISSION

1. To support the study, promotion and application of mineralogy and all related disciplines in society and to share that information with the wider public. The Society aims to be a voice which promotes diversity, equality and inclusivity in our science.

2. We achieve this by activities that include:

(a) Being involved in the publication of books, journals and other material.

(b) Supporting a range of special interest groups which represent the breadth of our science.

(c) Running conferences and other forms of discussion.

(d) Supporting our members at every stage of their careers, including students and early career scientists.

(e) Recognizing those in our community who have excelled.

EQUALITY, DIVERSITY, INCLUSIVITY

Since the end of 2020, the Society has prepared and run a survey of members and others willing to answer questions about equality (or equity), diversity and inclusivity (EDI, sometimes referred to as DEI). A draft report has been written and the Society's EDI committee will now consider it before presentation to Council (April 2022) and publication on our website (www.minersoc.org) and elsewhere (including excerpts in our pages here in *Elements*).

Among the >500 people who responded to our survey, it is clear that there are many people who have experienced or witnessed discrimination against themselves or others. There was a very significant degree of support for a series of proposed measures which the Society could investigate. When our report has been published, the Society will then begin a painstaking task of examining each of our areas of activity so that they can all adopt a more EDI-aware *modus operandi*.

The Society resolved early that this will be a meaningful set of actions and that EDI will become embedded in all of our activity from this point forwards. This is not a grey report to put on the shelf and be admired occasionally; this is a starting point from which there will be no turning back.

JUBILEE YEAR FOR THE CLAY MINERALS GROUP

2022 is the 75th anniversary of the foundation of the Clay Minerals Group.

To celebrate, the group will:

- host a series of monthly online interviews which will be available through our Youtube channel
- run a (hybrid) two-day conference in the Natural History Museum, London from 25–26 May 2022, with a series of invited speakers and including a talk on the history of the group
- launch a new CMG 'Research Grant'
- launch a new CMG Newsletter
- run a competition to find the 'best' new image to add to the Images of Clay
- run a Twitter campaign (@CMG_minsoc) to publicize the group and the work that it does

Check https://www.minersoc.org/jubilee-year-2022.html for updates and links to these new activities. A number of interviews have already been conducted including one by Anke Neumann with Adi Radian, available at https://youtu.be/W6dE2Kaw9yI

Adi Radian, clay mineralogist

MSG RIP 2022

The Metamorphic Studies Group 2022 Research in Progress meeting took place on 11th April 2022 at St. Andrews University and also included a two-day field trip. The meeting was organized by Dick White (rww3@st-andrews.ac.uk).

GGRIP 2022

The Geochemistry Group ran its GGRiP meeting on the week commencing 9th May 2022. This took place at Cardiff University, hosted by Marc-Alban Millet. More details are available at https://www.minersoc.org/geochem.html.

EUROPEAN MINERALOGICAL CONFERENCE 2024

Following a successful third iteration in Krakow during late 2021, it has been decided that the next European Mineralogical Conference will be hosted in Trinity College Dublin, from 18–23 August 2024. The Council and staff of the Society are grateful to our European colleagues for placing their faith in us to run this important meeting. We look forward to welcoming many of you to Dublin in a couple of years!

RECENT CONTENT IN *MINERALOGICAL MAGAZINE*

Calciolangbeinite-O, a natural orthorhombic modification of $K_2Ca_2(SO_4)_3$, and the langbeinite–calciolangbeinite solid-solution system

Igor V. Pekov, Natalia V. Zubkova, Irina O. Galuskina, Joachim Kusz, Natalia N. Koshlyakova, Evgeny V. Galuskin, Dmitry I. Belakovskiy, Maria O. Bulakh, Marina F. Vigasina, Nikita V. Chukanov, Sergey N. Britvin, Evgeny G. Sidorov, Yevgeny Vapnik, Dmitry Yu. Pushcharovsky

The Wombat Hole Prospect, Benambra, Victoria, Australia: a Cu–Bi–(Te) exoskarn with unusual supergene mineralogy

Dermot A. Henry, William D. Birch

Illoqite-(Ce), $Na_2NaBaCeZnSi_6O_{17}$, a new member of the nordite supergroup from Ilímaussaq alkaline complex, South Greenland

