Elements

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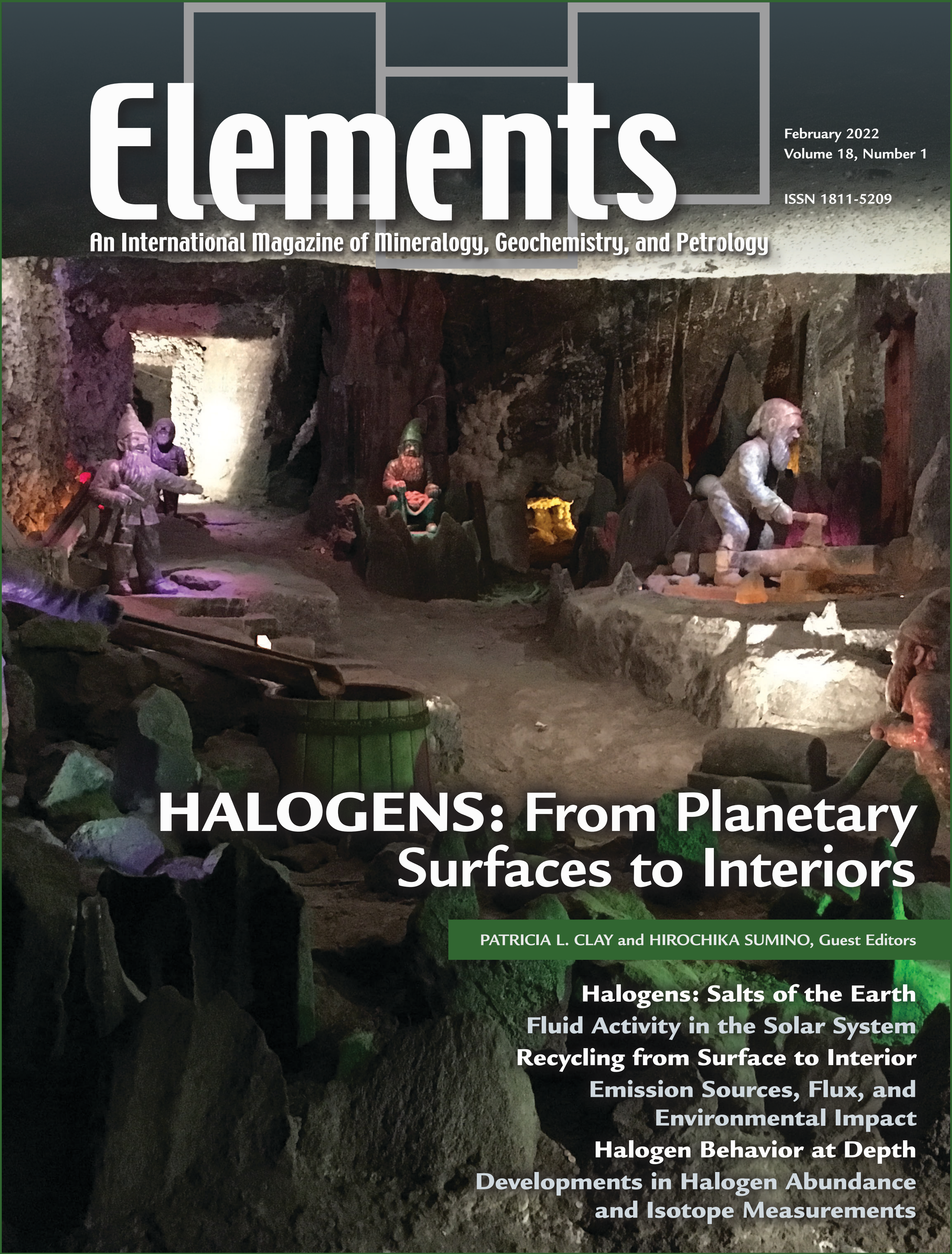

HALOGENS: From Planetary Surfaces to Interiors

PATRICIA L. CLAY and HIROCHIKA SUMINO, Guest Editors

Halogens: Salts of the Earth
Fluid Activity in the Solar System
Recycling from Surface to Interior
Emission Sources, Flux, and Environmental Impact
Halogen Behavior at Depth
Developments in Halogen Abundance and Isotope Measurements

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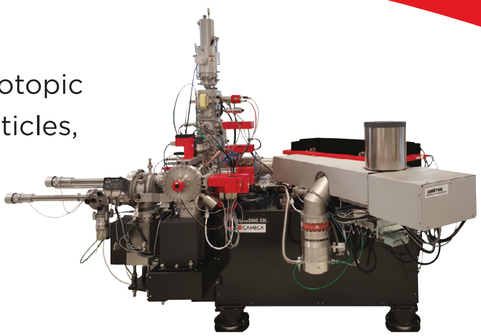

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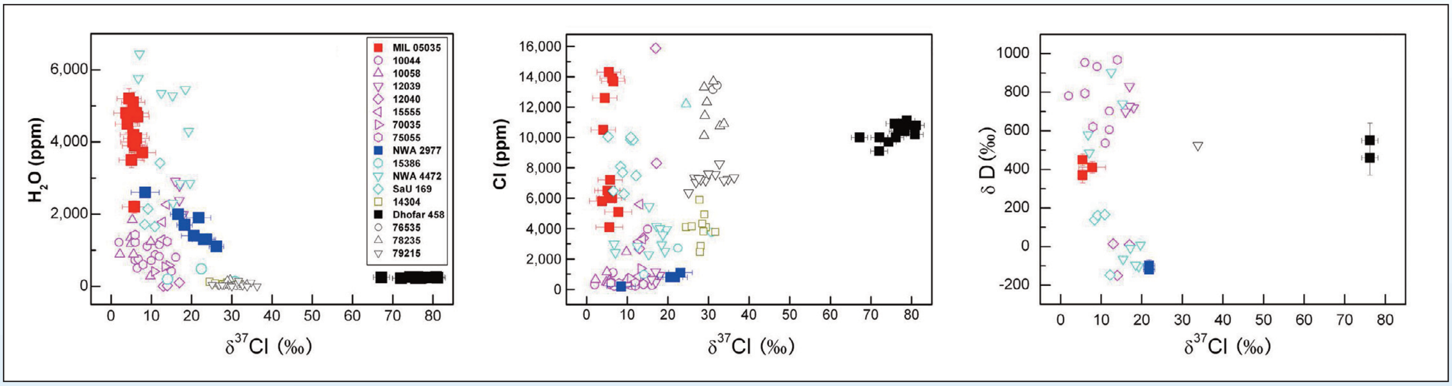
Measuring volatile content and chlorine isotope compositions of lunar apatite grains with NanoSIMS 50L, scientists explored the enigmatic provenance of the elevated δ^{37}Cl content in lunar apatite.



NanoSIMS measurements of H_2O content, Cl content, and δD versus δ^{37}Cl for lunar apatite from MIL 05035, NWA 2977, and Dhofar 458. Data from the literature (hollow symbols) are plotted for comparison. Red and magenta symbols represent mare basalts; blue and cyan symbols are KREEP-bearing basalts; black and grey symbols are highland rocks; and 14304 is a very high-K basalt. No apparent correlation can be observed among δ^{37}Cl, δD, and Cl content. *Data acquired on NanoSIMS 50L at Caltech. From Wang et. al. An extremely heavy chlorine reservoir in the Moon: Insights from the apatite in lunar meteorites. Nature Scientific Reports 9:5727 (2019).*

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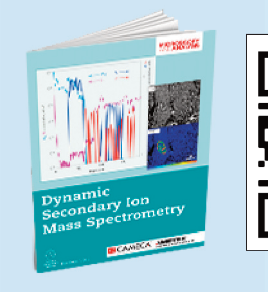

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Salt-carved sculptures in the Wieliczka Salt Mine (Poland) PHOTO: HIROCHIKA SUMINO.

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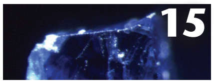

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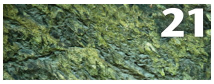

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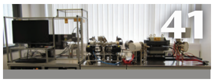

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Elements is published jointly by the Mineralogical Society of America, the Mineralogical Society of the UK and Ireland, the Mineralogical Association of Canada, the Geochemical Society, The Clay Minerals Society, the European Association of Geochemistry, 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.

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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

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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

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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.

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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.

BEWARE THE BROMIDES

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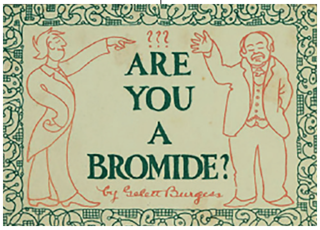
Becky Lange

In this issue of *Elements*, we are shown how the four halogens (F, Cl, Br, I) “punch well above their weight” in a whole plethora of Earth and planetary processes, from the atmosphere down to the core. This led me to wonder when each of us first became aware of the role of these trace elements in our daily lives. For myself, it was in childhood. Not necessarily the fluoride in toothpaste, which has greatly reduced cavities, nor iodized table salt, a boon for our thyroids. I was oblivious to such health-related matters as a kid. Rather, it was the intense burning of my eyes that followed countless hours of summer fun in strongly chlorinated public pools. To this day, my Pavlovian response to the pungent smell of bleach is a fond flood of childhood memories.



Cover image from *Are You a Bromide?* (Burgess 1906).

With respect to Br, I was not meaningfully introduced to the term “bromide” until I was an undergraduate at UC Berkeley. Not in chemistry lab, but rather in a Comparative Literature course. The term “**bromide!**” was scrawled in red, repeatedly, all over my essay on Moby Dick. Apparently, my deep, philosophical musings on Ahab’s obsessive quest were found to be “trite and unoriginal”. Oh dear! A well-earned, if stinging, instruction on how Br-bearing sedatives (no longer available due to their toxicity) entered the English lexicon to refer to boring and meaningless expressions, in large part due to Gelett Burgess’ 1906 essay, *Are You a Bromide*?

Although bromine solutions were not a feature of my undergraduate chemistry labs, there was plenty of hydrochloric acid (HCl) to be had. It was not until graduate school that I became familiar with the more dangerous halogen acid, HF. Although the weaker of the two acids, it is that very trait, namely HF’s low dissociation constant, that enables it to penetrate tissue (i.e., skin, eyeballs, lungs, etc.) as a neutral lipid-soluble molecule, where it can then do significant damage. As part of my pursuit of silicate-melt density data, I spent hundreds of days in the late 1980s cleaning out silicate-coated platinum crucibles with vast quantities of HF. This was an era when laboratory safety protocols were nowhere near what they should have been. Although I carefully donned a flimsy (and ineffective) pair of vinyl gloves when handling the HF, I watched my PhD advisor cavalierly and deftly work with the stuff with bare hands. Now, my graduate students and I don full-blown hazmat attire when using HF in quantity: goggles, face shields, HF-protective aprons, thick gloves (which unfortunately reduces our dexterity when handling small beakers), gaiters, the lot. Those safety videos that feature severe HF burns are effective!

The 1980s was also when many of us became increasingly aware of the problem with chlorofluorocarbons (CFCs) and their destructive impact on Earth’s protective ozone (O_3) layer, subjecting all forms of life to dangerous levels of UV radiation. A decade earlier, the Molina and Rowland (1974) landmark paper predicted the breakdown of CFCs in the stratosphere and showed how one measly chlorine atom can efficiently destroy over 100,000 ozone molecules.

But scientific papers, even when they lead to Nobel prizes, do not move public opinion. What caught most people’s attention was the actual discovery in 1985 of a large ozone “hole” over Antarctica, which had formed far more rapidly than scientists had predicted. That the unrelated Chernobyl nuclear accident occurred the very next year may have contributed to public alarm over the ozone hole, owing to the frightening resonance the term “radiation damage” has in the collective public imagination, whatever the source – nuclear or solar.

Global action on curbing CFCs with the 1987 Montreal Protocol was surprisingly swift and united. It appears that two factors drove sustained success in healing our ozone layer in the ensuing decades: i) widespread public alarm and ii) business opportunities to profit from CFC substitutes. Many have asked if the recipe for success in curbing CFCs can be applied to greenhouse emissions and our unfolding climate crisis.

Perhaps there are thin silver strands of hope that can be gleaned from otherwise dark news headlines over the past year. The sheer number of record-breaking, climate-related disasters has left virtually no part of the globe unscathed and it’s going to get a lot worse. Has the devastation been enough to move public opinion on the urgent need to transition from fossil fuels? Or is more suffering required? With respect to profitable green technologies, it is noteworthy that today’s richest person in the world (and in history) vaulted to that status just last year due to the success of Tesla’s electric cars. Some news headlines suggest that high-temperature fusion power plants may be attainable within a decade or two; others feature transformative, cheap methods to store energy (e.g., Form Energy; Energy Vault). Even if these specific examples don’t quickly come to fruition, at least substantial investment in green technologies is accelerating. As noted by Euripides, “Nothing has greater strength than dire necessity”. (Oops, I hope that’s not a bromide!)

Becky Lange
Principal Editor

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Molina MJ, Rowland FS (1974) Stratospheric sink for chlorofluoromethanes: chlorine atom-catalysed destruction of ozone. Nature 249: 810-812, doi: 10.1038/249810a0

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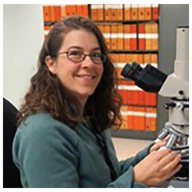
ABOUT THIS ISSUE

In this issue, we follow the halogen group elements (fluorine, chlorine, bromine, and iodine) from the Earth's interior to surface—and even beyond! In a similar vein to two previous *Elements* issues that also explored groups of elements united by common properties (Rare Earth Elements; October 2012 and Platinum Group Elements; August 2008), this issue similarly showcases the wide diversity of research that is encompassed by halogen mineralogy and geochemistry. Over the last several decades, the halogens have increasingly come into the spotlight, possibly due to improving methods for measuring ultra-low abundance bromine and iodine in geologic materials, as well as isotopes of chlorine and bromine. The result of this increased enthusiasm for halogens is deftly covered over six articles by this issue's authors—from halogens in Earth and planetary systems to experimental petrology and analytical developments, there truly is something for everyone.

This issue further highlights how halogens are relevant to society and human health, ranging from their role as essential elements to human health, to the more detrimental impacts of halogen emissions and radionuclide contamination. Eleven years ago, the Fukushima Daiichi Nuclear incident occurred on March 11, 2011, which prompted an *Elements* issue (Fukushima Daiichi; June 2012) the following year. On the ten-year anniversary of this issue, we revisit the specific impact of iodine radionuclide contamination in this issues' Perspective by Takeshi Ohno.

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

RISING LEADERSHIP



Dear *Elements* readers,

I would like to introduce myself as the next Chair of the *Elements* Executive Committee. First, however, I'd like to thank our outgoing chair, Dan Frost, for his years of service to *Elements*, and for a job well done.

I have been working with *Elements* since 2011 as the representative for the Meteoritical Society. In that time I have compiled the Met Soc Society news and worked on the CosmoElements feature (3x per year). I also co-edited the "Asteroids" issue in 2014. Working with *Elements* has been a great way to stay involved with the greater geologic community, both by working with representatives from other societies all over the world, and by reading the issues as they come out. As we all know, once we leave formal schooling it becomes much more difficult to stay current on the broader aspects of one's field, and *Elements* is a great way to overcome that hurdle. In addition, it has allowed me to become more involved in my society, and to get to know more of its members than I would have otherwise, including both the newer generation of researchers and those in more advanced stages of their careers.

Since 2008, I have been a research geologist and the curator of Antarctic Meteorites at the Smithsonian Institution's National Museum of Natural History in Washington, DC, USA. My research centers around the U.S. Antarctic Meteorite Collection, and has included work on a wide variety of meteorites and meteorite types, including the process of impact and how it has affected the evolution of the planetary materials within our Solar System. As a bonus of working in a large museum collection, I have been able to work on newly discovered meteorites and have also had the privilege of being able to delve into some of the history of our meteorite collection. I spend a significant portion of my time mentoring interns and fellows, as well conducting outreach to students and the greater public and *Elements* has been a big part of that outreach for me for over a decade.

I look forward to working with you to keep *Elements* moving into the future as the high-quality publication we've all come to know and love.

Sincerely,
Catherine (Cari) Corrigan

WELCOMING JANNE BLICHERT-TOFT

We are delighted to welcome Janne Blichert-Toft as the 2022–2024 geochemistry principal editor with *Elements*. Janne is an isotope geochemist and has served as a research director at CNRS at the Ecole Normale Supérieure de Lyon (France) since 1997. Janne completed her Ph.D. at the University of Copenhagen (Denmark) in 1993 and her Habilitation à Diriger des Recherches at Université Claude Bernard Lyon 1 (France) in 2000. Her research focuses on radiogenic and stable isotopes and dating techniques to constrain the origin and evolution of the Earth and other planetary bodies in the Solar System, extending also into crude oil provenance, geoarchaeology, and numismatics. She further applies isotopic data from archaeological settings and artifacts to address controversial historical questions, such as why the Roman empire collapsed, how Carthage survived the Punic wars, and what were the origins of the silver looted by Alexander the Great in his conquest of the Persian Empire. Janne is currently working with the guest editors of the "Cement and Concrete: From the Romans to Mars" issue, which is scheduled for October 2022.

NEW FACES, NEW FEATURE

Please join us in warmly welcoming Esther Posner to the *Elements* Editorial Team. Esther earned her M.S. in Geosciences at the University of Arizona (USA) in 2012 and Ph.D. in Experimental Geoscience at the Bayerisches Geoinstitut at the Universität Bayreuth (Germany) in 2017. Esther's passion for geoscience is uniquely complimented by her flair for the written word: she is an internationally acclaimed academic editor—having professionally edited more than 1000 scientific manuscripts—and is also an award-winning performance poet and composer. With Esther's oversight, *Elements* is defining a new platform for geoscience-inspired poetry/prose in our bi-annual **GeoScience Slam** feature. Be sure not to miss her rhyming rendition of the geological time scale on page 70 of this issue.

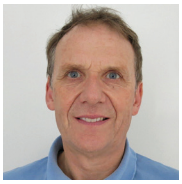
Meet the Authors

Alessandro Aiuppa is a professor of geochemistry and volcanology at the Università di Palermo, Italy. His current research focusses on volcanic gas chemistry, with special emphasis on the cycling of volatiles in and out the planet's interior, magmatic degassing processes, the role of gases in driving explosive basaltic volcanism, and volcanic gas–based instrumental volcano monitoring.

Jaime D. Barnes is a professor in the Department of Geological Sciences (Jackson School of Geosciences) at the University of Texas at Austin. She completed her M.S., Ph.D., and post-doctoral research at the University of New Mexico. Jaime uses stable isotopes as geochemical tracers of fluids in various tectonic and geologic settings from the upper mantle, the oceanic lithosphere, the subducting plate interface, and volcanic systems. Much of her research involves volatile cycling, metamorphism, and volatile transport in subduction zones, serpentinization, and fluid–rock interactions and metasomatism in high-temperature environments with the overarching goal to improve our knowledge of the chemical evolution of the Earth.

Jessica Barnes is an assistant professor of cosmochemistry in the Lunar and Planetary Laboratory at the University of Arizona. Her interests include geochemistry, geochronology, mineralogy, petrology, and planetary volcanology. Her research focuses on the geochemical evolution of the Moon, and the history and origins of volatiles in the Moon, Mars, and asteroids. Jessica is invested in the development of secondary ion mass spectrometry protocols in support of studies of extraterrestrial materials. She is a collaborator on NASA's OSIRIS-REx asteroid sample return mission, Lead Scientist for the Sample Elements and Isotopes Working Group, and is preparing her laboratory for the analysis of returned material from asteroid Bennu.

Hélène Bureau is Director of Research at the French National Center of Research CNRS, working at the Institut de Minéralogie, de physique des Matériaux et de Cosmochimie at Sorbonne Université Paris (France). Her research interests include high-pressure and high-temperature experimental petrology and geochemistry, mineralogy, and natural sample investigations of the Earth's deep volatile cycling. She is particularly interested in hydrogen and halogen storage in the deep Earth and in natural diamond growth processes in the Earth's mantle.



Ray Burgess is a professor of isotope geochemistry at the University of Manchester, UK. He obtained an undergraduate degree in geology from the University of Southampton and a PhD at the Open University where his research involved investigating sulfur isotope variations in meteorites. He then switched research interests to noble gas isotopes and helped to develop the neutron irradiation technique for measuring halogens during postdoctoral spells at University of Sheffield and SUERC, Glasgow before moving to Manchester nearly 30 years ago. In Manchester, he combines noble gas isotopes with halogens to investigate the origin, movement, and interaction of fluids in the Earth's crust and mantle.