Emil H. Gulbransen, Henrik Friis, Fabrice Dal Bo, Muriel Erambert

Stable isotope and geochemical evidence for genesis of secondary Copper deposits at Girilambone, New South Wales, Australia

Erik B. Melchiorre

Gachingite, $Au(Te_{1-x}Se_x)$ $0.2 \approx x \leq 0.5$, a new mineral from Maletoyvayam deposit, Kamchatka peninsula, Russia

Nadhezda D. Tolstykh, Marek Tuhý, Anna Vymazalová, František Laufek, Jakub Plášil, Filip Košek

Hellandite-(Y)–hingganite-(Y)–fluorapatite retrograde coronae: a novel type of fluid-induced dissolution-reprecipitation breakdown of xenotime-(Y) in the metagranites of Fabova Hoľa (Western Carpathians, Slovakia)

Martin Ondrejka, Alexandra Molnárová, Marián Putiš, Peter Bačík, Pavel Uher, Bronislava Voleková, Stanislava Milovská, Tomáš Mikuš, Libor Pukančík

Nomenclature of wöhlerite group minerals

Fabrice Dal Bo, Henrik Friis, Stuart J. Mills

Garpenbergite, $Mn_6As^{5+}Sb^{5+}O_{10}(OH)_2$, a new mineral related to manganostibite, from the Garpenberg Zn–Pb–Ag deposit, Sweden

Dan Holtstam, Luca Bindi, Hans-Jürgen Förster, Andreas Karlsson, Kjell Gatedal

YOUTUBE CHANNEL

Peer Review Workshop

A video recording of this workshop is now available from the Society's Youtube Channel which can be accessed via the Society website (find the youtube link on the slider on the homepage, or go direct to https://www.youtube.com/channel/UCJLEvvFJEAtt2SRHozqd7LQ/videos

Reviewing for academic journals: why is this essential and how does it benefit the reviewer?

New Topics in Mineralogy 2: The mineral–microbe interface through time and space

Also available from our Youtube channel is a set of video recordings of presentations made during our latest 'New Topics' meeting. Please check them out at https://www.minersoc.org/new-topics-in-mineralogy-2-the-mineral-microbe-interface-through-time-and-space.html

International Mineralogical Association

www.ima-mineralogy.org

2022 IMA MEDAL OF EXCELLENCE TO PATRICIA M. DOVE

The IMA is delighted to present its 2022 Medal of Excellence to Patricia M. Dove, Distinguished Professor and C.P. Miles Professor of Science at Virginia Polytechnic Institute and State University, USA. She has been praised as a "world leader in the field of mineral reactivity and biomineralogy" and a pioneer who "has combined key advances and development of new techniques at the atomic level with major insight into large scale processes including the long-term evolution of biomineral systems."

Patricia completed her BSc. and M.Sc. studies at Virginia Tech, USA (1981 and 1984, respectively) and earned her doctoral degree from Princeton, USA, in 1991. In the past 30 years, she has built an impressively successful research career at the crossroads of mineralogy, aqueous geochemistry, biochemistry, surface physics, and environmental science—first at Georgia Tech and since 2000 at Virginia Tech. Recognizing the critical role of interaction between rocks and biota in the critical zone, Professor Dove embarked on studying some of the least-understood aspects of that interaction, including the atomic-scale kinetics and molecular dynamics of dissolution and precipitation at mineral surfaces, and focused her research efforts on biologically relevant systems (quartz, amorphous silica, calcite, and amorphous $CaCO_3$). She pioneered the use of atomic force microscopy (AFM) for in-situ molecular imaging to observe crystal growth and resorption under carefully controlled conditions (Dove and Hochella 1993; Dove and Platt 1996). The parameters of these experiments ranged from ambient temperature and pressure to methodologically challenging simulated environments, which required ingenious experimental apparatus, such as a hydrothermal mixed-flow reactor for direct measurements of reaction rates at steady-state conditions (Dove and Crerar 1990) and fluid-tapping AFM for studying microbial interactions with minerals (Grantham and Dove 1996). This work was foundational to constraining the effects of physico-chemical parameters on the kinetics of crystal growth and dissolution, and to the development of quantitative molecular models describing these processes in surficial, hydrothermal and bio-mediated environments (e.g., Dove, 2010; Dove et al., 2008, 2019). Another important outcome of Professor Dove's research was the collaborative discovery of crystallization by particle attachment (De Yoreo et al. 2015). This "non-classical" crystallization mechanism has since been documented increasingly in synthetic and natural systems, yielding over 170 citations of the original publication annually! These papers have far-reaching implications, not only for our understanding of how minerals form and dissolve but also for the interpretation of rock textures, paleoclimate reconstructions, evolutionary biology, and such practically important areas as nanotechnology and crystal design. Professor Dove's outstanding contribution to science has been recognized through many awards and honors, including the F.W. Clarke Medal from the Geochemical Society (1996); Dana Medal from the Mineralogical Society of America (2014); fellowships with the Mineralogical Society of America (2000), American Geophysical Union (2008), and Geochemical Society (2010); and the US Department of Energy Best University Research Award (1999 and 2005).