Anita Cadoux is a volcanologist with expertise in field studies, petrology, and geochemistry. She obtained her PhD at the University Paris Sud XI (France) studying the geochronology and petrogenesis of silicic volcanism in central Italy (K-Ar dating, trace and isotope geochemistry). Since then, her research interests and tools have broadened to explore pre-eruptive magma storage conditions (in-situ analysis of dissolved gases in volcanic glasses, experimental petrology), the behaviour of halogens (notably bromine) in magmas, and the impact of volcanogenic halogens on atmospheric chemistry. She is an associate editor of the American Mineralogist Special Collection "Halogens in Planetary Systems".

Patricia Clay is a UK Research and Innovation Future Leaders Fellow at the University of Manchester (UK). She completed her B.S. and M.A. in the US (Syracuse University and Boston University, respectively) before moving to the UK to pursue a PhD at the Open University, which she completed in 2010. She is interested in the origin of volatile elements in the terrestrial planets. In particular, she studies how volatiles are stored in, and distributed between, geochemical reservoirs to better understand their role in planetary evolution. To achieve this, she uses the noble gas and halogen group elements as geochemical tracers in a variety of geologic environments, linking geochemical measurements with petrographic observation, mineralogy, and experimental petrology.

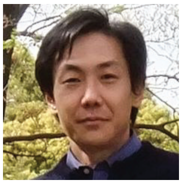
Mitsuru Ebihara is a professor of Earth Sciences at Waseda University (Japan). After completing his PhD (chemistry) at the University of Tokyo in 1979, he worked as a postdoc with Professor Edward Anders at the University of Chicago (USA) from 1979 to 1982, when he moved to Gunma University (Japan). He then moved to Tokyo Metropolitan University in 1988 and took mandatory retirement in 2017, becoming an emeritus professor. In 2018, he became a professor at Waseda University. In 2008 and 2021, he received society awards of Geochemical Society of Japan and Japan Society of Nuclear and Radiochemical Sciences, respectively, for both of which he has served as president. In 1989, he was appointed as a fellow of the Meteoritical Society. His research area is cosmochemistry, for which he developed analytical procedures for determining elemental contents in meteorites and lunar samples using neutron activation and ICP-MS.

Hans Eggenkamp is a scientific associate at the Department of Petrology and Mineral Resources of the Eberhard-Karls-Universität-Tübingen (Germany). He obtained his PhD from Utrecht University (The Netherlands). His research interest and scientific expertise focus on the geochemistry of stable chlorine and bromine isotopes. He studied these isotope systems during his PhD and during stays at the University of Reading (UK), the Instituto Superior Técnico (Lisbon, Portugal), the Institut de Physique du Globe de Paris (France), and finally in Tübingen. He is the author of the handbook "The Geochemistry of Stable Chlorine and Bromine Isotopes", published by Springer. He applies his knowledge on stable halogen isotope geochemistry mostly to studies on groundwater, salt, and more recently magmatic systems. He has worked on geothermal energy solutions for industrial and agricultural heating, as well as isotopic and chromatographic analysis solutions for the oil and gas exploration industry.

Bastian Joachim-Mrosko is an assistant professor at the University of Innsbruck (Austria). He specializes in high P-T experiments and likes to combine mineralogical, petrological, and geochemical approaches to investigate the abundance, distribution, storage, and transport of volatiles in the Earth's crust, mantle, and core. He is also interested in the effect of volatiles on physical and chemical processes such as the dynamics of metamorphic and metasomatic reactions. He studied Earth Sciences at the Leibniz University Hannover and did his PhD at the GFZ German Research Centre for Geosciences in Potsdam and TU Berlin (both in Germany) followed by several postdoctoral appointments at the University of Vienna (Austria), the University of Manchester, and the University of Oxford (both UK).

Tatsuhiko Kawamoto is a professor of petrology and geochemistry at Shizuoka University (Japan). After completing his PhD at Kyoto (Japan), he enjoyed a postdoc at Tokyo (Japan), Tempe (USA), and Bayreuth (Germany). He worked on magmas and aqueous fluids under high-pressure and high-temperature conditions at the Institute of Geothermal Sciences, Kyoto University (Japan); he took a sabbatical leave to Paris and Clermont-Ferrand (France). Since he happened to find seawater-like saline fluid inclusions in Pinatubo mantle xenoliths, the importance of being salty in subduction-zone fluids has been his theme. He conducts hydrothermal experiments to learn about carbonation of ultramafic rocks, and often goes to the theaters.

Mark A. Kendrick is an associate professor of geochemistry at the University of Queensland (UQ). His research interests are focused on the origins of crustal fluids, mantle volatiles, and subduction zone processes, which he investigates using innovative combinations of halogen, noble gas, and trace element geochemistry and geochronology. Prior to joining UQ, he held research positions at the Australian National University and University of Melbourne including the Australian Research Council QEII and Future Fellowships. Before moving to Australia, Kendrick held a postdoctoral position at the Geological Survey of Norway and obtained his PhD from the University of Manchester.



Hirochika Sumino is a professor of geochemistry in the Research Center for Advanced Science and Technology at the University of Tokyo, Japan. He completed his M.S. and Ph.D. at the University of Tokyo, and investigates the origins and behavior of volatiles in the terrestrial mantle using highly sensitive noble gas mass spectrometry. Since learning a technique for trace halogen determination that combines neutron irradiation and noble gas mass spectrometry while visiting the University of Manchester, UK in 2006, he has applied this method to decipher the origin of water subducted into the mantle at subduction zones.

Susann Tegtmeier is an assistant professor at the University of Saskatchewan (Canada), working in the field of atmospheric chemistry-climate interactions. Her research explores Earth-system processes and interactions of the atmosphere with the marine and terrestrial biosphere based on observational and model data. One focus of her research program is on marine halogenated and sulfur-containing substances, their industrial and agricultural sources, as well as their current and future impact on atmospheric chemistry and climate.

Michael Zolensky is an astromaterials researcher and curator of Stardust, Hayabusa, and spacecraft micro-impact samples at NASA Johnson Space Center. He characterizes the chemical weathering record of asteroids and their associated meteorites, especially aqueous fluid inclusions, and the primitive mineralogy of comets. Among other activities, Mike led sample analysis teams for the Stardust comet coma dust return mission and the Hayabusa asteroid regolith sample return mission. He is now on the Hayabusa2 mission science team and the sample analysis working team for the Mars Moons eXploration Mission. He is the namesake of minor planet 6030/Zolensky and the mineral zolenskyite.

RADIOIODINE CONTAMINATION CAUSED BY THE FUKUSHIMA DAIICHI NUCLEAR POWER PLANT ACCIDENT

Takeshi Ohno[1]

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INTRODUCTION

The Great East Japan Earthquake and Tsunami happened on 11 March 2011, which caused the Fukushima Daiichi Nuclear Power Plant (FDNPP) accident. The accident resulted in a substantial release of radionuclides, including ^{131}I, ^{134}Cs, and ^{137}Cs, into the atmosphere, causing significant environmental contamination. This was a particular issue in many parts of eastern Japan, especially in the Fukushima Prefecture (Yoshida and Takahashi 2012). Among the above-mentioned radioactive isotopes, ^{131}I is one of the most critical radionuclides to be monitored after an accidental reactor release due to its tendency to accumulate in the human thyroid gland. Because of the short half-life of ^{131}I (8 days), it is difficult to determine its radioactivity within a few months after such an accident. Estimating the effective dose of released ^{131}I is important, but the lack of data on the deposition of ^{131}I immediately following such accidents makes retrospective dosimetry a challenge (Michel et al. 2005). This article summarizes what is known about the amount of ^{131}I released into the environment due to the Fukushima Daiichi Nuclear Power Plant accident and also introduces the Fukushima Health Management Survey Project for the long-term health care of the residents of Fukushima Prefecture.

RELEASE OF ^{131}I FROM THE FDNPP AND BEHAVIOR OF THE PLUME

Knowledge of the total ^{131}I released from the FDNPP accident is critical when estimating the exposure doses for Fukushima residents. However, it is difficult to obtain direct and accurate source information on the amount of ^{131}I released by the FDNPP accident. This is because the radiation monitors were affected by earthquakes and tsunamis, and because the core meltdown of several reactors caused various sources of release from the plant. For this reason, atmospheric dispersion simulations and environmental monitoring were adopted to estimate the ^{131}I release from the Fukushima accident. From this methodology, the total release amount was ~1.5 × 10^{17} Bq (Fig. 1) (Katata et al. 2015). Using the UNSCEAR dosimetry protocol, the total release of ^{131}I was ~1–5 × 10^{17} Bq (UNSCEAR 2014).

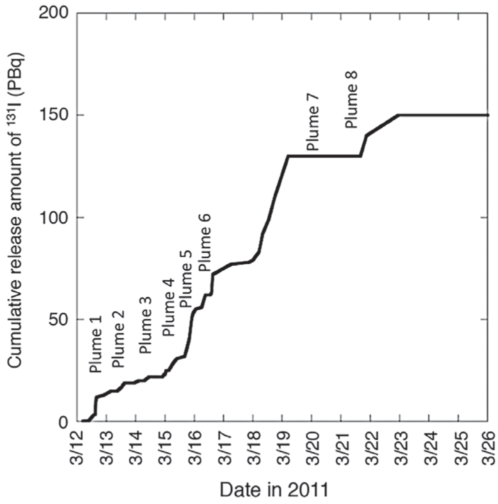

FIGURE 1 Temporal changes in the cumulative release of ^{131}I versus plume movement of the eight major releases during the Fukushima Daiichi Nuclear Power Plant accident. Plume 1 on afternoon of 12 March. Plume 2 on afternoon of 13 March. Plume 3 from noon on 14 March to afternoon of 15 March. Plume 4 from night of 14 March to afternoon of 15 March. Plume 5 from morning to evening of 15 March. Plume 6 from afternoon 15 March to morning of 16 March. Plume 7 on 20 March. Plume 8 on 21 March. DATA FROM KATATA ET AL. (2015).

The behavior of the contamination plume that contained ^{131}I was investigated using an atmospheric dispersion model based on the aforementioned information on the release and on measurements made at various locations (Katata et al. 2015). Tsuruta et al. (2019) summarized the transit periods of major plumes at the FDNPP and reported that the ratios of ^{131}I to ^{137}Cs in the radioactive plumes were divided into three groups: A, having a ratio of 10; B, having a ratio of 75; C, having a ratio of 360. The ratios in group C were much higher than those of groups A and B and were observed from the afternoon of 21 March 2011 to 25 March 2011 in Tokyo, 200 km from the plant. Tsuruta et al. (2019) pointed out that these high ^{131}I concentrations could have been released after emergency cooling water had been supplied to the FDNPP.

After the accident, ^{131}I levels of 210 Bq/kg on 22 March and 190 Bq/kg on 23 March were detected in tap water derived from the Kanamachi Water Treatment Plant in Tokyo, exceeding the provisional standard value of ^{131}I at 100 Bq/kg set by Japan's Ministry of Health, Labor and Welfare to restrict the intake of tap water by infants. This was probably due to the fact that the timing of the radioiodine plume reaching Tokyo coincided with a period of rainfall, and the rainwater containing radioiodine made its way into rivers which flowed into the water purification plant. In general, iodine exists in rainwater in the form of iodide ions (I^-) and iodate ions (IO_3^-), which are difficult to remove with activated carbon. This suggests that radioiodine in rainwater flowed into the river and was detected in the tap water after some degree of dilution. The Bureau of Waterworks of the Tokyo Metropolitan Government conducted an experiment to reduce the concentration of radioactive iodine by oxidizing iodide ions through chlorination and then adsorbing them on activated carbon (Ministry of Health, Labor and Welfare 2011).

ESTIMATING DEPOSITION IN SOIL OF ^{131}I RELEASED FROM THE FDNPP

In order to understand the dispersion of radionuclides, a large-scale soil sampling campaign was organized in June 2011 by the Ministry of Education, Culture, Sports, Science and Technology (MEXT) with the cooperation of many researchers from a variety of universities and institutes. Radiocaesium was detected at all locations, and deposition maps for these nuclides were constructed (Saito et al. 2014). In the case of ^{131}I, however, and because of its short half-life (8 days), there was not enough data to provide regional information on the deposition of ^{131}I.

Muramatsu et al. (2015) focused on the long-lived iodine isotope ^{129}I (half-life of 1.57 × 10^7 y), analyzed by accelerator mass spectrometry (AMS) from surface soil samples collected by the MEXT team in Fukushima Prefecture. In order to obtain information on the ^{129}I/^{131}I ratio released from the accident, the group determined ^{129}I concentrations in soil samples in which ^{131}I concentrations had been previously determined. Analytical results yielded a positive correlation ($R^2 = 0.82$) between the two radioiodine isotopes, and the atomic number ratio of ^{129}I/^{131}I was determined to be 21, after a decay correction from 11 March 2011. Miyake et al. (2015) reported that the ^{129}I/^{131}I in soil samples collected in Fukushima was 26.1 ± 5.8, which is in good agreement with the reported values. Based on these results, ^{129}I concentrations (Bq/kg) in approximately 400 soil samples were determined and the radionuclide deposition densities (Bq/m^2) of ^{131}I were then estimated so one could reconstruct a deposition map of ^{131}I (Fig. 2) (Muramatsu et al. 2015). It was found that the areas with high ^{131}I values (>5000 Bq/m^2) extended to the northwest and south. Compared to the contamination map of ^{137}Cs, the distribution of ^{131}I was different, and it was reported that ^{131}I/^{137}Cs tended to be higher in the south of the plant (Saito et al. 2014; Muramatsu et al. 2015).

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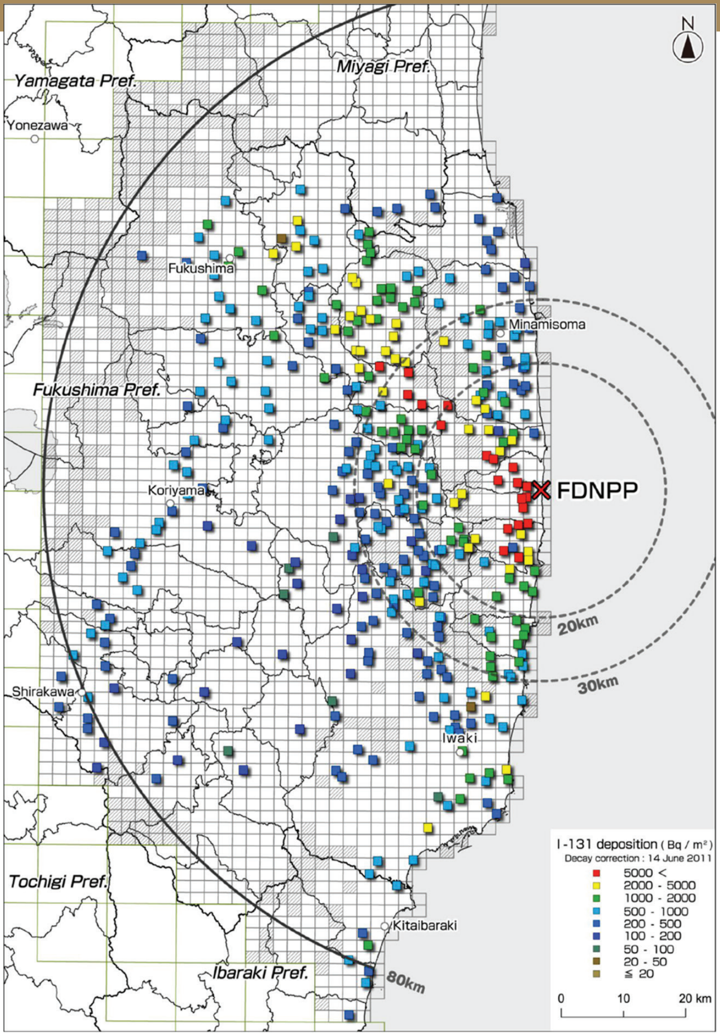

FIGURE 2 Deposition map of ^{131}I in Bq/m^2 as reconstructed from soil ^{129}I analyses in the Fukushima Prefecture.' USED WITH PERMISSION OF ELSEVIER FROM MURAMATSU ET AL. (2015).

THYROID CANCER AFTER THE FDNPP ACCIDENT

Fukushima Prefecture conducted the Fukushima Health Management Survey Project for the purpose of long-term health-care administration and medical early diagnosis and treatment for the prefecture residents. The large-scale ultrasound screening in Fukushima Prefecture demonstrated a high detection rate of thyroid cancer in young individuals, revealing 187 cases after testing ~300,000 subjects (Yamashita et al. 2018).

The exposure doses for the Fukushima residents were much lower than radiation doses from the accident at Chernobyl (Tokonami et al. 2012). There is no strong evidence that supports a causal relation between thyroid cancer and radiation exposure in Fukushima. However, recent studies report a positive correlation between the incidence of thyroid cancer, the air-dose rate, and ^{131}I in soils (FIG. 3) (Toki et al. 2020). The correlation between ^{131}I in soil and the incidence of thyroid cancer is very weak; therefore, the causal relation of thyroid cancer with radioiodine exposure in Fukushima is still controversial. It is very important when interpreting thyroid cancers in Fukushima to understand the causal relation between thyroid cancer and radiation exposure. Thus, future studies will be needed to avoid any misinterpretation of the high detection rate of childhood thyroid cancer.

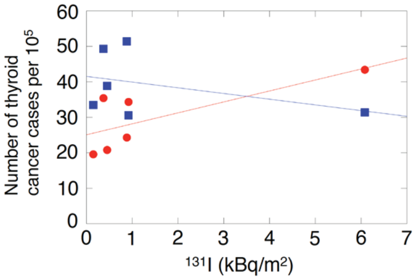

FIGURE 3 Thyroid cancer cases per 10,000 children observed in the Fukushima Health Management Survey as a function of the amount of radioactivity from ^{131}I in six selected areas. Symbols: blue squares = results of the preliminary baseline survey started in 2011; red circles = results of the full-scale survey started in 2014. DATA FROM TOKI ET AL. (2020).

CONCLUDING REMARKS

I started writing this article after returning from my field research in Fukushima. With the fifth wave of COVID-19 now under control in Japan, I was able to resume my fieldwork after almost two years. I am very grateful to the late Professor Yasuyuki Muramatsu. He was a leading researcher of radioiodine, and, after the FDNPP accident, he was appointed as an advisor to the Fukushima Prefecture. In April 2011, I joined Professor Muramatsu's laboratory as an assistant professor, and I learned from him not only about radioiodine research but also about behavior that is appropriate for a researcher. The researchers who engage in curiosity-driven research can be of use to society as experts in geochemistry when catastrophes occur. I feel that there is still much left for me to contribute. In particular, the behavior of ^{129}I in the ecosystem needs to be documented. The full-scale operation of the reprocessing facility in Japan is scheduled to start in 2022. Once the facility is operational, a large amount of ^{129}I will be released into the environment but in a safe and controlled manner. As a generation that experienced these events firsthand, it is important to pass on the knowledge we have gained to the next generation.

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Halogen-rich materials, (FROM LEFT) morishio or "piled salt", Blue John fluorite, a KBr plate, and iodine-rich seaweed.

Halogens: Salts of the Earth

Patricia L. Clay[1] and Hirochika Sumino[2]

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The halogen group elements (F, Cl, Br, and I) and the stable isotopes of Cl and Br collectively are powerful tracers of terrestrial volatile cycling. Individually, their distinct geochemical affinities inform on a variety of fluid-mediated and magmatic processes. They form a wide-range of halogen-bearing minerals whose composition reflects the source fluids from which they evaporated or crystallized. Fluorine's geochemical cycle is generally decoupled from that of the heavier Cl, Br, and I, which are concentrated into Earth's surface reservoirs. Throughout history, the salt-forming halogens have been integral to human health and are key constituents of many industries. These common elements have an important role in tracing geochemical processes across many geologic environments – from the surface to the deep planetary interior.

KEYWORDS: halogens; anions; halide minerals; evaporites; geochemical tracers; volatiles

INTRODUCTION

Fluorine (${}_{9}$F), chlorine (${}_{17}$Cl), bromine (${}_{35}$Br), and iodine (${}_{53}$I) collectively comprise the halogen group elements. The natural and short-lived radioactive halogen astatine (${}_{85}$At) and the synthetic halogen tennessine (${}_{117}$Ts) are not included in this review because they lack relevance to geologic systems. The group name "halogen" was aptly assigned by the Swedish chemist Jöns Jacob Berzelius in 1826, deriving from the Greek *háls* (salt) and *gen* (to form). The name refers to the readiness with which they form ionic salts of metallic elements, such as calcium, sodium, or magnesium. The halogens reside in Group 17 (formerly VIIa) of the periodic table and, as such, share common properties that define their behavior across different geologic environments and geochemical processes (Enghag 2004) (FIG. 1).

In his 1956 review of the geochemistry of the halogens, geochemist Carl W. Correns noted, "By far the greatest part of geochemical work is concerned with cations. It therefore seems desirable, for once in a way, to consider the behavior of anions." And indeed, the anionic halogens' role in a variety of geochemical systems is significant; more so, perhaps, than their relatively low abundance in most crustal and mantle minerals and bulk rocks would initially suggest. The halogens impact many of the physical and chemical processes that have shaped Earth's evolution. In magmatic systems, the halogens are important to volcanism through their influence on mantle melting (Aiuppa et al. 2009). When released to the atmosphere through volcanic emissions, oceanic aerosols (e.g., sea salt aerosols), or as anthropogenic halogen emissions they influence the environment both locally and globally (Pyle and Mather 2009; Broadley et al. 2018). Halogens also play a critical role in hydrothermal and metasomatic systems, acting as ligands that help to mobilize both base metals and precious metals during mineralization (Pirajno 2018).

IN THIS ISSUE

This issue explores the applications of halogen geochemistry to a wide range of geologic environments—from the surfaces of planets to the deep Earth. An overview of the important role that halogens play across natural systems is considered, from tracing important fluid–rock reactions in extraterrestrial environments (Barnes and Zolensky 2022 this issue), and the recycling of abundant surficial halogens into the Earth's mantle at subduction zones (Kendrick and Barnes 2022 this issue), to their subsequent return to the atmosphere through volcanic emissions and sea salt aerosols (Cadoux et al. 2022 this issue). The role that experimental petrology plays in shaping our understanding of halogen behavior at depth within the Earth, including applications to natural systems, is explored by Joachim-Mrosko et al. (2022 this issue). Finally, the variety of techniques capable of measuring halogen elements and isotopes, including important recent advances, is examined by Burgess et al. (2022 this issue).

COMMON ELEMENTS, COMMON PROPERTIES

Halogens are present in every terrestrial geochemical reservoir, from the surface to the deep Earth (FIG. 2). Our understanding of halogen abundance and behavior in these reservoirs, collected from measurements of natural samples and data from experimental determinations, is advancing, allowing for a comprehensive picture of terrestrial halogen geochemistry to be developed. The collective geochemical properties of the halogens, which changes in an orderly fashion from fluorine to iodine, define their geochemical behavior in the terrestrial planets (FIG. 1). These properties include measures of electronegativity, incompatibility (related to ionic radii), volatility, and oxidation potential. Fluorine and chlorine are regarded as "hard" bases, forming ionic bonds with hard acids such as Na, K, Mg, and Ca, whereas Br and I are "soft" bases with a stronger affinity for soft acids, such as Hg, Au, and Ag (e.g., Enghag 2004), forming bonds in which covalent interaction is more

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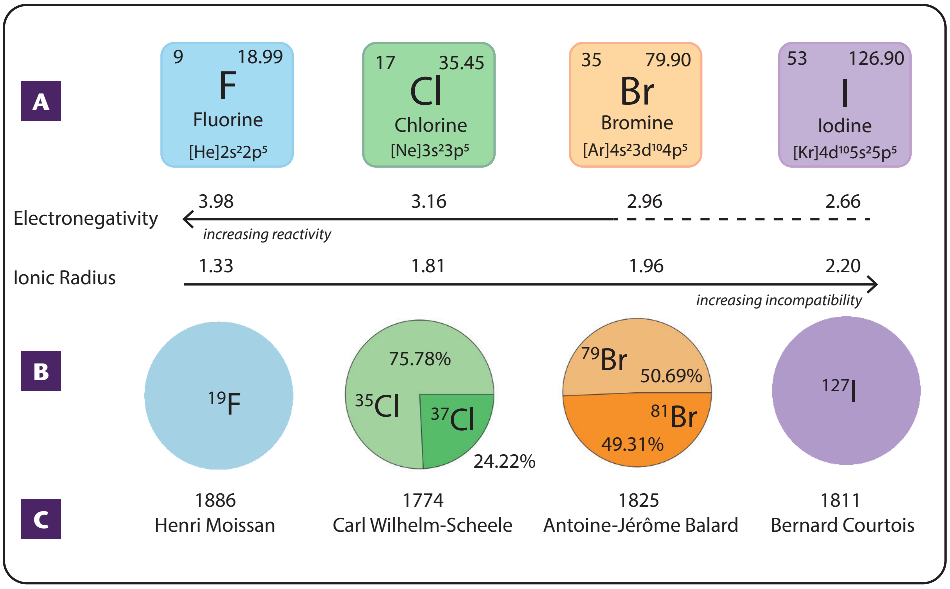

Figure 1 (**A**) The basic chemical properties of the four main (i.e., geologically relevant) halogen group elements. (**B**) The natural isotopic composition of each halogen. (**C**) The year of discovery and the name of the individual credited with the discovery of each halogen. Electronegativity is Pauling scale; ionic radius is the effective ionic radius in units of Ångströms. Sources: Enghag (2004) and the Commission on Isotopic Abundances and Atomic Weights (https://www.ciaaw.org).

important. This different behavior results from variation in the polarizabilities of each halide ion.

Each halogen also has a specific geochemical affinity that determines where they are stored in the terrestrial inventory and that influences how they partition between Earth's reservoirs (Fig. 2). For the heavy halogens (Cl, Br, I), it is these collective properties, coupled with their high solubility and relative scarcity in the Earth's interior compared to the surface, that make them excellent geochemical tracers, both in their own right and as tracers of other important volatile species (e.g., H_2O).

THE HISTORY OF HALOGENS: A LONG AND DANGEROUS PERIOD OF DISCOVERY

The discovery of the halogen elements (F, Cl, Br, and I) took over 100 years (1774 to 1886) and was not without significant trial by the discoverers and their associated researchers, particularly in the case of fluorine, which forms deadly gases during purification. The first to be discovered was chlorine in 1774 by the Swedish chemist Carl Wilhelm Scheele, when he reacted pyrolusite (MnO_2) with *spiritus salis*, or hydrochloric acid (Weeks 1932). Chlorine was thought to be a compound of oxidized hydrochloric acid, or "muriatic acid," as it was known. This view persisted until 1810 when British chemist Sir Humphrey Davy demonstrated that chlorine was, indeed, an element, naming it after its green colour, from *chloros*.

Iodine was discovered in 1811 by French chemist Bernard Courtois. In Courtois' time it was common practice to burn seaweed washed ashore at low tide, leaching the ash with sulfuric acid to extract valuable Na–bearing and K–bearing compounds, such as NaCl and K_2SO_4. Courtois discovered iodine when he fortuitously added an excess of sulfuric acid to the ash and produced a violet-hued vapor that would come to be known as iodine, from *iodes* (or "violet").

Bromine's discovery in 1826 originated in French saltmarshes. At the age of only 23, French chemist Antoine Jérôme-Balard made the discovery of the new element, one that he initially called "muride". The element was eventually called "bromine", after *bromos* for "stench", reflecting the element's foul odor. Balard would later go on to perfect industrial methods of salt extraction from seawater. Bromine was discovered in parallel by German chemistry student Carl Löwig, who observed bromine in 1825 in Heidelberg, but Balard reported his findings first and is credited with the discovery.

It would be another 60 years before the isolation and confirmation of fluorine in 1886 by French chemist Henri Moissan, though fluorine's story started much earlier in 1764 with the first systematic study of hydrofluoric acid (HF) by German chemist Andreas Marggraf, later formally described in 1771 by Scheele. There were many pioneering scientists along the road to the discovery of fluorine, including Scheele and Davy, and many suffered significant ill-health effects due to the inhalation of HF vapor. Those who succumbed to injury or death in their attempts to isolate fluorine became known as the "fluorine martyrs". Henri Moissan received the Nobel Prize in Chemistry in 1906 for his efforts to isolate fluorine, two months prior to his death.

Later efforts to better understand halogen behavior, particularly that of fluorine, were driven in part by World War II (1939–1945) during America's so-called Manhattan Project (to build the first nuclear bomb), with uranium hexafluoride (UF_6) being essential to the separation of uranium isotopes and the enrichment of fissile ^{235}U (Roesky 2010). Studies focused on methods to measure halogen abundances became more commonplace; today there are numerous methods for measuring both halogen abundances and isotopes (Burgess et al. 2022 this issue).

HALOGEN DISTRIBUTION ON EARTH: KEY TRACERS

The "geochemical cycling" of the halogen elements on Earth refers to the transfer and exchange of halogens between Earth's main geochemical reservoirs (Fig. 2). Specific materials (e.g., sediments) and reservoirs (e.g., the oceans) tend to exhibit characteristic halogen element abundances and relative distributions (e.g., their F/Cl, Br/Cl, and I/Cl ratios). With estimates of ~60%–90% of the halogens being concentrated in Earth's surface (e.g., Kendrick et al. 2017 and references therein), they are ideally placed as tracers of surface-to-interior exchange. Understanding

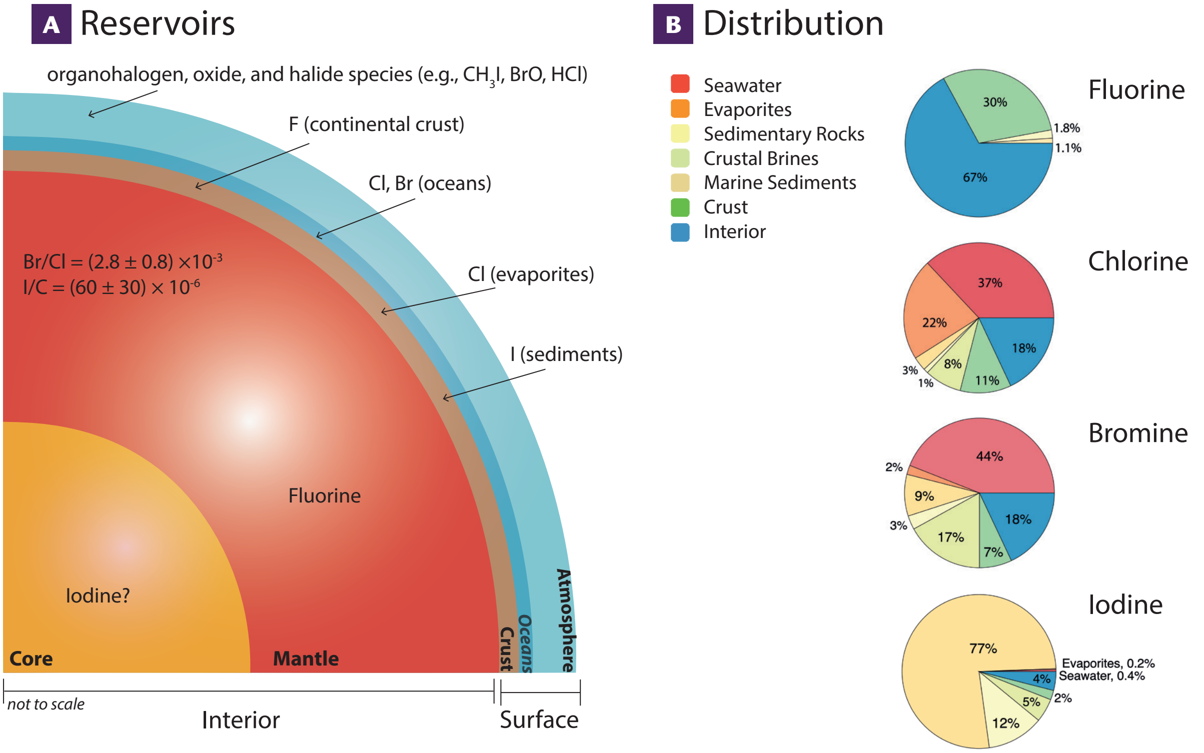

FIGURE 2 (**A**) Schematic of the halogen budget of Earth's main geochemical reservoirs and their general terrestrial distribution in the silicate Earth. (**B**) Surface reservoirs, which include the atmosphere, oceans, evaporite deposits, saline formation waters, oceanic crust, and continental crust. Interior reservoir includes the mantle and core. Chlorine and bromine exhibit similar terrestrial distribution patterns, concentrated into the surface reservoirs, whilst iodine, although concentrated in the surface, is predominantly held in sediments and brines. In contrast, fluorine's distribution is dominantly in the mantle. Crust in FIGURE 2B encompasses oceanic and continental crust. Mantle Br/Cl and I/Cl ratios are representative of mid-ocean-ridge basalt (MORB) and ocean island basalt (OIB) (Kendrick et al. 2017 and references therein). DATA ARE FROM KENDRICK ET AL. (2017).

the terrestrial halogen inventory is, therefore, essential to exploiting their unique geochemical cycle to better understand volatile storage and transfer processes on Earth. The concentration of halogens in, and their distribution between, Earth's main geochemical reservoirs is largely governed by their place in the periodic table, but also by their individual geochemical affinities and the processes that can result in their fractionation (FIG. 1). Collectively, these differences result in the decoupling of the halogens' geochemical cycles: fluorine is strongly decoupled from chlorine, bromine, and iodine, resulting in a largely different geochemical cycle for fluorine compared to its' heavier halogen relatives (FIG. 2). Chlorine and bromine are decoupled from iodine, though to a lesser extent.

Earth's Surface Reservoirs: Atmosphere, Hydrosphere, and Crust

The atmosphere is not a significant reservoir for halogens in terms of abundance (<0.001% of terrestrial halogens), but, once present in the atmosphere, their influence there is considerable. Natural volcanic and oceanic emissions, as well as anthropogenic halogen sources, contribute to the atmospheric halogen inventory. Halogens are present as organic and inorganic halocarbons, halides, and oxide species, where they contribute to the degradation of the terrestrial ozone (O_3) layer (Cadoux et al. 2022 this issue) and detrimentally influence the reaction cycles of other important greenhouse gases (e.g., NO, CH_4). The release of magmatic halogens potentially contributed to ancient climate events (Broadley et al. 2018), which may themselves be linked to mass extinction events.

Despite being a small reservoir by mass and volume when compared to the mantle, the surface is important when considering the terrestrial halogen distribution (FIG. 2). Chlorine, bromine, and iodine are heavily concentrated into the oceans (Cl and Br), evaporite salts (Cl), crustal brines, and, in the case of I and Br, in algae and in organic-rich sediments. The oceans account for a significant portion of the terrestrial chlorine budget (as the dominant anion in seawater) and the bromine budget. By contrast, fluorine and iodine are significantly depleted in seawater. Iodine's biophilic affinity means that it is sequestered into organic-rich sediments as organohalide compounds, such as methyl iodide (CH_3I^-). Under the oxidizing conditions of the modern Earth, iodine is present in the oceans as iodate (IO_3^-) and is a tracer of redox conditions in the geologic past (Lu et al. 2018). In contrast, fluorine is moderately compatible in many crustal minerals, due to its high electronegativity and small ionic radius. Unlike the heavy halogens, it generally has a low solubility in aqueous fluids (T-dependent). Fluorine is, therefore, abundant in the mantle and the crust, where it readily substitutes for OH^- in hydroxyl-bearing minerals, such as biotite, muscovite, apatite, and amphibole (Mi and Pan 2018).

Earth's Interior: Mantle and Core

Mid-ocean-ridge basalt (MORB) and ocean island basalt (OIB) show consistent heavy halogen ratios Br/Cl = (2.8 ± 0.8) × 10^{-3} and I/Cl = (60 ± 30) × 10^{-6} (Kendrick et al. 2017 and references therein), though concentrations of the halogens vary significantly. Because the halogens are not significantly fractionated from one another during partial melting or fractional crystallization processes, their ratios can fingerprint specific halogen sources, such as seawater, altered oceanic crust, or sediments, delivered from the surface to the mantle at subduction zones to depths of ~100 km (Sumino et al. 2010; Kendrick and Barnes 2022 this issue). Similarly, halogen ratios (F/Cl, Br/Cl, I/Cl) and Cl-isotope compositions of hydrous mineral phases can be used to fingerprint fluid sources (Barnes et al. 2018). However, the extent of halogen recycling from the surface to the mantle is not well known. The mantle is a significant source of terrestrial fluorine (Kendrick et al. 2017), where it is present in low concentrations in the abundant mantle minerals olivine and pyroxene.

The core has been suggested as a potential reservoir for chlorine, bromine, and iodine. Iodine has experimentally been shown to behave in a siderophile manner, with metal–silicate partition coefficients ranging from ~1.0 to 5.5 over different metal compositions at ~20 GPa and 3,000 K (Armytage et al. 2013). In contrast, the core is not thought to host chlorine, which has a low metal–silicate partition coefficient (D<<1) (Sharp et al. 2013). The core's role in storing bromine remains relatively unexplored.

THE MINERALOGY OF HALOGENS: HALIDES AND BEYOND

Halogens are present in the solid Earth in a variety of mineral phases (Table 1). Halogen-rich minerals are those with at least one halogen in a major crystallographic site and are diverse with respect to both mineral group and environment of formation. Approximately 15% of approved International Mineralogical Association (IMA) mineral species are halogen-rich (Mi and Pan 2018). However, a great many more contain appreciable amounts of halogens, particularly fluorine and chlorine (in hundreds-to-thousands of parts per million F and Cl).

This diversity in mineralogy means that halogens can act as recorders of a wide range of geologic processes. The mineral compositions can inform on the halogen concentrations in, and relative abundances of, the fluids or melts from which they evaporated or crystallized in a variety of environments. Thus, from low-temperature solar evaporation of the brines that form evaporite minerals (Warren 2021) to the high-temperature fluids that are essential to base-metal and precious-metal ore formation in hydrothermal systems (e.g., Pirajno et al. 2018), halogen-rich minerals act as fluid archives. Such minerals can also be a dominant control on halogen budgets and geochemical cycles. This is true also for halogen-bearing minerals in extraterrestrial materials. The chlorine-bearing sulfide djerfisherite [$(K, Na)_6(Fe,Cu,Ni)_{25}S_{26}Cl$)], whilst common in alkaline igneous intrusions on Earth, is primarily known from the reduced enstatite chondrite meteorites, which host up to 1.5 wt% chlorine. Apatite is a common accessory phase in many extraterrestrial materials, including lunar, martian, and chondritic meteorites, where their halogen abundance and chlorine isotope composition can reveal the source, composition, and complex histories of fluids or melts in planetary bodies (Barnes and Zolensky 2022 this issue).

Mineral species containing fluorine and chlorine are abundant in the geologic record, but mineral lattices generally cannot easily accommodate bromine and iodine (though there are notable exceptions, such as iodine in carbonate) (Lu et al. 2018). There are many niche occurrences of halogen-bearing minerals occupying numerous terrestrial environments, the diversity of which is too broad to be covered here. The reader is referred to Mi and Pan (2018) to explore these wonderfully complex species and their unique environments of formation. The more common halogen-rich minerals, and their importance to the geologic environments in which they form, are briefly described below.

Halides

Halogens are the dominant anion in the halide group minerals, such as common rock salt (halite, NaCl). There are over 80 halide mineral species and, despite the global ubiquity of salts such as halite or sylvite (KCl) which form from evaporative processes, most halide minerals are not widespread but rather restricted to local occurrences (Mi and Pan 2018; Warren 2021). Halide minerals are of economic importance, particularly to agriculture and as ores of metals. Some halide occurrences are especially prized for their ornamental value, such as the purple-banded "Blue John" fluorite (CaF_2), which has been mined since the mid-18th century (Fig. 3A) in Derbyshire (UK). Hosted in Carboniferous limestone and the result of Mississippi Valley type mineralization by Ca- and Na-chloride–rich fluid(s), Blue John accompanies galena (PbS) ore.

Silicates and Phosphates

Chlorine and fluorine are important anions in accessory phosphates, mostly chlorapatite [$Ca_5(PO_4)_3Cl$] and fluorapatite [$Ca_5(PO_4)_3F$], readily substituting with each other and OH^-. Apatite is an important carrier of F and Cl in planetary interiors (Barnes and Zolensky 2022 this issue; Joachim-Mrosko et al. 2022 this issue) and is prevalent in a broad range of geological environments. Apatite can record the composition of parental melt or the composition of fluids during metasomatic and metamorphic events, making it an important mineral for understanding halogen abundance and behavior in numerous terrestrial and extraterrestrial environments.