Professor Dove is an award-winning educator and promoter of science, who has shared her passion for biomineralogy with hundreds of university and school students through the National Science Foundation programs, Virginia Tech's CurVinci Living Learning Communities, Kids Tech, and other outreach platforms. At Georgia and Virginia Techs, she has developed and taught an impressive spectrum of courses, from *Resources of the Earth* to *Oceanography* and *Biomimetic Materials and Design*.

We congratulate Professor Dove on this prestigious award and look forward to reading about her new exciting discoveries in biomineralogy and beyond!

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Dove PM, Han N, Wallace AF, De Yoreo JJ (2008) Kinetics of amorphous silica dissolution and the paradox of the silica polymorphs. Proceedings of the National Academy of Sciences 105: 9903-9908, doi: 10.1073/pnas.080379810

Dove PM, Hochella MF (1993) Calcite precipitation mechanisms and inhibition by orthophosphate: in situ observations by scanning force microscopy. Geochimica et Cosmochimica Acta 57: 705-714, doi: 10.1016/0016-7037(93)90381-6

Dove PM, Platt FM (1996) Compatible real-time reaction rates of mineral dissolution by atomic force microscopy. chemical geology 127: 331-338, doi: 10.1016/0009-2541(95)00127-1

Grantham ME, Dove PM (1996) Investigation of bacterial-mineral interactions using Fluid Trapping Mode^{TM} atomic force microscopy. Geochimica et Cosmochimica Acta 60: 2473-2480, doi: 10.1016/0016-7037(96)00155-X

MINERAL OF THE YEAR AWARD

The IMA is pleased to announce that for 2021, the "Mineral of the Year" award has been assigned to **seaborgite**. The mineral was found and fully characterized by a research team led by Anthony R. Kampf, from the Mineral Sciences Department of the Natural History Museum of Los Angeles County, Los Angeles, California, USA (Kampf et al., 2021).

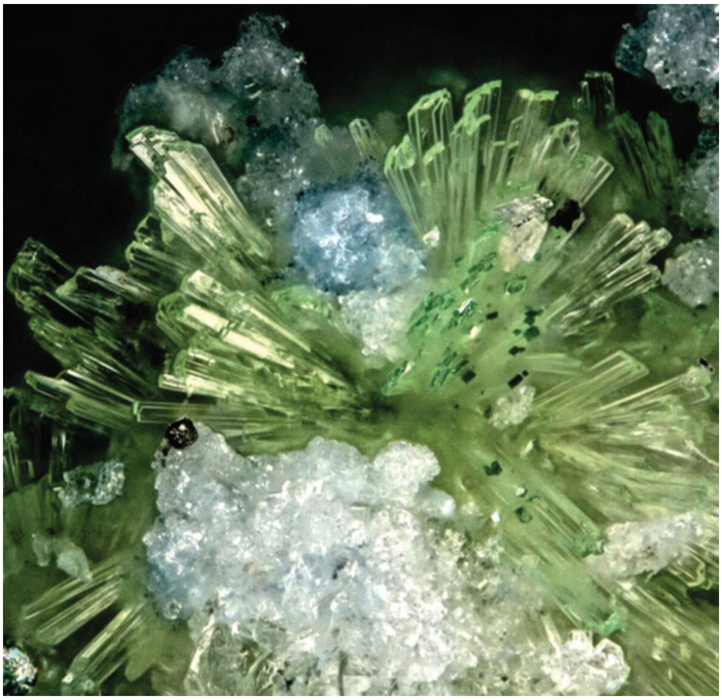

Figure 1 Diverging group of bladed seaborgite crystals (associated with ferrinatrite)