Halogens are important constituents of many silicate minerals, including amphibole, muscovite and biotite micas, and the more niche minerals of scapolite and sodalite. Fluorine- and chlorine-rich amphiboles and micas occur by halogen substitution for the hydroxyl ion, with F-rich varieties generally more common, particularly in the case of the micas. Scapolite may be of primary igneous origin, although it more commonly results from metasomatic or metamorphic processes, where its halogen abundance can inform on fluid source composition (Mi and Pan 2018). Serpentine can be halogen-rich, with abundances of up

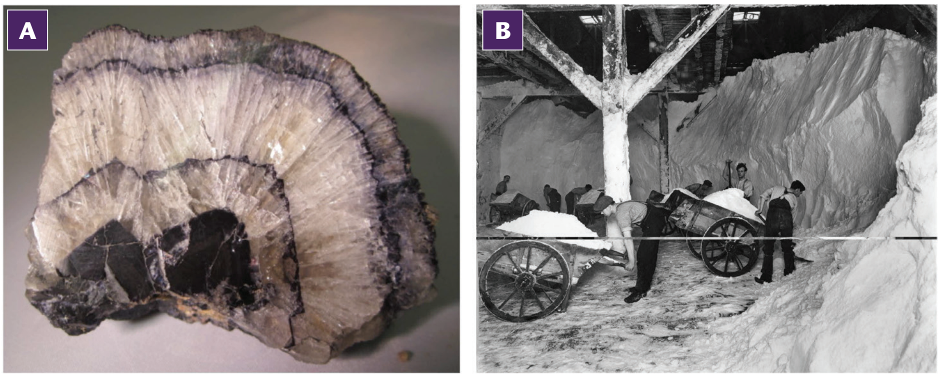

Figure 3 (**A**) Specimen of "Blue John" fluorite (CaF_2) from the Witches Miller's Vein at Treak Cliff Cavern in Castleton, Derbyshire (UK). Blue John is prized for the banded nature of the stone, although the exact cause of this distinct colouration is unknown. Specimen is approximately 15 cm in diameter. Photo used with permission of Treak Cliff Cavern. (**B**) Workers putting salt into salt barrows at the Winsford Salt Union warehouse (Winsford, UK) from the period 1920–1929. Winsford has the largest salt mine in the UK. Photo used with permission from the West Cheshire Museums and the Cheshire Image Bank.

to ~1 wt% Cl, 24 ppm Br, and 45 ppm I as documented in lizardite–chrysotile serpentine (Kendrick and Barnes 2022 this issue). This has implications for the recycling of halogens into the mantle. The nominally anhydrous minerals olivine and pyroxene may also be an important control on the halogen geochemical cycle of the mantle due to the high volumetric proportions of these minerals and despite their typically low halogen abundances.

HALOGENS IN SOCIETY AND THE ECONOMY

Halogens are key to human health and industry. Since the halogens do not exist in their elemental form in nature under normal conditions, consideration of their relevance to society and the economy tends to unite around the property that they are collectively named for: salt formers.

Salt: A Matter of Health and Wealth

Salts of halide ions are necessary for human health, and the use of salt is embedded in daily life. Historically, salt has been central to many cultures through tradition and ritual. To some, a pinch of salt over the shoulder brings good fortune whilst to others the spilling of salt is considered a bad omen (in Japan, *morishio* or "piled salt" is often placed at the entrance of a business to bring luck). Salt is now common and inexpensive, but it was once a highly sought-after commodity. Human dependence on salt has been the source of conflict throughout history, including through taxation and restrictions on production.

Recovery of salt, through evaporation of seawater and mining of rock salt hosted in evaporite deposits, has occurred throughout human history. Salt was key to ancient civilizations in the preservation and transport of food. Evidence for salt production by brine boiling, technology utilized by the Mayans (AD 300–900), exists in the form of "briquetage" or salt-boiling pottery vessels preserved at the Paynes Creek Salt Works (Belize) (McKillop and Aoyama 2018). In the United Kingdom, thick Triassic halite beds and brine springs that have formed from halite dissolution have been exploited for salt production likely since the Iron Age (Zant 2016). This heritage is preserved in towns with names containing the term "wich," or saltworks, such as Northwich and Nantwich in the salt-rich county of Cheshire (Fig. 3B). Worldwide, evidence of salt production likely extends to ~6,000 BC, with the harvesting and gathering of salt produced from the solar evaporation of saline lakes in China's Shanxi Province.

From the early 20th century, iodine (as KI or NaI) was added to table salt to address the widespread iodine-deficiency that currently affects an estimated 2 billion people globally (Fuge and Johnson 2015). Fluoride intake for dental health has been supplemented through addition of fluorine to toothpastes and drinking water. Today, salt is key to several major industries, including agriculture, medicine, chemical processing, road de-icing, and water treatment. The necessity of salt, sourced from diverse geologic environments, is reflected in both the volume of production and the value of the salt industry. Approximately one-third of the world's industrially produced iodine is sourced from iodine-rich brines in fore-arc basins in Japan (Muramatsu et al. 2001), possibly derived from subducted iodine-rich sediment. Mined rock salt, evaporated salt, and sea salt account for the ~39 million tons of salt produced in 2020 in the US alone, worth an estimated $US2.4 billion (Bolen 2021). Approximately 43% of salt consumption is actually used for highway de-icing, in which we rely on solutions of Na-, Mg-, and K-chloride salt to depress the freezing point of ice on the roads. An implication is that the demand for salt now and in the future is, and will be, linked to climate.

FURTHER READING

Halogen research in the Earth, environmental, and planetary sciences is dynamic and currently thriving. The techniques available for measuring halogen abundances, ratios, and isotopic compositions are developing and expanding in application. Whilst this is excellent news for those engaged in halogen-related research, it does mean that the scope of available topics is too broad to be accommodated in this one issue. Many active areas of research are, therefore, unfortunately left unexplored herein, including the role of anthropogenic halogens, halide minerals, radionuclide isotopes (in the I–Xe system), and cosmogenic isotopes (e.g., ^{36}Cl) of the halogens. To partially remedy this, a summary of some of the other avenues of halogen-based research not covered in this issue is provided here, with references for the reader to explore.

- For an exploration of the unique role that redox-sensitive iodine plays in tracing ancient ocean chemistry and environments, the reader is referred Lu et al. (2018).

Table 1 SOME EXAMPLES OF COMMON HALOGEN-BEARING MINERAL SPECIES BY GROUP AND THEIR OCCURRENCE. General mineral formulae are from the International Mineralogical Association database (https://rruff.info). See Mi and Pan (2018) for a comprehensive discussion of halogen mineralogy.

Mineral Group	Mineral Name	General Formula	Occurrence
Halides	Halite	$NaCl$	Common evaporite minerals
	Sylvite	KCl	
	Carnallite	$KMgCl_3 6H_2O$	
	Fluorite	CaF_2	Hydrothermal veins, granites, pegmatites, or other high-temperature veins
	Lawrencite	$(Fe,Ni)Cl_2$	Alteration product, meteorites
Silicates	Sodalite	$Na_4(Si_3Al_3)O_{12}Cl$	Alkaline-rich rocks, phonolites, syenites, meteorites
	Marialite (scapolite)	$Na_4Al_3Si_9O_{24}Cl$	Ca-rich metamorphic assemblages
Phosphates	Chlorapatite	$Ca_5(PO_4)_3Cl$	Common accessory phase in sedimentary, igneous, and metamorphic systems and meteorites
	Fluorapatite	$Ca_5(PO_4)_3F$	
Sulfides	Djerfisherite	$(K)_6(Fe,Cu,Ni)_{25}S_{26}Cl$	Kimberlites, pegmatites, hydrothermal ores, skarns, meteorites
	Thalfenisite	$Tl_6(Fe,Ni,Cu)_{25}S_{26}Cl$	Associated with, and included within, ore minerals

- For an overview of the effects of the release and transport of radionuclides of iodine (^{129}I and ^{131}I) to the environment during the Fukushima Daiichi Nuclear Power Plant accident in Japan during March of 2011, see Muramatsu et al. (2015).
- For a review of the mineralogy and global distribution of evaporite deposits and the geochemistry of brines, the reader is referred to Warren (2021).
- For the role that halide ligands play in metal mineralization in diverse hydrothermal systems, the reader is referred to Pirajno (2018).
- For an overview of the short-lived and extinct ^{129}I, the I–Xe system, and the chronology of the early Solar System, the reader is referred to Gilmour et al. (2006).
- For a review of the applications of ^{36}Cl cosmogenic nuclide studies to dating and as a geochemical tracer, see Bierman et al. (2021).

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A Halogen Record of Fluid Activity in the Solar System

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Halogens are mobile in geological fluids, making them excellent tracers of volatile activity. Halogen-bearing minerals in diverse planetary materials, coupled with chlorine isotope compositions of bulk samples and minerals, can be used to infer the presence of fluids on planetary surfaces, crusts, and interiors. Halogen element and isotopic evidence helps define the role that halogens play in diverse planetary environments (e.g., asteroids, the Moon, and Mars), which offers insights into fluid activity in the early Solar System and in the role such fluids have played in volatile transport, alteration processes, and habitability throughout geological history.

KEYWORDS: meteorites; asteroids; isotopes; astrobiology; Mars; Moon

INTRODUCTION

Halogens (F, Cl, Br, I) are fluid (vapor or liquid) mobile elements, making them excellent tracers of fluid activity in geological systems. Halides are important components of fluids and affect the chemical (e.g., pH) and physical (e.g., freezing point) properties of such fluids. Therefore, halogens influence the ability of surface or subsurface liquid water to host life. In the context of the early Solar System, halogens are not only linked to aqueous solutions but also played important roles in fluid-assisted thermal metamorphism (metasomatism) and in the mass transport of elements within planetary crusts. Knowledge regarding the abundances, mineral hosts, and isotopic composition of halogens therefore is key to improving our understanding of planetary origins, magmatic and thermal evolution, and habitability.

To understand the chemical evolution of the Solar System we can study the composition of planetary materials. Chondritic meteorites, also called "chondrites", are physical representatives of the unmelted material from which the terrestrial planets formed. The parent planetesimals to the chondrites accreted variable amounts of dust, metal, and ice from the solar nebula. Today, we recognize those differences as unique chondrite groups, including carbonaceous, ordinary, and enstatite chondrites. Whereas the parent bodies did not undergo differentiation, they did experience variable degrees of heating and/or aqueous activity. These differences manifest themselves in a petrologic scale to which chondrites can be ascribed (Van Schmus and Wood 1967). The most primitive and least altered are called type 3; types 2 and 1 show increasing aqueous alteration, respectively; and petrologic types greater than type 3 show progressive heating. Unlike the chondrites, achondrites derive from bodies that underwent partial to complete melting to form a metallic core, silicate mantle, and crust.

The abundances of halogens in planetary materials are important to constrain because they, together with highly volatile elements (e.g., C and H), provide insights into the origin of bioessential elements to the terrestrial planets. Unfortunately, the bulk-rock abundances of halogens are challenging to measure, and, currently, there is no robust way to measure all four elements simultaneously (Burgess et al. 2022 this issue). Historical reports of F in planetary materials appear variable and questionable; moreover, chondrites display a wide range of halogen abundances that reflect their intrinsic diversity and parent body processing, as well as issues such as nugget effects and complications from any terrestrial weathering of the meteorites (e.g., Clay et al. 2017; Brearley and Jones 2018). In contrast, recent advancements in electron microbeam techniques and mass spectrometry are opening new avenues by which to investigate ancient extraterrestrial fluid activity. Studies of the mineralogical hosts of halogens, together with their textures, chemistry, and isotopic compositions in meteorites, are illuminating the sources of the halogens (nebular or planetary) and the fluids, the mobilization of volatiles, and the past existence of habitable conditions on bodies throughout the Solar System's history. These new developments are the focus of this paper.

FLUID ACTIVITY ON ANCIENT CARBONACEOUS CHONDRITE ASTEROIDS

Because chondrites escaped complete melting and differentiation processes, they provide us with primitive material from the birth of our Solar System. Chondritic planetesimals accreted different amounts of dust, metal, and ice, and accreted greater ice-to-rock ratios with increasing distance from the proto-Sun. Early on, the dust contained varying amounts of "live" ^{26}Al (half-life $t_{1/2}$ = 0.73 million years, Ma) and ^{60}Fe ($t_{1/2}$ = 1.5 Ma). Rapid decay of these short-lived radioisotopes produced the heat necessary to melt ice and generate free fluids without melting chondritic planetesimals.

Hydrated Chondrites

The consequences of low temperature aqueous alteration in carbonaceous chondrites include the formation of minerals that possess structural OH^- or H_2O, collectively called "phyllosilicates". Despite containing measurable amounts of bulk-rock halogens and Ivuna-type (CI) chondrites

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containing the highest abundance of chlorine (e.g., Clay et al. 2017), the minerals containing the halogens in these chondrites remain mysterious, aside from a few reports of halite (NaCl), sylvite (KCl), and F-bearing hydroxylapatite [$Ca_5(PO_4)_3(OH)$] (e.g., Piralla et al. 2021). Textural relationships and the co-occurrence with other minerals precipitated from hydrothermal fluids, such as magnetite, indicate apatite is a secondary phase. Using the chemical composition of apatite and partitioning relationships between apatite and fluid, Piralla et al. (2021) determined that asteroidal fluids from which hydroxylapatite precipitated were low-temperature (<100 °C), relatively alkaline (pH ~10–13), undersaturated in F and Cl, and likely represented the late stages of hydrothermal alteration on the parent body.

Anhydrous Chondrites

On carbonaceous planetesimals with low water-to-rock ratios, fluids facilitated the transport and concentration of halogens into specific phases during alteration. Some of the dry, oxidized Vigarano-type (CV) carbonaceous chondrites contain an array of minor minerals of low abundance, including sodalite ($Na_4Al_3Si_3O_{12}Cl$), wadalite ($Ca_6Al_5Si_2O_{16}Cl_3$), rare apatite ($Ca_5(PO_4)_3(F,Cl,OH)$), chlormayenite ($Ca_{12}Al_{14}O_{32}[_{-4}Cl_2]$), and adrianite ($Ca_{12}(Al_4Mg_3Si_7)O_{32}Cl_6$) (Brearley and Jones 2018). These minerals are typically found as mineral alteration products in the first Solar System solids, calcium-aluminum–rich inclusions (Fig. 1A), and, to lesser degrees, in chondrule glass and chondrite matrix. The resulting alteration assemblage appears to be dependent on the composition of the primary minerals present in different chondrite components. Such alteration is called "Fe-alkali-halogen metasomatism" because it describes the fluid-assisted mobilization, redistribution, and deposition of Fe, K, Na, and halogens on chondrite parent bodies.

Oxygen isotope analyses of secondary halogen-bearing minerals show a mass-dependence trend consistent with their precipitation from fluids. While a host phase for iodine has not yet been identified, it is expected to follow Cl and be incorporated in sodalite during metasomatism (Brearley and Jones 2018). The decay of ^{129}I to ^{129}Xe ($t_{1/2}$ = 15.7 Ma) shows this period of alteration was protracted, lasting for ~14 My (Pravdivtseva et al. 2003). Such metasomatic reactions are considered to have taken place over a range of temperatures (>200–600 °C), at pressures of a few tens of bars, and at low water:rock ratios.

Using Chlorine Isotopes

Chlorine is the most abundant halogen in chondritic meteorites, followed by F (Clay et al. 2017). Variations in the stable Cl isotope ratio ($R = {}^{37}Cl/{}^{35}Cl$) of a sample are expressed using "δ notation" [$\delta^{37}Cl$ (‰) = ($R_{sample}/R_{standard}$ – 1) × 1,000 (where standard = SMOC, standard mean ocean chloride of $\delta^{37}Cl$ = 0.0‰]. Measurements are made either in situ within a particular phase or on bulk-rock specimens, with the results of the latter often reported as water-soluble Cl (i.e., the Cl in salts such as NaCl and $FeCl_2$) or as structurally bound Cl (meaning Cl is locked into a mineral).

Figure 2 shows overlap between the $\delta^{37}Cl$ values of terrestrial samples and bulk chondrites, indicating a common provenance for Cl among these materials (e.g., Sharp et al 2013). Sodalite in the CV-type chondrite Allende has been analyzed in situ and shows lower $\delta^{37}Cl$ values (average –1.3 ± 0.6‰, 1σ) than the bulk rock (–0.4‰) (Sharp et al. 2013) (Fig. 2), which could be explained by low-temperature equilibrium fractionation of Cl isotopes between sodalite and NaCl on the CV parent body.

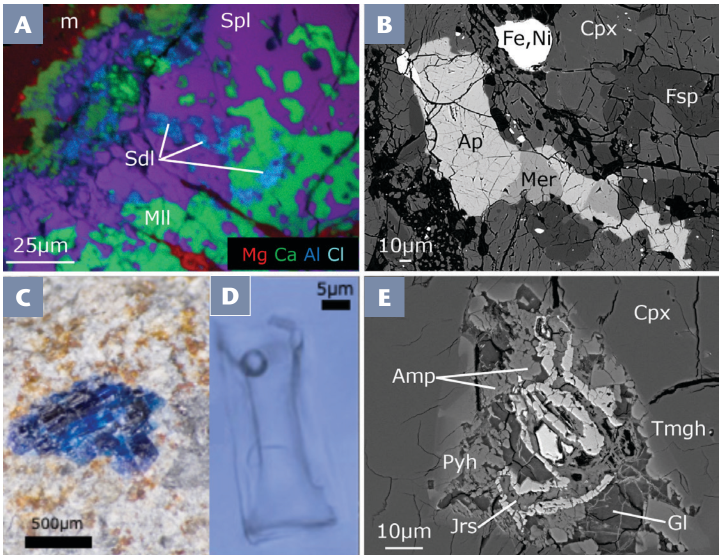

Figure 1 Halogen-bearing minerals in planetary materials. (**A**) False color X-ray composite of a sodalite-bearing refractory inclusion in Vigarano CV3 chondrite. (**B**) Phosphate intergrowth in a type-6 portion of the Zag H3-6 brecciated meteorite. From Jones et al. (2016). (**C**) Blue halite from the Zag H3-6 meteorite. (**D**) Transmitted light view of a fluid inclusion (with vapor bubble) in halite from the Monahans (1998) meteorite. From Bodnar et al. (2019). (**E**) Amphibole-bearing melt inclusion in Martian meteorite Miller Range 03346. From McCubbin et al. (2009). Abbreviations: Ap = apatite; Jrs = jarosite, Amp = Cl-amphibole; Cpx = clinopyroxene; Fsp = feldspar; Sdl = sodalite; Mer = merrillite; Pyh = pyrrhotite; Tmgh = titanomaghemite; Gl = glass; Spl = spinel; Mll = melilite; m = matrix. Images reproduced with permission from *Geochimica et Cosmochimica Acta*, the *Mineralogical Society of America*, and *The Royal Society*.

Halogen-bearing minerals, together with low degrees of heating and the presence of phyllosilicates, indicate that halogens were important constituents of low-temperature fluids on primitive chondritic parent bodies. Even though the carbonaceous chondrites are representative of materials that underwent a wide range of alteration conditions, including a high degree of aqueous activity, it is surprising that they contain a limited range of halogen-bearing minerals (except for the CV group). It is possible that the dearth of minerals reflects reaction of halogen-bearing minerals in meteorites with the terrestrial environment (Brearley and Jones 2018).

FLUID-ASSISTED THERMAL METAMORPHISM ON PLANESTIMALS

Ordinary chondrites are so-called because they are the most common meteorite type, even though their source asteroids (S-class asteroids) are not the dominant type in the asteroid belt. The parent bodies to the ordinary chondrites are thought to have formed in relatively dry and more reducing (i.e., higher metal:ice ratios) parts of the solar nebula (i.e., closer to the Sun) compared to carbonaceous chondrites. The ordinary chondrites are subdivided into H (high), L (low), and LL (very low) groups based on their iron content. These meteorites display a range of metamorphic grades from relatively unaltered type 3 to heated type 6 (temperatures up to ~700 °C) and contain an array of halogen-bearing minerals (Brearley and Jones 2018). Unequilibrated ordinary chondrites contain clay minerals, sodalite, and apatite, and all except apatite decompose upon prograde metamorphism. Therefore, apatite is a key tool by which to trace fluid activity and evolution on the ordinary chondrite (OC) parent bodies (McCubbin and Jones 2015).

Phosphates

Recent studies have demonstrated that the composition, grain size, and textures of phosphates and feldspar in ordinary chondrites preserve a record of fluid activity during the first ~100 My of Solar System history (e.g., Jones et al. 2016) (Fig. 1B). A generalized model for the metamorphism and fluid alteration of primitive OC asteroids is as follows. Initial low-temperature metamorphism facilitated the solid-state diffusion of phosphorous out of Fe–Ni metal, which reacted with silicate minerals to form merrillite $[Ca_9NaMg(PO_4)_7]$. Fine-grained intergrowths of apatite and merrillite in low petrologic type meteorites indicate reaction of merrillite with a halogen-rich fluid. With prograde metamorphism, phosphate minerals coarsen to hundreds of micrometers in the longest dimension (McCubbin and Jones 2015).

In many equilibrated ordinary chondrites, textural analysis indicates apatite formed either via an interface-coupled dissolution–reprecipitation reaction between a halogen-rich fluid and an existing merrillite or via direct precipitation from a brine. Although generally Cl-rich and OH-poor, the composition of apatite in ordinary chondrites does not equilibrate with increasing temperature, implying the local passage of late-stage dry, Cl-rich, F-bearing brines during retrograde metamorphism (cooling) at low fluid:rock ratios (e.g., Jones et al. 2016).

Bulk-rock ordinary chondrites show a range in Cl isotope compositions from –1.7‰ to ~1‰ (Fig. 2) that do not correlate with petrologic type. The Parnellee meteorite (an LL3 stone from India) is an exception, having very light (–4.1‰ ± 0.3‰) structurally bound Cl, which has been interpreted as a nebular signature possibly inherited from HCl hydrate ices or indigenous light pore waters (Sharp et al. 2013).

Not all apatite in ordinary chondrites is Cl-rich. Some are F-rich and, therefore, represent a key repository of F in primitive meteorites. The occurrence of F-apatite in brecciated ordinary chondrites and in clasts of various petrologic types suggests that impact processing of asteroid regolith was important in the genesis of the F-rich fluids from which F-apatite precipitated. The source of the F is unclear but could have originated in the OC regolith or from an exogenous source (Jones et al. 2016).

Extraterrestrial Salt

Terrestrial halite is often found with water, occurring as an evaporite mineral. This association with water highlights the importance of evaporites for understanding the origin of life, because such minerals provide crystalline surfaces that act as adsorption sites for catalytic synthesis, polymerization, and the organization of prebiotic molecules. Two witnessed ordinary chondrite meteorite falls, the "Zag H3-6 regolith breccia" (hereafter "Zag") and the "Monahans (1998) breccia" (hereafter "Monahans"), contain millimeter- to centimeter-size aggregates of extraterrestrial halides (Zolensky et al. 1999).

In these meteorites, halite (NaCl) and sylvite (KCl) are predominantly found in the grey matrix material (Fig. 1C). In addition to containing Cl, sylvite is an important host of Br and I (e.g., Bridges et al. 2004). The I–Xe ages of the salts are consistent with aqueous processing on the parent asteroid occurring only ~8 My after the start of the Solar System (Busfield et al. 2004). Halite and sylvite in Zag are characterized by light Cl isotope compositions ($\delta^{37}Cl$ values of −1.7 ‰) (Bridges et al. 2004) (Fig. 2), which are consistent with the isotopic composition of water-soluble chlorine (−1.8‰) for the bulk rock (Sharp et al. 2013). These compositions are lighter than structurally bound chlorine in bulk Zag (−0.2‰ to −0.7‰), perhaps indicating an isotopic fractionation process within the parent body environment (Jones et al. 2016).

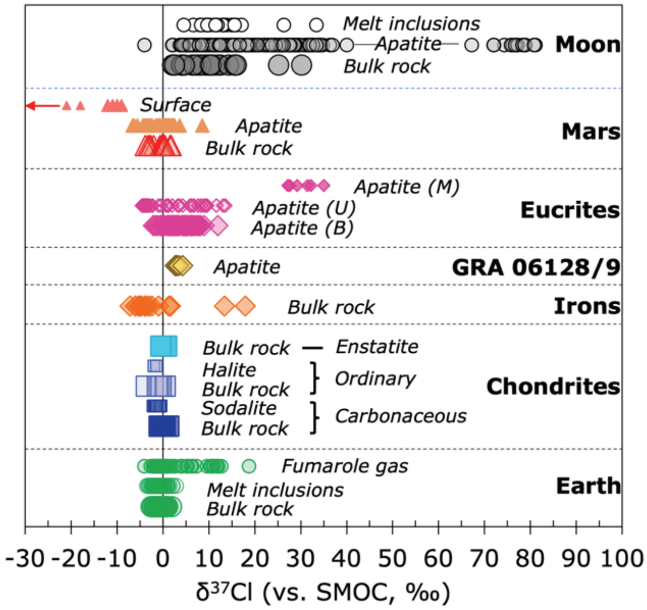

Figure 2 Bulk rock, in-situ, and gas chlorine isotope compositions for a variety of terrestrial and extraterrestrial materials (refer to the text and online supplement for data sources). For eucrites, in situ Cl isotopes were measured in apatite from metamorphosed (M), brecciated (B), and unbrecciated (U) samples. Martian surface measurements extend to ~–60‰ as indicated by the arrow. From Farley et al. (2016). Abbreviations: SMOC = standard mean ocean chloride; GRA = Graves Nunataks (Antarctica).

Whether or not halite in these meteorites is indigenous or exogenous to the parent bodies remains unresolved. But the Zag meteorite also contains a carbonaceous chondrite xenolith that itself contains halite. Oxygen, H, N, and C isotope data indicate that the halite originated on a P- or D-class asteroid (Kebukawa et al. 2019). Thus, it is possible that the halides found in Zag originated in the outer Solar System and were subsequently transported inward to the S-class asteroid parent of the Zag meteorite. This scenario is consistent with the solid mineral phases trapped within the halite and sylvite, which are consistent with a carbonaceous, rather than an ordinary chondrite, heritage (Kebukawa et al. 2019).

TRAPPED ASTEROIDAL BRINES

On Earth, tiny, trapped parcels of fluids found within minerals allow us to monitor paleofluid composition, pH, and temperature through geological time. In extraterrestrial samples, such records are rarely preserved. Halite in both Zag and Monahans meteorites contain low-temperature (25–100 °C) aqueous fluid inclusions that offer a rare snapshot of the asteroidal fluids from the first ~10 My of Solar System history. Fluid inclusions can be either trapped in a crystal during crystal growth (referred to as "primary inclusions") or trapped later in healed fractures ("secondary inclusions"). In both samples, secondary inclusions are more dominant. The trapped fluids are dominated by NaCl–KCl brines that contain divalent cations (Fe, Mg, Ca) and abundant organic molecules (e.g., including CH_3^+, $C_2H_3^+$, and $C_2H_2NO_2$) (Bodnar et al. 2019). Notably, the presence of both primary and secondary inclusions suggests local episodic brine-rich fluid activity.

The fact that the fluid inclusions in halite in these meteorites have remained intact is a signal that either the halite precipitated from the same late-stage brines as the Cl-rich apatites or that they were added to the ordinary chondrite asteroid regolith after the thermal metamorphism that produced the Cl-rich apatite (Zolensky et al. 1999). Coupled oxygen and hydrogen isotope studies of the fluid inclusions show that the brines have compositions more deuterium-rich and ^{16}O-poor than that which is known from chondritic water sources, suggesting a link to cometary or interstellar ice origins (Yurimoto et al. 2014). The astrobiological significance of such inclusions is heightened when we consider that the trapped fluids are rich in organic compounds and that there are associated trapped solid inclusions of organics (Fig. 1D) (Bodnar et al. 2019).

To date, there is no consensus on whether halite in these meteorites is original to the parent body or exogenous. If halite and trapped fluids are exogenous, then they could represent direct samples of outer Solar System brines, perhaps like those now present within the moons of the giant planets or in large C-class asteroids or the dwarf planet Ceres.

HALOGEN ACTIVITY ON DIFFERENTIATED ASTEROIDS

Achondrites are pieces of bodies that started accreting within a million years of the start of the Solar System, during the time when short-lived radioisotopes were live, and so they experienced substantial heating (thermal energy produced from the decay of these radioisotopes) that then promoted partial-to-complete melting. The achondrites provide an important intermediary for understanding fluid activity between the chondrites and planets.

Eucrites are basaltic achondrite meteorites that represent pieces of the crust from the asteroid 4-Vesta. Eucrites contain mostly magmatic endmember fluorapatite (McCubbin and Jones 2015). Thermal metamorphism among eucrites is nearly ubiquitous and occurred during the first 50 My of the Solar System. In the Graves Nunataks 98098 eucrite (recovered from Antarctica), metasomatism has been invoked for the precipitation of large (<300 μm), Cl-bearing, F-rich apatites (Sarafian et al. 2017). The D/H ratio of trace OH in the apatite is consistent with other eucrites, indicating a similar volatile source, but the Cl is highly fractionated (average +7.7 ± 1.3‰, 2σ) compared to other unbrecciated basaltic eucrites (−3.8 ± 1.1‰) (Sarafian et al. 2017). With the sparce evidence, it is equally plausible that the relatively high Cl isotopic composition (1) is from fluid interaction, or (2) reflects a heterogeneous eucrite source with respect to Cl/F and Cl isotopes. The uncertainty surrounding the presence and nature of fluids on the eucrite parent body warrants future sample analysis aimed at characterizing the full suite of halogens, together with detailed petrological context and in situ chronology.

Fluid-derived phosphate replacement textures are observed in the paired ungrouped achondrite meteorites Graves Nunataks (GRA) 06128 and 06129. These stones crystallized from felsic melts through low-to-moderate degrees of partial melting of a volatile-rich chondritic precursor. In these meteorites, merrillite formed within 2–3 My of the start of the Solar System and was replaced by apatite ~100 My later (Tartèse et al. 2019 and references therein). Apatites in GRA 06128/9 are Cl-rich and OH-poor, reflecting the chemistry of the metasomatizing fluids. The apatites contain heavy Cl (Fig. 2) which, like the Cl in the eucrite, is significantly heavier than in bulk chondrites (Fig. 2). Together with hydrogen isotope data, the replacement features in the GRA 06128/9 meteorites could be explained by the alteration of preexisting merrillite from fumerolic, low-H_2O fluids with high D/H ratios (Tartèse et al. 2019). The source of the fluids is intriguing given the nonchondritic, D-rich compositions measured and is most compatible with interstellar D-rich and HCl-rich ices that condensed in the cold (<150 K) region of the outer Solar System, possibly of a similar source to the fluids sampled by Zag fluid inclusions.

Overall, phosphates demonstrate their usefulness in recording parent body processes and the nature of altering fluids, and they permit us to trace the ancient origins of volatile elements. We note that the examples presented here are unique and, generally, there is limited evidence for fluid activity in achondrite meteorites. This could be related to the dehydration of early formed planetesimals.

VAPOR TRANSPORT IN THE MOON'S CRUST

Compared to the Earth, the Moon is extremely volatile-depleted and this depletion is an expected consequence of the violent impact event thought to have formed the Moon and its subsequent thermal evolution. Despite this, the Moon retains endogenous volatiles, including hydrogen and halogens. The major halogen reservoir on the Moon is expected to be the residual liquid of the putative lunar magma ocean. Progressive fractional crystallization of the lunar magma ocean to thereby form the cumulate mantle and floatation crust would result in a final liquid (at the point where the mantle is >95% solid) rich in incompatible trace elements and halogens (so-called KREEP, for its enrichment in potassium, rare earth elements, and phosphorous). The KREEP reservoir likely contained ~1,100 ppm Cl and ~660 ppm F (McCubbin et al. 2015). Several studies have postulated that the KREEP reservoir had a fractionated Cl isotope composition (δ^{37}Cl > +30‰) obtained through lunar magma ocean degassing or via impact-loss of ^{35}Cl (e.g., Barnes et al. 2016). Indeed, crustal rocks and rocks produced by interaction with the KREEP residual liquid are enriched in Cl and F and record fractionated Cl isotope compositions (Fig. 2). Unlike other rocky bodies, namely the Earth or Mars, the Moon does not (nor ever did) host water as a free fluid. Therefore, the mechanisms for volatile transport and cycling within the Moon are distinct.

The most famous sample to show evidence of volatile enrichment is the Apollo 16 breccia "rusty rock" 66095 in which the halogens are heterogeneously distributed and are housed in FeO(OH,Cl), phosphates, and chlorides (McCubbin et al. 2015 and references therein). Volatiles were likely transported via a S-rich, metal–chloride-bearing, H-poor gas phase. Such low-H content vapors were also responsible for transporting other metals (Zn, Cu, Pb, Fe) and for fractionating chlorine isotopes up to +15.7‰. Direct evidence for vapor deposition of halogens is preserved in Apollo 14 Fra Mauro regolith samples. In those samples, Cl-rich (>2 wt%) apatites occur in void spaces of recrystallized breccia fragments (McKay et al. 1972).

Vapor deposition, however, is not always as easily observed as mineralization of void spaces or co-enrichments of halogens with other volatile elements. In many samples, however, the records are more cryptic. Magmatic volatile records may have been partially-to-fully overprinted by metasomatism, which would involve volatile-rich vapors during the crystallization of basalts, breccias, and impact melts. This manifests as highly variable Cl isotopes in apatites from impact-processed samples, which usually trend towards high ^{37}Cl/^{35}Cl ratios. For example, based on the curvilinear appearance of apatites that cross-cut Apollo 17 feldspathic granulite 79215, it is thought that apatites were added to the protolith by a fluid phase that penetrated along cracks, and that they record the passage of this fluid. The 79215 apatites are Cl-bearing fluorapatite (F/Cl ~ 10) and have fractionated δ^{37}Cl values > +30‰ (Treiman et al. 2014) (Fig. 2). Cryptic metasomatism is a plausible explanation for the Cl signatures in apatite in other impact processed samples like high-aluminum Apollo 14 basalts, impact melt rocks, and cryptomare basaltic meteorite Kalahari 009 (e.g., Potts et al. 2018). Collectively, these samples date from ~3.9 Ga to 4.3 Ga, suggesting that similar fractionation process operated in the lunar crust over that time interval.

The Moon's surface preserves 4.5 billion years' worth of scars from impact bombardment because the Moon lacks plate tectonics. Impact heating, a fundamental aspect of the cratering process, is arguably the most likely mechanism to facilitate the transport of volatiles through the lunar crust. Volatile transport could have occurred in hot (1,000–1,200 °C) ejecta blankets following impact events, which would scavenge elements like Zn, Cl, and Pb, and transport and redeposit them in cooler locations in the ejecta blanket (McKay et al. 1972). It is also possible that volatiles could have been scavenged and fractionated from underlying volatile-bearing crust when hot lavas erupted onto the surface. If the metasomatic process was driven by impact events, then vapor metasomatism and mass transport of halogens within the lunar crust could have been widespread geographically and temporally.

HALOGENS AND HABILITABILITY ON MARS

Decades of research on the red planet have revealed that Mars had a watery past, although it does not have oceans on its surface today (Carr and Head 2015). Remote sensing and in situ measurements of the Martian atmosphere indicate that Mars lost volatiles, such as water, throughout its history. Because the heavy halogens (Cl, Br, and I) are important components of aqueous fluids in which salts dissolve and microbes have been detected in some hypersaline environments on Earth, halogen-rich brines have been posited as potentially habitable environments on Mars. Therefore, determining the character, distribution, and concentration of halogens is an important thread in Martian exploration, because it is related to discussions of habitability, and is integral to the search for past and present water on the planet.

Mars is more halogen-rich than Earth, especially at its surface (e.g., Rampe et al. 2018). Of the halogens, Cl appears in the largest abundances and is the only one to have been detected by all three methods of observation: remote-sensing by orbiting spacecraft, in situ surface exploration by landers and rovers, and laboratory investigation of Martian meteorites. Fluorine and Br have been detected by the *Mars Science Laboratory* rover.

Fluorine, Cl, Br, and I abundances and Cl isotopes have been measured in Martian meteorites. The Martian mantle seems to record a Cl isotopic composition that is light compared to Earth (Fig. 3), which could indicate a nebular component (Shearer et al. 2018). Of the Martian meteorites, the chassignites and nakhlites contain the most evidence for interaction with halogen-bearing fluids. These meteorites are considered cogenetic igneous cumulates (dunites and clinopyroxenites, respectively) with similar crystallization ages of ~1.4 Ga to 1.3 Ga (Borg and Drake 2005). Petrogenetic models indicate that they were emplaced as distinct lava flows and/or magmatic bodies close to the Martian surface. These rocks contain halogen-bearing minerals (F–Cl apatite and Cl-rich amphibole) (Fig. 1E) that record a history of high-temperature (>700 °C) and low-temperature (~200 °C) halogen-dominated hydrothermal alteration (e.g., McCubbin et al. 2009).

In addition to magmatic-hydrothermal fluids, variable amounts of low-temperature postmagmatic, Martian, hydrous alteration are recorded in all Martian meteorites. Collectively, halogen-rich surface alteration on Mars dates between 1 Ma and ~633 Ma (Borg and Drake 2005). Thermochemical modeling of alteration in nakhlites indicates that low-temperature (<200 °C) aqueous fluids altered olivine phenocrysts and some isolated portions of mesostasis under oxidizing conditions in the shallow subsurface. This is significant because whereas surficial acidic fluids have been implicated in the formation of sulfates on Mars, the action of near-surface fluids at habitable conditions (low temperature, alkaline) could have transported bioessential elements, such as K, Na, P, and the halogens (Bridges and Schwenzer 2012).

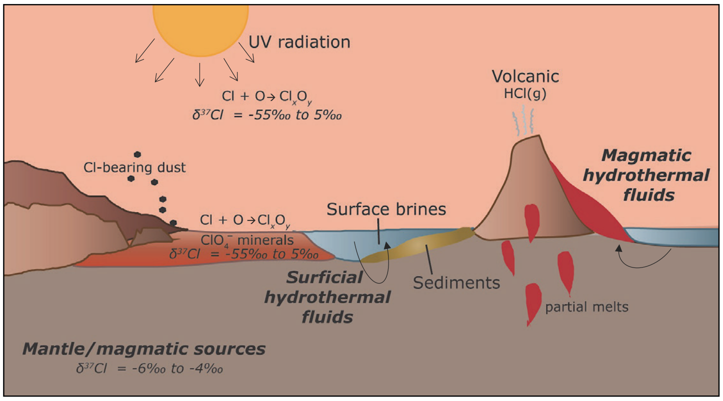

Figure 3 Cycling of chlorine on Mars. Oxychlorine compounds (Cl_xO_y) can be created either in the atmosphere or at the surface. The mantle is characterized by light Cl (Shearer et al. 2018) whereas the surface and regolith (mid-orange color) are mixtures of extremely light oxychlorine compounds and heavy crustal fluids (>0‰). The heat sources required to generate subsurface hydrothermal fluids are debated but could have been provided by impact events. Modified from Bellucci et al. (2017).

Martian surface deposits, as sampled by the *Phoenix* lander and *Mars Science Laboratory* rover, contain considerable amounts of Cl in the form of oxychlorine compounds, such as chlorate (ClO_3^-) and/or perchlorate (ClO_4^-) (e.g., Rampe et al. 2018). Explored terrains on Mars, rare Martian regolith breccia meteorites, and hydrothermally formed minerals show that Cl at the surface of Mars is highly fractionated, with extreme variations beyond that seen on Earth (δ^{37}Cl values −55‰ to +8‰) (Farley et al. 2016; Bellucci et al. 2017) (Fig. 2). The most extreme depletions in ^{37}Cl are associated with oxychlorine-bearing surface materials as measured by the Sample Analysis at Mars instrument on *Mars Science Laboratory*. The detection of oxychlorine compounds in Hesperian-age (3.0–3.7 Ga) sedimentary units (i.e., after the wetter Noachian period, 3.7–4.1 Ga, on Mars) and modern sediments indicates formation conditions for oxychlorine persisted throughout Martian history. Oxychlorine compounds could have been formed in a variety of ways, including oxidation on mineral surfaces, radiolysis by ionizing radiation, and/or UV irradiation (Fig. 3). The highly variable isotopic records of surface materials could be accounted for by interaction of surface fluids with ^{35}Cl-bearing oxychlorine deposits and/or volcanic outgassing of HCl (Fig. 3).

Oxychlorine compounds may, therefore, signal liquid water and mark locations where microbial life may have been sustained and may be preserved. On the other hand, an overabundance of salts could have had a detrimental effect on wider Martian habitability.

FUTURE WORK

Fluids played an important role in mobilizing and redistributing halogens within primitive planetesimals and in the crusts of differentiated bodies. There remain challenges to determining the nature of ancient fluids, in part due to preservation issues, to complex sample histories, and to a lack of planetary-relevant experimental data.

While we are one step closer to understanding the fluid activity preserved in chondritic meteorites, we still do not understand the relationship, if any, between apatite and halite, whether there were multiple sources of halogens (indigenous versus exogeneous), and what the mineralogical hosts of the halogens (especially Br and I) were in aqueously altered chondrites. To address these issues, future studies aimed at combining detailed chemical and textural analysis of phosphates and salts in chondrites should be coupled with trace element, isotopic, and chronological studies. The diligent sample storage, handling, and sample preparation required to preserve and locate salts and other reactive halogen-bearing minerals, and the fragile fluid inclusions within them, makes it especially exciting to see whether samples returned from asteroids Bennu and Ryugu by the OSIRIS-REx and Hayabusa2 missions, respectively, will add to our understanding of ancient fluid activity on primitive, carbon-rich parent bodies.

There is a paucity of aqueous fluid activity recorded on achondrite bodies compared to primitive bodies, which likely reflects the fast accretion in the inner Solar System of the former followed by internal heating and dehydration early in Solar System history. This makes apatite, which is often the only mineral to contain halogens (and OH^-), a very important mineral, because it might be the only one we can use to trace fluid processes on partially melted or differentiated bodies.

Better constraints on the overall halogen budget of Mars will be important to better understand the past and current habitability of the red planet. This might be achieved by two means: (1) the identification of halogen-bearing minerals in newly recognized Martian meteorites and on rocks from the surface of Mars, through samples currently being cached by the Mars 2020 *Perseverance* rover for future return; (2) experimental investigations into their origins.