Seaborgite was found in the Blue Lizard mine, Red Canyon, White Canyon District, San Juan Co., Utah, USA, where it occurs on a thick crust of gypsum overlaying a matrix comprising mostly quartz. Associated phases are copiapite, ferrinatrite, ivsite, metavoltine, römerite, and other currently unknown minerals. Seaborgite occurs as attractive bladed crystals of light-yellow color up to 0.2 mm in length. Crystals typically occur in radiating sprays (Fig. 1). The ideal chemical formula of seaborgite is $LiNa_6K_2(UO_2)(SO_4)_5(SO_3OH)(H_2O)$; hence, it is an uranyl sulfate mineral. Seaborgite is the only known mineral species containing both Li and U as species-forming elements, and it is also one of very few minerals containing three distinct alkali metals.

Seaborgite is triclinic, with space group $P\bar{1}$, and unit cell parameters a = 5.4511(4) Å, b = 14.4870(12) Å, c = 15.8735(15) Å, α = 76.295(5)°, β = 81.439(6)°, and γ = 85.511(6)°. Its crystal structure has been determined by single-crystal X-ray diffraction methods to R = 3.77%. The structure of seaborgite is new and unprecedented, although it is based on the same uranyl sulfate cluster that is topologically identical to the one in the crystal structure of bluelizardite.

The mineral was named after Glenn Seaborg (1912–1999), an American chemist who was involved in the synthesis, discovery, and investigation of ten transuranium elements, including seaborgium. These studies led him to win the 1951 Nobel Prize in Chemistry.

Seaborgite is the third "Mineral of the Year" with its type locality in the USA. The previous winners were ophirite (2014, from the Ophir mine in Utah) and rowleyite (2017, from the Rowley mine in Arizona). The Blue Lizard mine was a prolific mineralogical site and the type locality for 22 other mineral species besides seaborgite.

The full description of the new mineral is available courtesy of the American Mineralogist from https://pubs.geoscienceworld.org/msa/ammin/article/106/1/105/593632/Seaborgite-LiNa6K2-UO2-SO4-5-SO3OH-H2O-the-First?guestAccessKey=195c8c0d-8405-407e-8990-0f002e75bade

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Kampf AR, and 5 coauthors (2021) Seaborgite, $LiNa_6K_2(UO_2)(SO_4)_5(SO_3OH)(H_2O)$, the first uranyl mineral containing lithium. American Mineralogist 106: 105-111, doi: 10.2138/am-2020-7540

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APPLIED GEOCHEMISTRY EXCELLENCE IN REVIEW AWARDS

Since the founding of *Applied Geochemistry* in 1986, many outstanding reviewers have helped shape our Society's journal and our success as a Society. We are indebted to those contributions, and starting last year, we began highlighting the reviewers who deserve extra recognition. The editorial board of *Applied Geochemistry* launched our annual "Excellence in Review Award" to recognize the dedicated community of expert reviewers inside and outside of our organization. We offer a big THANK YOU to all our awardees, and congratulations!

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LianGe Zheng – Energy Geosciences Division, Lawrence Berkeley National Lab, USA

International response to COVID-19 has resulted in scientific meetings being canceled or postponed. Check meeting web pages for ongoing updates.

2022

September 11–14 **22nd Congress of the Carpathian-Balkan Geological Association**, Plovdiv, Bulgaria. Web page: cbga2022.geology.bas.bg/.

September 11–15 **GeoMinKöln 2022**, Cologne, Germany. Web page: www.geominkoeln2022.de/

September 12–15 **Earth Mantle Workshop (EMAW)**, Toulouse, France. Web page: emaw2021.sciencesconf.org/.

September 18–23 **Europlanet Science Congress 2022**, Granada, Spain. Web page: www.epsc2022.eu/.

September 19–23 **Chapman Conference: Distributed Volcanism and Distributed Volcanic Hazards**, Flagstaff, AZ, USA. Web page: www.agu.org/Chapmans-Distributed-Volcanism.

October 9–12 **Geological Society of America National Meeting**, Denver, CO, USA. Web page: community.geosociety.org/gsa2022/home.

October 9–12 **Materials Science and Technology 2022**, Pittsburgh, PA, USA. Web page: www.matscitech.org/MST22.