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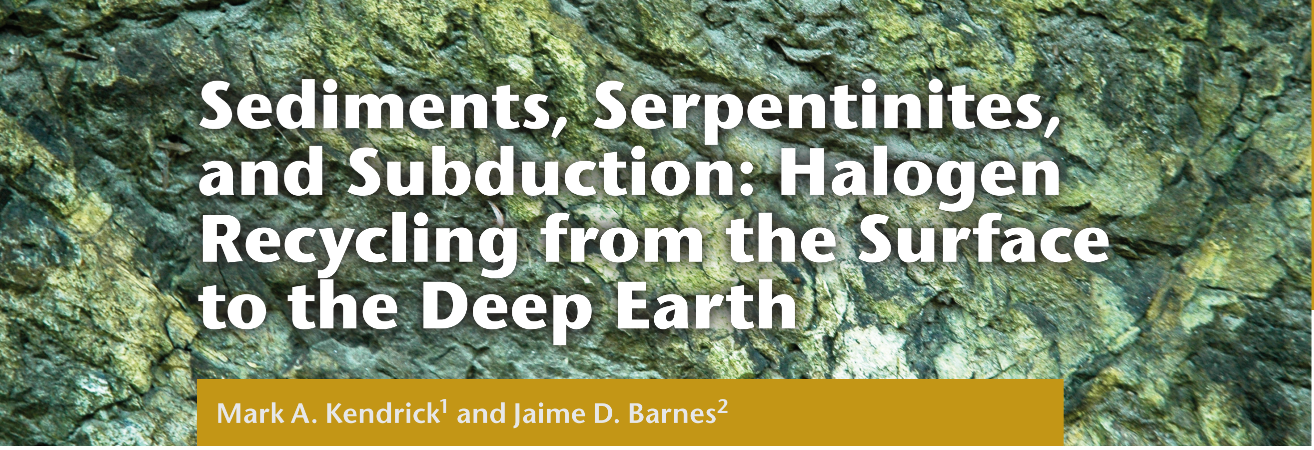

Sediments, Serpentinites, and Subduction: Halogen Recycling from the Surface to the Deep Earth

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Halogens are important elements that participate in a variety of biogeochemical processes and influence the solubility of metals in subduction-zone fluids. Halogens are powerful tracers of subducted volatiles in the Earth's mantle because they have high abundances in seawater, sediments, and altered oceanic lithosphere but low concentrations in the mantle. Additionally, Br/Cl and I/Cl ratios, as well as Cl-isotope ratios, have characteristic ranges in different surface reservoirs that are not easily fractionated in the mantle. Current data suggest that subduction of serpentinised lithosphere is a major source of halogens in the Earth's mantle.

KEYWORDS: altered oceanic crust; basalt glass; volatile cycling

INTRODUCTION

The ability of the halogens (F, Cl, Br, and I) to form halide anions makes them a uniquely important group of elements that are essential for the transport of metals in geofluids and for life on Earth. The high concentrations of Cl, Br, and I in the Earth's surface reservoirs of seawater, sediments, and altered oceanic crust, relative to the mantle, also means that halogens are important tracers of subducted surface volatiles in the Earth's mantle (e.g., Straub and Layne 2003; Barnes et al. 2008; John et al. 2010; Kendrick et al. 2017, 2020; Urann et al. 2020).

This article will outline how the combination of multiple halogens and Cl isotope ratios identify the presence of subducted halogens in the Earth's mantle and help distinguish between the major pathways by which volatiles are subducted. This is possible because while Cl isotope (^{37}Cl/^{35}Cl) and Br/Cl and I/Cl ratios are relatively constant within basaltic melts and the mantle (e.g., Sharp et al. 2013; Kendrick et al. 2017), they are fractionated in surface reservoirs and seafloor settings to produce characteristic signatures in different subduction zone reservoirs (see review of Barnes et al. 2018). Characteristic Cl isotope, Br/Cl, and I/Cl signatures within these different reservoirs can be recognised in subduction-related lavas and used to distinguish between, for example, the subduction of carbonated basalts versus amphibolitised gabbros or the subduction of serpentinites formed in forearc settings versus the lithospheric mantle (Kendrick et al. 2020).

Sediments, altered oceanic crust, and serpentinites all contribute to volatile subduction. However, there is evidence that serpentinisation of olivine-rich rocks in the lower crust and lithospheric mantle is a major control on the concentrations of halogens and other volatile elements recycled into the deep mantle. This is based on the following factors: 1) the concentrations of halogens in different subduction zone lithologies; 2) the Cl isotope and Br/Cl and I/Cl ratios of different subduction zone lithologies; 3) the enrichment and depletion of different mantle reservoirs in halogens and H$_2$O relative to each other and to lithophile elements of similar compatibility; and 4) how these data can best be reconciled with experimental petrology, seismology, and other lines of geological evidence.

HALOGEN RESERVOIRS IN THE MANTLE AND SUBDUCTING SLAB

The primitive mantle (bulk silicate Earth) has estimated concentrations of 17 ± 6 μg/g F, 26 ± 8 μg/g Cl, 76 ± 25 ng/g Br, and 7 ± 4 ng/g I (e.g., Kendrick et al. 2017). On average, the modern mantle is depleted in strongly incompatible Cl, Br, and I by ~70%–95% of the primitive values and in moderately incompatible F by 15%–50% of the primitive value (TABLE 1) (Kendrick et al. 2017). Mid-ocean-ridge basalt (MORB) glasses typically contain ~20–250 μg/g Cl with values outside of this range influenced by the assimilation of seawater components or derived from unusually depleted or enriched mantle domains (e.g., Schilling et al. 1980; Le Voyer et al. 2015; Kendrick et al. 2017).

In comparison with the mantle, subducting slabs including both oceanic lithosphere and overlying marine sediments are strongly enriched in halogens. The dominant form of ocean crust today is produced at fast spreading ridges (e.g., East Pacific Rise). This type of crust comprises: 1) ~1.5−2.5 km of basalt in lavas and sheeted dykes; 2) ~4−5 km of gabbro; and 3) underlying depleted peridotite, all of which can be altered and overlain by sediments (FIG. 1) (Grevemeyer et al. 2018). The sheeted dykes and lavas are subjected to high-temperature alteration by seawater-derived hydrothermal fluids at the spreading axes, with deeper penetration of seawater and high temperature alteration of the gabbros following crystallisation of the melt lens. Low-temperature alteration and carbonation continue off-axis, gradually decreasing in intensity as the crust cools and gets covered by an impermeable blanket of sediments (Staudigel 2014). However, seismic data and heat flow measurements suggest that renewed alteration occurs prior to subduction at the slab-bend, where newly developed faults penetrate more than ~25 km into the lithosphere enabling serpentinization of the lithospheric mantle (e.g., Grevemeyer et al. 2018). Further alteration of the slab occurs as slab fluids migrate through the slab

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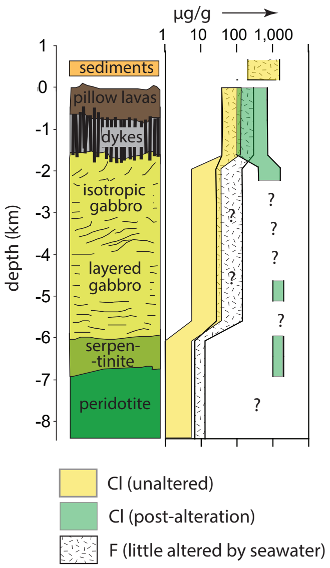

FIGURE 1 Schematic diagram of oceanic lithosphere produced at fast spreading ridges correlated to representative F and Cl concentrations (TABLE 1). Cumulates in the lower ocean crust are initially much more depleted in Cl than overlying lavas but can be strongly enriched by seawater alteration. The highest concentrations of Cl are found in amphibolites and serpentinised olivine-rich rocks in the lower oceanic crust. DATA SOURCES FOUND AT HTTP://ELEMENTSMAGAZINE.ORG/SUPPLEMENTS.

during subduction, with serpentinisation of the forearc mantle wedge commonly attributed to dewatering of sediments by compaction and to low-grade diagenetic reactions (Barnes et al. 2018 and references therein).

Fresh basalts have halogen concentrations 20%–80% lower than related glasses (Schilling et al. 1980), whereas fresh cumulate gabbros have much lower concentrations: less than ~10–30 μg/g Cl (TABLE 1). In comparison, altered basalts and gabbros are enriched in Cl, Br, and I (TABLE 1). Altered basalts recovered from the Integrated Ocean Drilling Program (IODP) Hole 1256D, close to the East Pacific Rise, have concentrations of ~100—700 μg/g Cl, ~0.5—2 μg/g Br, and 5—25 ng/g I ; and the uppermost gabbros have 500—1,600 μg/g Cl, 0.1–2.7 μg/g Br, and 1—12 ng/g I (e.g., Chavrit et al. 2016; Kendrick 2019). In contrast, altered basalts and gabbros have ~100—250 μg/g F that is probably close to the pre-alteration concentration (Kendrick 2019). The strong enrichment of Cl, Br, and I and the lack of F enrichment in altered oceanic crust is explained by the low solubility of F in seawater. Seawater contains only 1.3 μg/g F (less than in the mantle), but is strongly enriched in heavy halogens, having 1.9 wt. % Cl, 67 μg/g Br, and ~58 ng/g I (TABLE 1). The uppermost lavas and dykes of IODP Hole 1256D host halogens in clay minerals, including smectites and chlorite, with amphibole and fluid inclusions becoming important in the lower sheeted dykes.

Several studies have shown the Cl content of amphibole increases with metamorphic grade from tens to a few hundred μg/g Cl in actinolites formed under greenschist facies conditions to thousands of μg/g Cl in hornblendes and pargasitic amphiboles formed under amphibolite facies conditions. The increase in amphibole Cl concentration with depth results partly from the involvement of progressively higher salinity fluids at lower water:rock ratios in the deeper parts of the crust (Kendrick 2019 and references therein). Most Cl-rich amphiboles have low F/Cl ratios of <1, which is consistent with having formed from seawater-derived fluids. High F/Cl ratios of 6–20 can be related to the involvement of late-stage magmatic fluids (e.g., Kendrick 2019), although amphibole F/Cl is also influenced by element compatibility.

Analysis of serpentinites have been reported for drill-core samples of seafloor (abyssal) serpentinite, forearc serpentinites, and ophiolitic serpentinites (TABLE 1). Average seafloor serpentinites contain ~2,000 μg/g Cl (TABLE 1) (see review of Barnes et al. 2018 and refs therein); however, serpentinites can have whole-rock concentrations as high as ~1 wt% Cl, 5—24 μg/g Br, and 1–45 μg/g I (see TABLE 1 and Supplemental Material). Bulk analyses of chrysotile-bearing "seafloor" serpentinites indicate typical concentrations of 1—30 μg/g F (John et al. 2011; Kendrick et al. 2018), which is close to the expected range of depleted peridotites. In comparison, serpentine from the Kane Fracture Zone of the Mid-Atlantic Ridge has higher concentrations of 50—300 μg/g F, which must reflect either prolonged alteration at a high water:rock ratio (Debret et al. 2014) or the involvement of F-rich fluids.

The thickness and composition of subducting sediments is tremendously variable. A substantial part of the total Cl, Br, and I within sediments is initially hosted by pore waters (TABLE 1), which have near-seawater salinities that occupy up to ~80 volume % of unlithified sediments. Relative to seawater, the pore fluids are strongly enriched in Br, I, and CH_4 released by the degradation of organic matter (e.g., Muramatsu et al. 2001). Marine sediments have high concentrations of structurally bound halogens: authigenic or detrital clay minerals often dominate the F and Cl budgets, and organic matter often dominates the Br and I budget. However, when present, carbonate minerals can host significant F (~200—1,500 μg/g) and I (~1—9 μg/g) (TABLE 1). The reported range of halogen concentrations in sediments is influenced by sample preparation and washing procedures. Washed sediments that are free of pore fluid salts are probably most representative of compacted dewatered sediments subducted into the mantle. Lithified

TABLE 1 REPRESENTATIVE HALOGEN CONCENTRATIONS IN FLUIDS AND SUBDUCTION RESERVOIRS[1]

	F (μg/g)	Cl (μg/g)	Br (μg/g)	I (μg/g)
Seawater	1.3	19,300	67	0.058
Sediment pore water	0.04–2	17,000–23,000	60–260	0.1–220
Unlithified sediments[2]	400–1500	40–2,000	0.3–70	0.5–76
Lithified sediments	700–1300	30–1,200	0.03–22	0.1–10
Mid-ocean-ridge basalt glass	80–300	20–250	50–800	0.001–0.020
Altered ocean crust	20–300	20–2000	0.02–3	0.001–3
Eclogites	<100–800	100–200	0.01–0.4	0.001–0.04
Seafloor serpentinites	1–30	100–4,000	0.4–7	0.003–0.6
Forearc serpentinites	50–650	400–2,300	0.03–24	0.03–45
Antigorite-serpentinites	7–150	80–600	0.3–2	0.04–0.2
Secondary peridotites[3]	11–200	40–400	0.1–0.8	0.008–0.07
Average modern mantle[4]	12 ± 2	5 ± 2	0.013 ± 0.006	0.0003 ± 0.0001

[1] Data sources at http://elementsmagazine.org/supplements.

[2] Pore fluid salt is removed by washing.

[3] Formed by serpentinite dehydration.

[4] Concentrations in average processed mantle. FROM KENDRICK ET AL. (2017).

sediments contain less Br and I than is present in unlithified pelagic sediment (TABLE 1). However, the concentrations of halogens in sediments depends strongly on the mineralogy and maturation of organic matter.

HALOGEN FRACTIONATION IN SURFACE RESERVOIRS

The relative abundances of halogens (F/Cl, Br/Cl, and I/Cl) vary systematically between each of the previously described surface reservoirs, reflecting the limited number of processes that fractionate these elements.

First and foremost, F is strongly decoupled from Cl, Br, and I by its higher compatibility in mantle minerals (e.g., Schilling et al. 1980; Kendrick et al. 2017) and its low solubility in seawater and low-temperature pore fluids (e.g., Seyfried and Ding 1995). As a result, seawater is strongly enriched in Cl, Br, and I compared to the mantle, but not F (TABLE 1) and consequently altered ocean crust is strongly enriched in Cl, Br, and I, but not F (e.g., Kendrick 2019).

Due to the enrichment of Br and I in organic matter, sedimentary pore fluids are systematically enriched in Br and I relative to Cl in seawater and define a limited range of Br/I ratios (FIG. 2A). Ophiolitic and forearc serpentinites typically have elevated Br/Cl and I/Cl ratios that overlap sedimentary pore waters (FIG. 2A). This is consistent with forearc serpentinisation being driven by dewatering of sediments early in the subduction cycle and the juxtaposition of serpentinites and sediments during ophiolite emplacement.

The high oxidation potential of I means that seawater is dominated by iodate rather than iodide, whereas all the other halogens are present in seawater as halides. Iodate is more readily adsorbed onto oxyhydroxides than iodide and can substitute for the CO_3^{2-} group in carbonate minerals (e.g., Kendrick 2019; Kendrick et al. 2020 and refs therein). As a result, low temperature alteration on the Atlantis Bank (IODP Hole 1473A) is characterised by uniquely elevated I/Cl ratios (FIG. 2A). Importantly, this oxidised I-rich alteration lacks the strong enrichment of Br/Cl that accompanies I/Cl enrichment in sediment pore waters, meaning that these alternative causes of I-enrichment can be distinguished (FIG. 2).

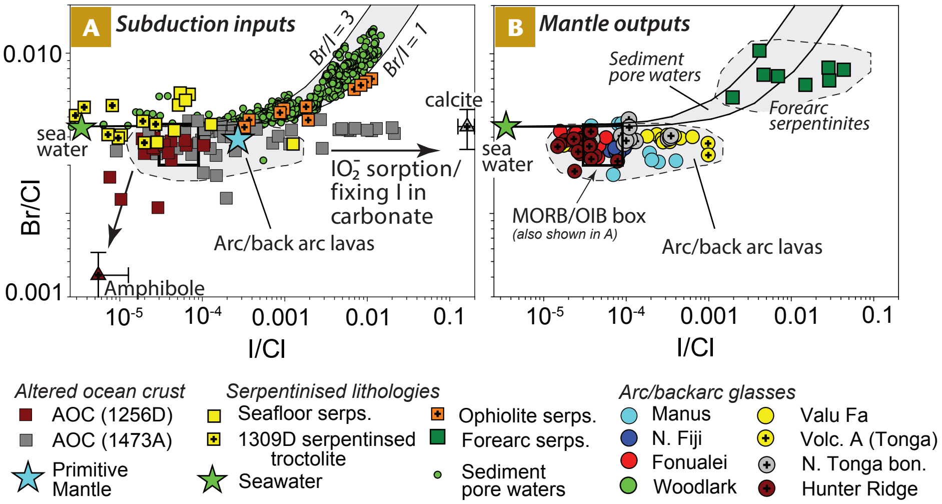

FIGURE 2 Summary of Br/Cl and I/Cl ratios of selected (**A**) subduction zone inputs and (**B**) mantle outputs. The compositional range of mid-ocean-ridge basalt (MORB) and ocean island basalt (OIB) are shown by the boxes in panels A and B. Abbreviations: serps = serpentinites; bon. = boninite; AOC = altered ocean crust. Note submarine arc glasses are distinguished from submarine back-arc glasses by a cross. DATA SOURCES FOUND AT HTTP://ELEMENTSMAGAZINE.ORG/SUPPLEMENTS.

All alteration minerals in the oceanic lithosphere have the potential to influence halogen abundance ratios. However, to date, significant fractionations have been linked to only carbonate and amphibole (FIG. 2A). Carbonate preferentially incorporates F and I over Cl and Br, whereas amphibole preferentially incorporates the smaller F^- and Cl^- anions over Br^- and I^-. The available data indicate serpentine (and, potentially, other clay minerals) preserve Br/Cl and I/Cl ratios similar to the alteration fluid. This is indicated by serpentinites from forearc and from ophiolite settings preserving Br/Cl and I/Cl ratios similar to sediment pore waters (Kendrick et al. 2018). And serpentinised olivine-rich troctolites from IOPD Hole 1309D on the Mid-Atlantic Ridge preserving very different Br/Cl and I/Cl ratios that are similar to seawater (FIG. 2A).

Chlorine isotope ratios ($\delta^{37}Cl$) range from about −3‰ to +2‰ in sediments, altered ocean crust, and serpentinites (FIG. 3). The lowest $\delta^{37}Cl$ values in the altered ocean crust and serpentinites are systematically related to low-temperature formation of clay minerals and serpentinisation by sedimentary pore waters (FIG. 3). In comparison with the solid phases, sedimentary pore waters have distinctly lower $\delta^{37}Cl$ values of about −8‰ to 0‰ (FIG. 3). In contrast to the variability of $\delta^{37}Cl$ in subducting reservoirs, the Earth's mantle has a $\delta^{37}Cl$ of −0.2‰ ± 0.3‰ (Sharp et al. 2013), which is within the uncertainty range of seawater. Given the homogeneity of $\delta^{37}Cl$ in most of the mantle (Sharp et al. 2013), Cl isotopes have proven to be an effective means to trace distinct subducted components in arc lavas (Barnes et al. 2008; Barnes et al. 2018 and references therein) and some enriched mantle reservoirs (e.g., John et al. 2010).

METAMORPHIC DEHYDRATION

A variety of continuous and discontinuous metamorphic dehydration reactions occur during subduction, which means that slab-fluid composition evolves during subduction and progressive slab dehydration. A large number of studies have investigated the Cl content of blueschist and eclogite facies metasediments, metabasites, and serpentinites/secondary peridotites (e.g., Philippot et al. 1998; Scambelluri et al. 2015); however, much less data are available for the other halogens (John et al. 2011; Pagé et al. 2016; Hughes et al. 2018; Kendrick et al. 2018). All studies agree that the halogen content of slab lithologies decreases with prograde metamorphism and suggest that Cl isotopes are not fractionated during subduction (e.g., John et al. 2011). However, questions remain about the efficiency of halogen loss and the extent to which halogens are fractionated from one another during subduction.