November 27 – December 2 **MRS Fall Meeting**, Boston, MA, USA. Web page: https://www.mrs.org/meetings-events/fall-meetings-exhibits/2022-mrs-fall-meeting-exhibit

December 12–16 **AGU Fall Meeting**, Chicago, IL, USA. Web page: www.agu.org/Events/Meetings/Fall-Meeting-2022.

2023

January 9–11 **1st Workshop on Ices in the Solar System: A Volatile Excursion from Mercury and the Moon to the Kuiper Belt and Beyond**, Montreal, Canada. Web page: www.hou.usra.edu/meetings/ices2023/

January 22–27 **47th International Conference and Expo on Advanced Ceramics and Composites (ICACC2023)**, Daytona Beach, FL, USA. Web page: ceramics.org/event/47th-international-conference-and-expo-on-advanced-ceramics-and-composites-icacc2023.

January 30 – February 3 **IAVCEI Meeting**, Rotorua, New Zealand. Web page: confer.eventsair.com/iavcei2023/.

February 23 **41st Tucson Mineral Symposium**, Tucson, AZ, USA. Web page: www.friendsofmineralogy.org/call-for-papers/.

February 26 – March 2 **Microscopy Conference**, Darmstadt, Germany. Web page: https://www.microscopy-conference.de/.

March 13–17 **54th Lunar and Planetary Science Conference**, Houston, TX, USA. Web page: www.hou.usra.edu/meetings/lpsc2023/.

March 26–30 **American Chemical Society Spring Meeting, Indianapolis, IN, USA**. Web page: www.acs.org/content/acs/en/meetings/acs-meetings/about/future-meetings.html

April 10–14 **MRS Spring Meeting**, San Francisco, CA, USA. Web page: www.mrs.org/meetings-events/spring-meetings-exhibits/2023-mrs-spring-meeting.

April 23–28 **EGU General Assembly 2023**, Vienna, Austria. Web page: forthcoming.

May 4–7 **4th International Planetary Caves Conference**, Lanzarote, Spain. Web page: www.hou.usra.edu/meetings/4thcaves2023/.

May 20–25 **Clay Minerals Society Meeting**, Austin, TX, USA. Web page: forthcoming.

May 24–27 **Geological Association of Canada – Mineralogical Association of Canada Annual Meeting**, Sudbury, Ontario, Canada. Web page: event.fourwaves.com/Sudbury2023/pages.

June 12–15 **XVIII International Symposium on Experimental Mineralogy, Petrology and Geochemistry**, University of Milano, Italy. Web page: www.empg2023.it.

July 9–12 **2023 Goldschmidt Conference**, Lyon, France. Web page forthcoming.

July 23–27 **Microscopy & Microanalysis 2023**, Minneapolis, MN, USA. Web page forthcoming.

July 24–27 **EuroClay 2023**, Bari, Italy. Web page: euroclay.aipea.org/.

August 2023 **86th Annual Meeting of the Meteoritical Society**, Los Angeles, CA USA. Website forthcoming.

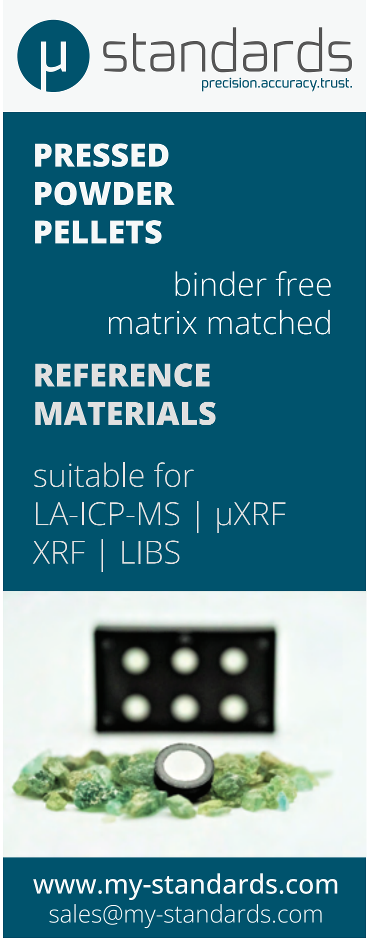
August 13–17 **American Chemical Society Fall Meeting**, San Francisco, CA, USA. Web page: www.acs.org/content/acs/en/meetings/acs-meetings/about/future-meetings.html.