Analyses of minerals in ophiolites from the Western Alps indicate that blueschist and eclogite facies metagabbros have <60 µg/g F, <80 µg/g Cl, <120 ng/g Br, and <40 ng/g I, which are substantially lower than that of altered ocean crust (Debret et al. 2016; Hughes et al. 2018). The implied loss of halogens from blueschists and eclogites in the Western Alps coincides with the decrease in Cl and F concentration between low-pressure amphibole and glaucophane (Debret et al. 2016). However, while lawsonite blueschists from Turkey have similarly low concentrations of 10–50 µg/g Cl and 100–500 ng/g Br, they are substantially enriched with 200–800 µg/g F and 100–1,500 ng/g I (Pagé et al. 2016). Similarly, eclogites from Ecuador have less than 10 µg/g Cl, but have calculated concentrations of 100–400 µg/g F (Urann et al. 2020). The reported moderate enrichment of F in some eclogites, or its lack of depletion relative to likely protoliths (Pagé et al. 2016; Urann et al. 2020), suggests that variable quantities of F (and other halogens) might be introduced into metabasites by fluid migration within subducting slabs. Marine carbonates and clay minerals can contain 300–1,500 µg/g F, which is preserved within metasediments and only mobilised during high-grade metamorphism. Evidence for F migration in eclogites is clearly preserved within eclogite lenses and surrounding metasediments in the Erzebirge (Germany), where amphibole, phengite, and garnet in eclogite contains thousands of µg/g of F introduced from the surrounding metasediments (Gross et al. 2008).

Eclogites are known to trap fluid inclusions with a range of compositions, including high-salinity brine inclusions that are relatively enriched in Br and I, as well as low-salinity fluid inclusions and CO_2 fluid inclusions (Svensen et al. 2001). Allowing for the presence of fluid inclusions, Phillipot et al. (1998) estimated typical concentrations of 100–200 µg/g Cl in eclogite facies oceanic crust subducted into the mantle. The lower limit of ~100 µg/g Cl is only slightly higher than the range of 60–80 µg/g Cl suggested based on in situ analyses of eclogite minerals (ignoring fluid inclusions) from the Western Alps (Debret et al. 2016). In contrast, Ecuadorian eclogites prepared as washed whole-rock powders (which removes fluid inclusion salts) have much lower concentrations of Cl (Urann et al. 2020). These data indicate that the amount of Cl preserved in minerals in different terranes is variable but suggest that, if fluid inclusion salts are included, whole-rock concentrations of more than 100 µg/g Cl in eclogites are realistic.

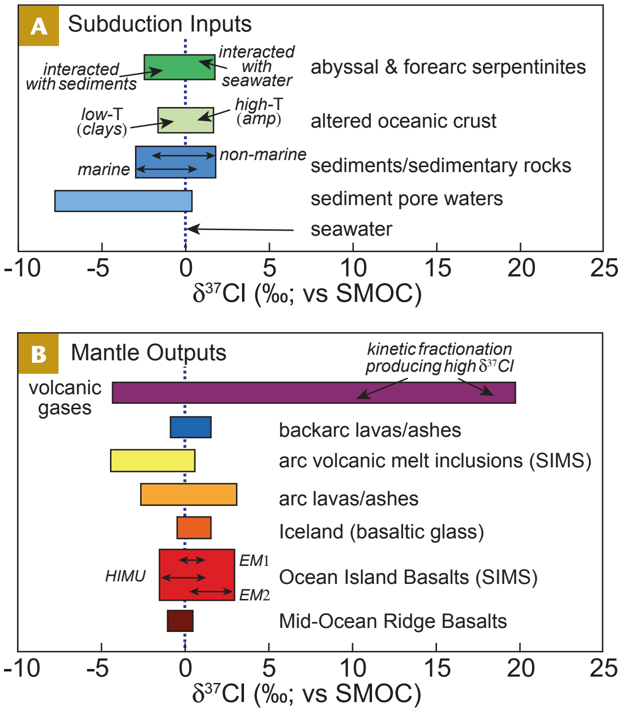

Figure 3 The chlorine isotope composition, expressed as δ^{37}Cl relative to Standard Mean Ocean Chloride (SMOC), of various (**A**) subduction zone inputs and (**B**) mantle outputs. Data were obtained by isotope ratio mass spectrometry, except where secondary ion mass spectrometry (SIMS) is indicated. Note that the large range of δ^{37}Cl in volcanic gases is a result of kinetic fractionation and is not representative of the chloride's source. Abbreviations: HIMU, EM1, and EM2 represent distinct mantle reservoirs, see text. Data sources found at http://elementsmagazine.org/supplements.

Eclogite-facies antigorite serpentinites from Erro Tobbio (Italy) and chlorite harzburgites from Cerro del Almirez (Spain) retain concentrations of 10–200 µg/g F, 200–400 µg/g Cl, 2–2,000 ng/g Br, and 4–200 ng/g I: these values are substantially higher than for typical eclogites and reflect the initially high concentrations of halogens in seafloor serpentinites (John et al. 2011; Kendrick et al. 2018). The peak metamorphic mineral assemblage in secondary garnet peridotites from Cima di Gagnone, which formed by the complete dehydration of serpentinites, are estimated to preserve ~11 µg/g F, ~40 µg/g Cl, 180 ng/g Br, and ~9 ng/g I (Kendrick et al. 2018). The abundances of halogens preserved by nominally anhydrous minerals and desiccated fluid inclusion remnants within this lithology (Scambelluri et al. 2015) remains significantly higher than halogen concentrations in the depleted upper mantle (Table 1).

In summary, the available data confirm that halogens (and other seawater-derived volatiles) are progressively removed from the slab during metamorphism but that devolatilisation never reaches completion. Furthermore, variable enrichments or depletions of F and I imply that fluid exchange occurs between different rock units during subduction. This makes it difficult to accurately access the overall dehydration efficiency of each halogen from a single suite of metamorphic rocks. Furthermore, the halogen signature of subducted ocean crust may evolve to include some attributes inherited from sediments during subduction.

SUBDUCTION-RELATED LAVAS

Most studies have concluded that halogens are quantitatively retained in submarine glasses erupted in water depths of more than ~1,000 m (e.g., Straub and Layne 2003). The heavy halogens (Cl, Br, I) are all strongly incompatible in the mantle, comparable to K or Nb, whereas F is only moderately incompatible, comparable to Pr or Nd (e.g., Kendrick et al. 2017). As a result, the Br/Cl and I/Cl ratios of basalt melts (that have not assimilated seawater components) are representative of their mantle source and can be compared directly to possible sources in subducting slabs. In contrast, mantle F/Cl ratios vary systematically as a function of mantle depletion as well as the halogen source (Kendrick et al. 2017, 2020).

Fluorine, Cl, Br, and I have now been investigated in submarine glasses from all major tectonic settings: mid-ocean ridges; arcs and backarcs that have strong evidence for subduction components; and oceanic islands that sample distinct mantle reservoirs that are interpreted to have been enriched by the presence of deeply subducted slabs (i.e. EM1, EM2 and HIMU). The EM1 and EM2 reservoirs (enriched mantle 1 and 2)—characterized by low ^{143}Nd/^{144}Nd and high ^{87}Sr/^{86}Sr ratios—are commonly attributed to subducted sediments. The HIMU reservoir (i.e., "high µ" = high ^{238}U/^{204}Pb) is characterized by highly radiogenic Pb isotope ratios and is commonly attributed to subduction of altered ocean crust and lithosphere (e.g., Kendrick et al. 2017).

Relative to mid-ocean-ridge basalts (Fig. 2A), arc and backarc lavas are strongly enriched in H_2O, Cl, Br, and I and weakly enriched in F (Fig. 4). This reflects the much stronger enrichment of Cl, Br, and I in the slab compared to F, and the relatively low mobility of F in slab fluids

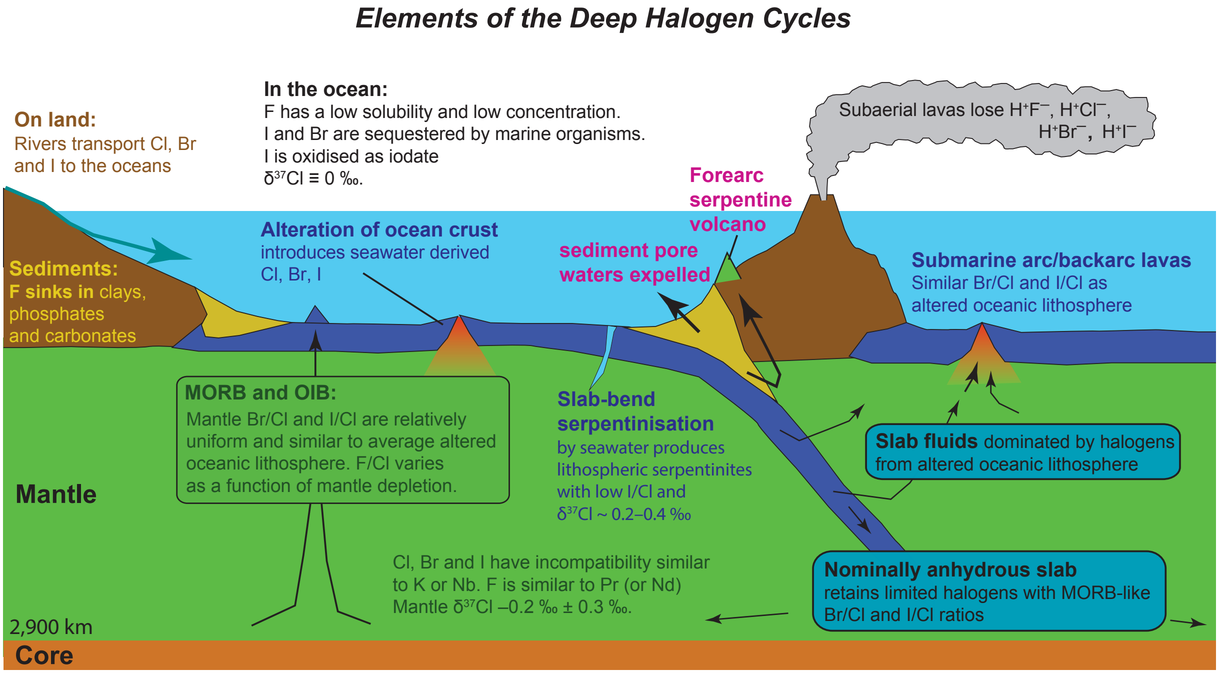

FIGURE 4 Schematic diagram highlighting important processes that fraction halogen abundance ratios or isotopes in the global halogen cycles. Abbreviations: MORB = mid-ocean-ridge basalt; OIB = ocean island basalt. MODIFIED FROM KENDRICK ET AL. (2020).

(Straub and Layne 2003; Kendrick et al. 2020). Compared to mid-ocean-ridge basalts, the enriched mantle reservoirs (EM1 and EM2) are depleted in H_2O, Cl, Br, and I relative to lithophile elements of similar compatibility and have F/Cl ratios of ~2–4 (FIG. 4). Allowing for fractionation of F/Cl during mantle melting and depletion events, this is consistent with the presence of dehydrated slab residues with F/Cl of ~5 ± 2 (Stroncik and Haase 2004; Kendrick et al. 2017, 2020). Relative to MORB, HIMU mantle reservoirs are depleted in fluid mobile lithophile elements, which is expected for dehydrated altered ocean crust. However, HIMU lavas have H_2O/Ce and Cl/K ratios that are both higher and lower than MORB and higher than EM reservoirs (Stroncik and Haase 2004; John et al. 2010; Kendrick et al. 2017). The enrichment of H_2O and Cl relative to EM reservoirs has been attributed to the hybrid nature of the HIMU reservoir, which probably represents dehydrated crustal material (which dominates the lithophile trace element signature) variably re-enriched by H_2O, Cl, Br, and I derived from serpentinised lithosphere that continued to dehydrate after subduction beyond sub-arc depths (Stroncik and Haase 2004; Kendrick et al. 2017).

The Br/Cl and I/Cl signatures of forearc serpentinites and arc lavas provide further insights on the source of halogens (and other volatiles) subducted to sub-arc depths. Forearc serpentinites have variable Br/Cl and I/Cl signatures, reflecting the diversity of early released slab fluids (Pagé and Hattori 2017; Kendrick et al. 2018). However, the involvement of fluids with elevated Br/Cl and I/Cl that overlap sedimentary pore waters in the Marianas and Guatemala (Kendrick et al. 2018) suggests that sediment-derived halogens are lost relatively early in the subduction cycle. Forearc serpentine seamounts from the Izu and Marianas (~30 km above the subducting slab) are characterised by slightly positive $\delta^{37}Cl$ values that are higher than typical sedimentary pore fluids (FIG. 3). These fluids could be derived from dehydration reactions (e.g., chrysotile breakdown) suggesting sediment pore waters must be largely recycled to the surface during compaction at an even earlier stage of subduction (Barnes et al. 2008). This is consistent with I and Br recycling through accretionary prisms (e.g., Muramatsu et al. 2001), suggesting shallow loss of sediment pore waters globally (Barnes et al. 2018 and references therein).

Arc and backarc lavas in the southwest Pacific Ocean have elevated Cl/Nb ratios and overlapping ranges of Br/Cl and I/Cl that indicate halogens were probably derived from similar reservoirs in the subducting slab. The subducted halogens are characterized by lower-than-seawater Br/Cl ratios that are similar to the altered ocean crust and lithosphere and are distinctly different from the high Br/Cl ratios seen in organic-rich sediments and sediment pore waters (FIG. 2). The variable I/Cl ratios of arc lavas suggest origins from within different parts of the altered oceanic lithosphere, potentially including I-rich carbonated and oxidised alteration assemblages. The average I/Cl, Br/Cl, and Cl isotope signature of the subducted components in the lavas investigated are similar to mid-ocean-ridge and ocean island basalt lavas (FIG. 2). This is consistent with the possibility that subducted halogens from within different parts of the oceanic lithosphere are progressively homogenised during subduction and mixed throughout the Earth's mantle (Kendrick et al. 2020).

Questions remain about the extent to which small volumes of I-rich and Br-rich fluid can be subducted to sub-arc depths (e.g., Sumino et al. 2010), and the extent to which non-zero $\delta^{37}Cl$ values in arc-related melt inclusions, or some enriched mantle reservoirs, require the subduction of distinct sedimentary components (John et al. 2010; Bouvier et al. 2019). However, the majority of data suggest that halogens are subducted predominantly in oceanic lithosphere rather than sediments. The mantle now has an I/Cl ratio of substantially less than the calculated primitive mantle value (based on the sum of Cl and I in Earth reservoirs), which cannot be explained by subduction of iodine-rich sediments. Kendrick et al. (2017, 2020) have argued that Cl and Br are subducted more efficiently than I, causing a reduction in the mantle I/Cl ratio over Earth's history. Serpentinised troctolites from IODP Hole 1309D on the Mid-Atlantic Ridge provide evidence that serpentinised lithologies formed from seawater can have low I/Cl ratios (FIG. 2A). Therefore, subduction of I-poor serpentinites formed from seawater, either on the seafloor or at the slab-bend, is consistent with a reduction in mantle I/Cl ratio over time and could help balance the global halogen cycle (Kendrick et al. 2020). In contrast, forearc serpentinites that formed from sediment pore waters have elevated I/Cl ratios, implying that forearc serpentinites have a limited role in subduction of halogens to sub-arc depths or the deep mantle (Kendrick et al. 2020).

SUMMARY

The extent of variation in halogen concentrations, relative abundance ratios, and isotopic composition in the ocean crust and lithosphere, and in the Earth's mantle, is much better known now than 10 years ago. Furthermore, most of the observed variation can be explained by known processes and differences in the chemical behaviors of F, Cl, Br, and I. Nonetheless, substantial uncertainties still exist in several parts of the halogen cycle (Fig. 4). The difficulty of estimating halogen abundances in heterogeneous and under-sampled reservoirs means that subduction budgets will only be incrementally improved by the traditional mass balance approach. However, future investigations of multiple halogens and Cl isotope compositions in carefully selected natural samples that combine in situ and bulk methods, and experimental studies of halogen partitioning in selected minerals, will enable the continued development of a process-orientated understanding of halogen subduction (Fig. 4). Future in-depth studies, therefore, hold the potential to significantly improve our quantitative understanding of the halogen subduction cycles.

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Natural Halogen Emissions to the Atmosphere: Sources, Flux, and Environmental Impact

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Sea-spray is the major natural source of inorganic Cl and Br in the MABL.

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Understanding the atmospheric geochemical cycle of both natural and anthropogenic halogens is important because of the detrimental effect halogens have on the environment, notably on tropospheric and stratospheric ozone. Oceans are the primary natural source for atmospheric Cl, F, Br, and I, but anthropogenic emissions are still important, especially for Cl. While emissions of human-made halocarbons (e.g., chlorofluorocarbons or CFCs) are expected to continue to decrease allowing progressive stratospheric ozone recovery, volcanic activity (e.g., clusters of mid-scale explosive eruptions or large-scale explosive eruptions) might disturb this recovery over the next decades. This review provides a synthesis of natural halogen fluxes from oceanic, terrestrial, and volcanic sources, and discusses the role of natural halogen species on atmosphere chemistry and their environmental impact.

Keywords: methyl halides; very-short lived substances; bromine; oceans; volcanic gases; ozone depletion

INTRODUCTION

Halogens (chlorine, fluorine, bromine, iodine) are present as trace gases in the atmosphere but, due to their high reactivity, exert a profound impact on tropospheric and stratospheric chemistry. Halogen-containing compounds from Earth's surface release their constituent atoms by exposure to ultraviolet light and oxidation upon reaching the stratosphere. The halogen atoms, particularly Cl and Br, then undergo a series of photochemical reactions that catalytically destroy ozone (O_3) (e.g., Saiz-Lopez and von Glasow 2012). Consequently, even very small amounts of halogens can produce dramatic ozone losses, such as those observed over the polar regions in springtime and in the exhaust plumes of rockets fuelled by Cl-containing propellants. Halogens may also affect climate by modifying tropospheric methane, ozone, and particles, all of which are powerful climate forcing agents through direct and indirect radiative effects. As tropospheric halogens impact the oxidation power of the atmosphere, they also influence the fate of many planetary boundary layer pollutants.

Over the past decades, attention in atmospheric chemistry has mostly centred on halogens of anthropogenic origin, such as the halocarbons—the chlorofluorocarbons (CFCs), halons ($CBrF_3$, CBr_2ClF), and chlorinated solvents (e.g., CH_3CCl_3, CCl_4)—and their replacements, the hydrochlorofluorocarbons (HCFCs). More recently, the methyl halides CH_3Cl and CH_3Br have received similar attention. CH_3Cl and CH_3Br result from both natural and anthropogenic emissions and have lifetimes of around a year, making them much shorter-lived than the CFCs, solvents, and halons banned by international agreement. Nevertheless, large fractions of their surface emissions reach the stratosphere, where they contribute to ozone depletion (Fig. 1). Finally, very short-lived substances (VSLSs; e.g., CH_2Cl_2, $CHCl_3$) with lifetimes of less than 6 months, play an important role for tropospheric and stratospheric halogen budgets. While VSLSs have large, mainly oceanic, natural sources, increasing anthropogenic production has recently gained much attention (e.g., Engel et al. 2018).

A key issue in the understanding of the global halogen cycles is the unbalanced atmospheric budget of natural Cl and Br, with the input flux (emissions to the atmosphere) being lower than that of the sinks (removal from the atmosphere) (Carpenter et al. 2014). The missing sources may not, however, be oceanic (e.g., Moore et al. 1996). In the 2000s, high emissions of methyl halides from terrestrial and coastal ecosystems were identified, notably as strong CH_3Cl emissions from tropical plants and trees (Yokouchi et al. 2002). Keppler et al. (2000) brought to light an abiotic mechanism of organic halide production in organic-rich soils (e.g., peatlands). In 2002, the first direct detection of BrO in the eruptive cloud of the Soufrière Hills Volcano (Montserrat) (Bobrowski et al. 2003), and the ensuing observations at other volcanoes (e.g., Aiuppa et al. 2005), have suggested that volcanic activity could also account for a substantial part of the missing natural sources of atmospheric Br (Fig. 1).

This article reviews the natural sources of atmospheric halogens, provides an up-to-date view of natural halogens fluxes, and discusses their past, present, and future impact on the environment.