October 15–18 **Geological Society of America National Meeting**, Pittsburgh, PA, USA. Web page: forthcoming.

November 26 – December 1 **MRS Fall Meeting**, Boston, MA, USA. Web page: www.mrs.org/meetings-events/fall-meetings-exhibits/2023-mrs-fall-meeting.

December 11–15 **AGU Fall Meeting**, San Francisco, CA, USA. Web page: forthcoming.

The meetings convened by the societies participating in *Elements* are highlighted in yellow. This meetings calendar was compiled by Andrea Koziol. To get meeting information listed, please contact her at akoziol1@udayton.edu



Inform *Elements* readers about upcoming short courses, workshops, meetings, and conferences.

Contact **Andrea Koziol (akoziol1@udayton.edu)** and **Esther Posner (editorialteam.elements@gmail.com)**

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geochemical society

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DIAMOND: GENESIS, MINERALOGY AND GEOCHEMISTRY

Wednesday 26 & Thursday 27 October 2022
9 am US eastern time – 5 pm US eastern time

with topics covered in
Reviews in Mineralogy and Geochemistry
Volume 88

For details on the program, fees & registration, go to:
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Earth Science for a Sustainable World

EARTH SCIENCE WEEK

This map shows the locations of a sample of initiatives that illustrate how the geosciences support specific Sustainable Development Goals (SDGs). Information about initiatives in these locations is provided through ArcGIS StoryMaps (see poster back).

Geoscience Supports the United Nations Sustainable Development Goals

www.earthsciweek.org

SDG 2: ZERO HUNGER

Chicago, Illinois, USA — Innovative urban farming techniques expand agriculture and increase access to food while reducing human impacts on the environment. Urban farming projects are also occurring in New York City, New York, and Detroit, Michigan.

SDG 6: CLEAN WATER AND SANITATION

Santa Monica, California, USA — Urban Waters Learning Network (UWLN) engages communities in the restoration of waterways and improving urban water quality. Other UWLN restoration projects take place in Denver, Colorado, and Matawan, New Jersey.

SDG 7: AFFORDABLE AND CLEAN ENERGY

Cerro Pabellon, Chile — Multiple data sources have been used to locate areas that could harness and benefit from the use of geothermal energy as a renewable energy source. There is also data from Paraguay, Argentina, and Bolivia that supports the use of geothermal energy.

SDG 11: SUSTAINABLE CITIES AND COMMUNITIES

Sydney, Australia — Urban greening has occurred over the past three decades which has resulted in benefits to both the environment and human health. There are still improvements to be made and targets to reach in the future.

SDG 12: RESPONSIBLE CONSUMPTION AND PRODUCTION

Ningde, China — One of the largest lithium-ion battery manufacturing plants uses raw materials sourced from northern China, the Democratic Republic of the Congo, Chile, and Australia to produce rechargeable batteries. Recycling of lithium-ion batteries reduces the need for new raw materials.

SDG 13: CLIMATE ACTION

Hokkaido, Japan — Natural and artificial wetlands used as rice farms could help combat climate change by increasing biodiversity and providing material for biofuel. Urbanization and modernization of farming techniques may impact the future of rice farms.

SDG 14: LIFE BELOW WATER

Illes Medes, Spain — The Marine Ecosystem Restoration in Changing European Seas (MERCES) Project works to restore marine ecosystems and populations that have been negatively impacted by human activity. Illes Medes houses 9 of the 128 MERCES project sites across 12 European countries.

SDG 15: LIFE ON LAND

Kinshasa, Democratic Republic of the Congo — Environmental "hot spots" within tropical forests affected by deforestation are identified using quantitative and spatial data. Actions are being taken to reduce the destruction. Mitigation efforts are also taking place in Brazil and Indonesia.

After reviewing these initiatives, think about additional ways the geosciences can support these SDGs and others shown below.

Map: USGS/J. Cody, using an Esri dataset with data from Airbus, USGS, NGA, NASA, NOAA, CGIAR, GEBCO, NCEAS, NLS, OS, NMA, Geodatastyrelsen, GSA, GSI and the GIS User Community.

https://sdgs.un.org/goals

Find all this and more at www.earthsciweek.org

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Specific materials shown here are not necessarily included in the Earth Science Week 2022 Toolkit.