NATURAL SOURCES OF HALOGENS

Oceanic Sources

The ocean acts as a source for various halogen species, including the longer-lived methyl halides and the halogenated VSLSs (Fig. 1). For the methyl halides CH_3Br and CH_3Cl, biogenic processes in phytoplankton species are believed to be the primary source, tropical phytoplankton

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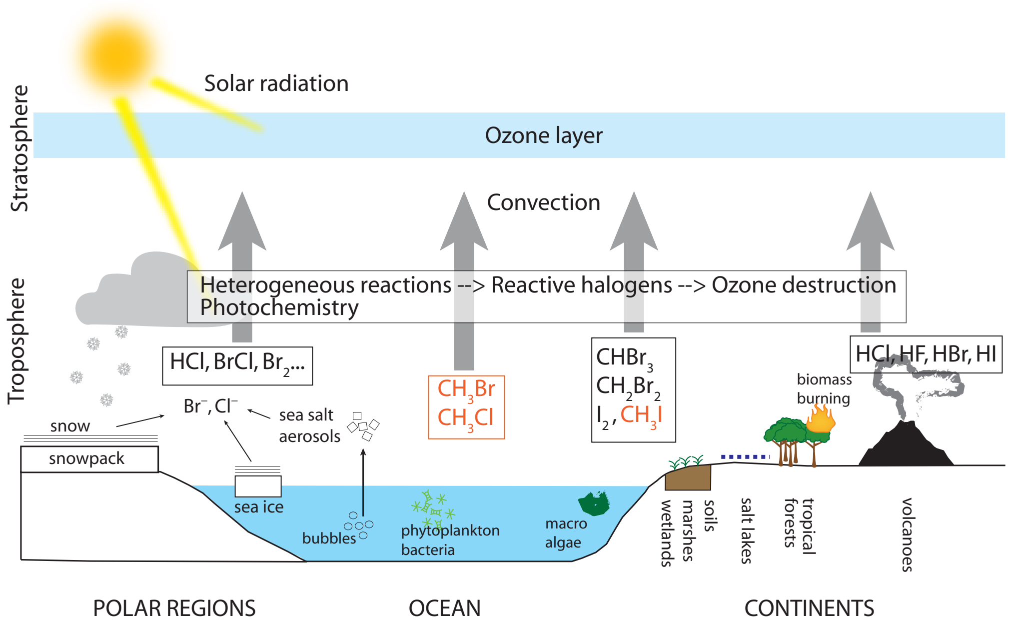

FIGURE 1 Schematic depiction of the main natural sources of halogens. Halogens are mainly emitted from the ocean via marine organisms such as phytoplankton and macroalgae, but also via sea salts. On land, terrestrial ecosystems (coastal salt marshes; soils, including fungi; tropical and subtropical plants; wetlands; salt lakes) are also significant contributors together with volcanoes (through passive and eruptive degassing of magma). In polar regions, halogens are emitted from sea ice and snow. The main source gases are indicated in boxes: orange colour indicates the long-lived gases (i.e., residence time in the stratosphere is longer than six months). Once emitted in the atmosphere, the halogenated compounds are rapidly involved in complex heterogeneous reactions (implying aerosols, solar radiation, clouds, etc.). During these reactions, they convert into reactive halogens species (see text and FIGS. 2 and 3), which destroy ozone molecules. A fraction of the natural halogens reaches the stratosphere, where other chemical reactions take place leading to stratospheric ozone depletion.

species having faster production rates than temperate species (Scarratt and Moore 1996). Coastal regions are also highly productive for CH_3Br, which is potentially related to phytoplankton blooms, while for CH_3Cl, phytoplankton communities in the open ocean might be more efficient producers (FIG. 2) (Hu et al. 2013). For both species, the ocean is also an effective sink due to chemical degradation and uptake by bacteria.

Oceanic production of halogenated VSLSs, such as $CHCl_3$, $CHBr_3$, CH_2Br_2, and CH_3I, occurs in macro- and microalgae (Gschwend et al. 1985). In a first step, bromide (Br^-), an abundant anion in seawater, is oxidized in the presence of the enzyme bromoperoxidase (FIG. 2). In a second step, the halogenation of organic compounds leads mainly to $CHBr_3$ production, with lesser amounts of CH_2Br_2. For macroalgae in coastal waters, halocarbon production is thought to be an antioxidant response that protects the algae from environmental stresses. In the open ocean, $CHBr_3$ synthesis is mainly related to phytoplankton (Moore et al. 1996); however, it is unclear whether it is formed extra- or intracellularly. In addition to the biotic processes, CH_3I is produced in abiotic processes, such as the photochemical breakdown of dissolved organic matter.

The major oceanic halogen source occurs via the release of halogens in inorganic form. One important mechanism is based on the reaction of ozone with I at the ocean surface, which leads to ozone deposition and the emission of inorganic HOI and I_2 to the atmosphere (see Carpenter et al. 2014). Another mechanism is based on the injection of Br and Cl into the atmosphere in association with sea-salt aerosol released by breaking waves on the ocean surface (FIG. 2). Observations of strong Br depletion in aerosols relative to seawater composition indicate that sea-salt aerosol debromination is an important source of tropospheric Br. Similarly, sea-salt aerosol dichlorination represents a large source of Cl gases to the troposphere.

Terrestrial and Cryosphere Sources

Snow and ice are known to be locally important bromine and iodine sources (FIG. 1). Fresh sea ice, multiyear sea ice, frost flowers, snowpack, and blowing snow all play a role in the formation and transformations of reactive halogenated species. In particular, first-year sea ice with highly saline surfaces and precipitating salts can lead to enriched bromide brine concentrations at the ice surfaces (Abbatt et al. 2012). The most efficient Br production was observed from tundra snow and snow above first-year sea ice, where exponential increase in gaseous Br radicals (the so-called Br explosion) and Br release through wind pumping act as efficient mechanisms for halogen activation. Algae growing under sea ice may also heavily contribute to the total I concentration in the atmosphere, especially in the Antarctic region (Saiz-Lopez et al. 2015).

Terrestrial ecosystems and natural biomass burning are efficient sources of atmospheric methyl halides (e.g., Yokouchi et al. 2002) and of some VSLSs (FIG. 1). Coastal-terrestrial ecosystem sources include salt marshes and mangroves, which have emissions associated with halophytic vascular plants. Tropical-forest ecosystem sources include living tropical plants, senescent or dead leaves, and wood-rotting fungi. Formation processes of CH_3Cl could be related to the widespread plant structural component pectin reacting with chloride ions. In addition, the oxidation of organic matter by Fe(III) can lead to abiotic emissions of methyl halides and chlorinated VSLSs from soil, sediments, and salt lake deposits (FIG. 1).

Volcanic Activity

Volcanoes emit large amounts of gas, including halogens, through magma degassing. At deep to mid-crustal depths, volatile species (i.e., gases) are dissolved in the liquid phase (silicate melt) of the magma, which eventually coexists with an exsolved free fluid phase (gas and/or

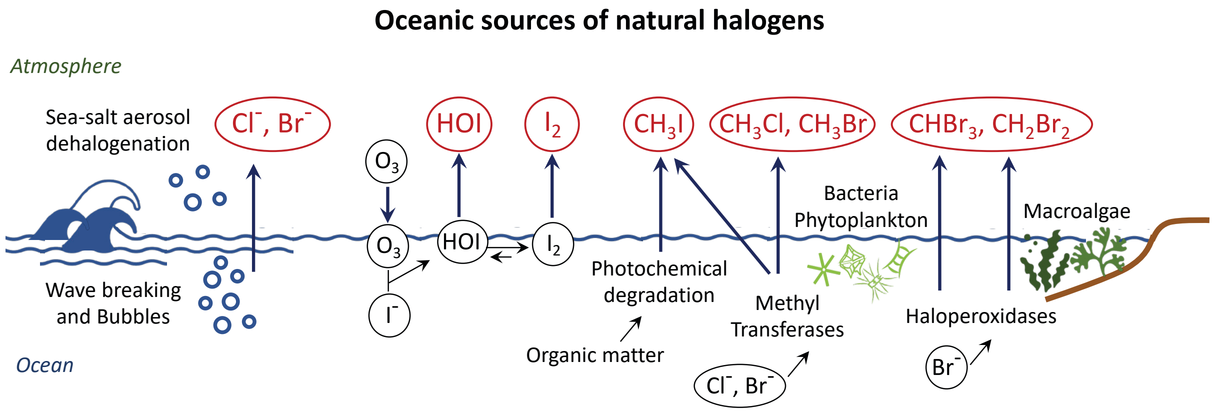

FIGURE 2 Schematic of oceanic sources of natural halogens, including sea-salt aerosol dehalogenation, iodine production due to ozone deposition, photochemical reactions, as well as biotic processes in phytoplankton and macroalgae. See text for details.

brine) (FIG. 3A). Upon magma ascent into the upper crust, the dissolved gases increasingly exsolve from the melt to form gas bubbles (FIG. 3A), which are ultimately released into the atmosphere with the coexisting free gas phase (if present). Crystal-hosted melt inclusions (FIG. 3B) indicate that halogens are primarily kept dissolved in the melt until very low pressures/depths owing to their relatively high solubilities in silicate melts. Shallow-emplaced melts can become enriched in halogens by magma crystallization (contrary to sulfur, which is typically released into gas bubbles at depths of < 3 km, i.e., $P < 100$ MPa) (FIG. 3B). At shallow depths, halogen partitioning into gas can become important (fluid/melt partition coefficients > 1) (FIG. 3B), leading to efficient Cl enrichment of volcanic gases and less so for other halogens (FIG. 3C). Ultimately, the coexisting magmatic gas and melt, which originate from this degassing process, evolve from S-rich to Cl–F–Br enriched (relative to S) upon increasing degrees of degassing and decreasing depth.

Volcanic gases can be released during a variety of processes, including explosive and effusive eruptions and noneruptive (quiescent) degassing. At most of the mafic, open-vent volcanoes, quiescent (passive) degassing is the dominant mode. Degassing of unerupted magma, representing a much larger volume than that of erupted magma typically leads to a large "excess degassing". In addition to crater degassing, other forms of "quiescent" halogen emissions include transport through hydrothermal solutions and groundwaters (FIG. 3A, and subsection "An under-explored volcanic source" below).

Despite being less abundant components of volcanic gas relative to water (H_2O), carbon dioxide (CO_2) and sulfur (S), the halogens (Cl and especially Br) have received particular attention over the last decade, owing to their high reactivity. Volcanic halogens are mostly emitted as hydrogen halides (HCl, HF, HBr, HI) (FIGS. 1 and 3A), which are strong, toxic acids. Part of these hydrogen halides are rapidly converted into oxidized halogen radicals (e.g., BrO, ClO, OClO, IO) by autocatalytic chemistry cycles (FIG. 3A).

NATURAL HALOGEN FLUXES

General Features

Around 22,000 Gg of halogens are emitted yearly from natural sources. These natural halogen emissions are dominated by chlorine (59%), followed by I (18%), Br (14%), and F (8%). FIGURE 4 shows that the most important carrier of halogens to the atmosphere is the ocean. It accounts for ~65% of the annual natural halogen flux, constituting most of the Br and I emissions and half of the Cl and F emissions. Volcanic degassing is the second largest emitting source (26%), contributing ~40% of natural Cl and F fluxes. Volcanic emissions of Br and I, however, are negligible in comparison with oceanic emissions. While oceanic and volcanic sources account for the majority of the natural halogen budget, the contribution of terrestrial ecosystems is also significant (9%).

Fluxes from Oceans to the Atmosphere

The flux of gases across the air–sea interface depends on the concentration difference between the water and the air and also on the efficiency of the transfer process. The transfer efficiency is controlled by several physical, biological, and chemical processes, including waves, large- and small-scale turbulence, bubbles, sea spray, rain, and surface films. Measuring the transfer velocity of gas exchange directly is challenging; therefore, it is often parameterized as a wind-speed dependent function. While the parametrizations can readily use available wind-speed estimates from satellites or surface wind-speed products, they do not capture all the forcing factors.

For oceanic chlorine fluxes, current estimates of emission rates of CH_3Cl in the surface ocean are 492 Gg Cl y^{-1} and uptake rates are −260 Gg Cl y^{-1}, making the ocean a net source (Hu et al. 2013). Oceanic chlorine can also be released in the form of short-lived $CHCl_3$ and CH_2Cl_2. Global flux estimates for these gases calculated from the wind-dependent transfer velocity and concentration differences are based on relatively few measurements, in particular for CH_2Cl_2. The ocean is a source for both gases, emitting in total 264 Gg Cl y^{-1} into the atmosphere (Khalil et al. 1999).

The flux of Br gases across the air–sea interface occurs in the form of CH_3Br and brominated VSLSs. Based on measurements in the Atlantic and Pacific oceans, Hu et al. (2012) derived local CH_3Br saturation anomalies and oceanic loss-rate constants. Extrapolations of the local values to global scales suggest emission rates of 27 Gg Br y^{-1} and uptake rates of −28 Gg Br y^{-1}. While these values suggest near-equilibrium concentrations of CH_3Br in the surface ocean and atmosphere, older measurements from before 1998 identified the ocean as a sink for CH_3Br. Declining anthropogenic emissions have driven these long-term changes and can be expected to lead to positive net air–sea fluxes in the future. Air–sea gas exchange of brominated VSLSs can be derived based on statistical gap-filling of an observational database (bottom-up approach) or by adjusting emissions in atmospheric modelling studies to produce agreement between the simulations and aircraft

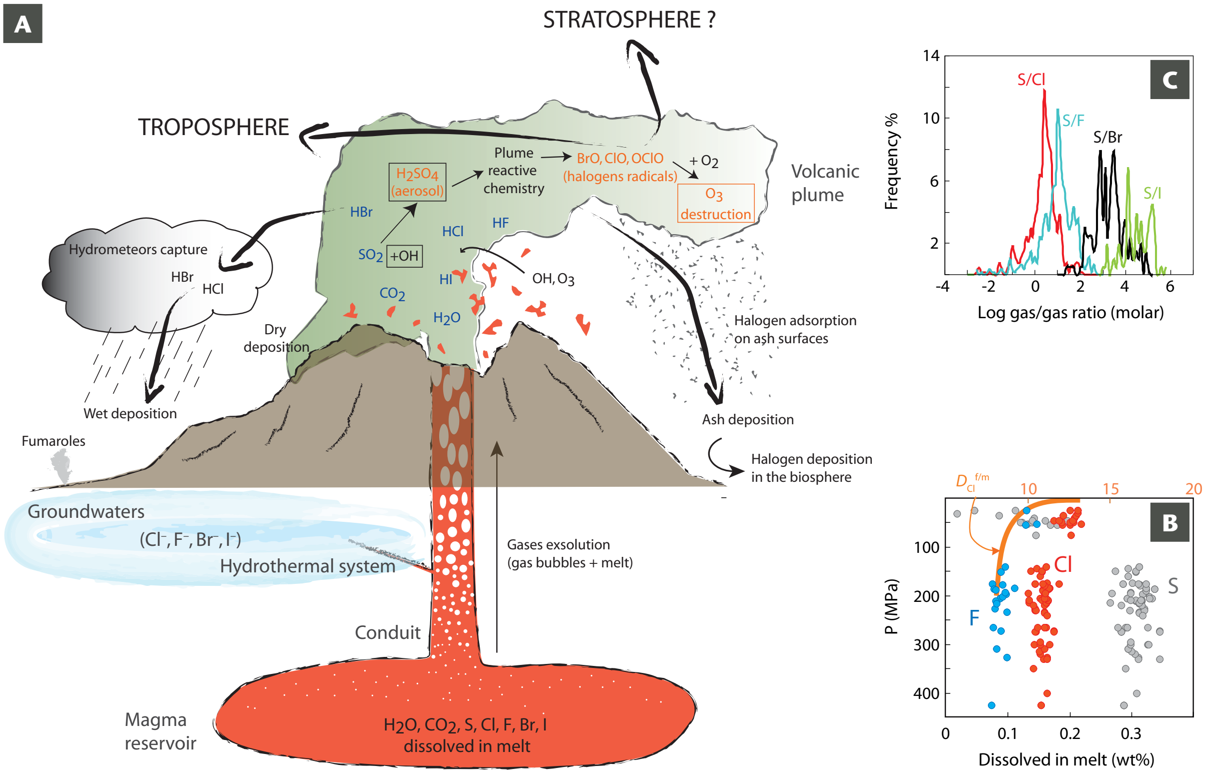

FIGURE 3 (**A**) Simplified diagram of a volcanic plumbing system, showing the different mechanisms governing halogen transport and deposition. (**B**) Crystal-hosted melt-inclusion record showing dissolved S, Cl, and F contents in melt upon magma decompression (DATA FROM MOUNT ETNA BASALTIC VOLCANIC SYSTEM, ITALY; SPILLIAERT ET AL. 2006). Below 100 MPa, the melt is enriched in halogens due to magma differentiation; Cl and F have less affinity for the gas phase than S, which is extensively degassed below 100 MPa. The chlorine fluid/melt partition coefficient ($D_{Cl}^{f/m}$) increases with decreasing pressure, leading to chlorine partitioning into the gas phase. (**C**) Emission of volcanic gases whose global compositional range, expressed as S/halogen molar ratios, is illustrated by the histograms. DATA FROM WEBSTER ET AL. (2018).

observations (top-down approach). For both approaches, the magnitude and distribution of VSLS emissions are poorly constrained given the sparse observational database (Ziska et al. 2013). As a consequence, global emission estimates show large variations, such as 120–820 Gg Br y^{-1} for $CHBr_3$ and 57–100 Gg Br y^{-1} for CH_2Br_2 (Engel et al. 2018).

Mobilization of Cl^- and Br^- from sea-salt aerosol (FIGS. 1 and 2) is believed to be the largest source of Cl and Br gases to the troposphere. However, the total amount of halogen radicals generated by the oxidation of chloride and bromide is highly uncertain as the underlying mechanisms and controlling factors are not well understood. Global modelling studies that take into account the dechlorination and recycling of inorganic Cl species on aerosols via heterogeneous reactions involving halogen and nitrogen species estimate a global source of 5,000–6,000 Gg Cl y^{-1}. For Br, modelling studies suggest that debromination on aerosol surfaces leads to an entrainment of 1,400–3,500 Gg Br/y (79% of the total Br emitted per year) (FIG. 4) (e.g., Engel et al. 2018).

Oceanic iodine is emitted in the form of CH_3I or other iodinated VSLSs. Air–sea fluxes of CH_3I from coastal and open-ocean environments are estimated to cause an input of 157–550 Gg I y^{-1} to the atmosphere (Carpenter et al. 2014). Other iodinated VSLSs, such as CH_2I, CH_2ICl, and CH_2IBr, account for an additional 340 Gg I y^{-1}. The largest source of oceanic iodine to the atmosphere is the emission of inorganic I compounds (HOI, I_2) that are formed from the uptake of O_3 to the ocean (FIGS. 2 and 4). According to global model simulations that parameterize ocean surface I^- concentration and that include active atmospheric ozone chemistry, inorganic I input amounts to 3,230 Gg I y^{-1} (i.e., ~81% of the total I annual budget) (FIG. 4). The oceanic fluorine flux is not well constrained: oceans could emit anywhere between 20 Gg F y^{-1} and 2,000 Gg F y^{-1} (Fuge 2019 and references therein).

Fluxes from Volcanoes to the Atmosphere

PASSIVE AND ERUPTIVE DEGASSING FLUXES

The fluxes of halogens released by volcanoes into the atmosphere cannot be measured directly but can be derived indirectly by scaling volcanic gas compositions to volcanic SO_2 fluxes, which can be remotely sensed by ultraviolet spectroscopy from either ground or space (e.g., Carn et al. 2017). As time-averaged SO_2 fluxes for individual volcanoes and for global volcanism are relatively well characterized (Carn et al. 2017), the matter resolves into assigning appropriate SO_2/halogen ratios to volcanic gas emissions. This effort has been undertaken since the 1970s (see Webster et al., 2018 for a review), but is complicated by (1) the incomplete volcanic gas catalogue available (many of the top volcanic SO_2 sources are still to be characterized for gas composition), and (2) the extreme heterogeneity of gas compositions globally. The most recent and robust (>600 individual samples) volcanic gas catalogue by Webster et al. (2018) indicates the following mean (global volcanism) gas molar ratios: SO_2/Cl is ~1.9; SO_2/F is ~7.8; SO_2/Br is ~2,200; and SO_2/I is ~26,600 (FIG. 3C). This catalogue is dominated by measurements made during persistent degassing activity, including the passive (quiescent) emissions of either open-vent or closed-vent (fumarolic) volcanoes, and/or emissions during mild, persistent (hawaiian to strombolian) explosive activity. If combined with a global SO_2 flux from persistent degassing of 16.6 Tg y^{-1} (Carn et al. 2017), these compositions confine the global persistent volcanic gas emissions for Cl at ~4.8 Tg y^{-1}, for F at ~0.6 Tg y^{-1}, for Br at ~0.009 Tg y^{-1}, and for I at ~0.0012 Tg y^{-1}, i.e., ~37% of total Cl and 33% of total F in annual natural emissions to the atmosphere, and <1% of Br and I (FIG. 4). It should be cautioned that, in view of the large intra- and inter-volcano variability in SO_2/halogen ratios (e.g., measured volcanic gas SO_2/Cl ratios vary from 0.0024 to 149) (Webster et al. 2018), these inferred fluxes should only be viewed as order of magnitude assessments.

The numbers above do not include the potential halogen fluxes sustained by degassing during individual eruptions. Recent SO_2 fluxes derived during multidecadal (1978–2019) satellite measurements indicate a cumulative "eruptive" SO_2 mass release of 98.6 Tg from 1,827 eruptions in 41 years, spanning 0 to 6 in the Volcanic Explosivity Index (VEI) (Carn 2019). This corresponds to an annual average SO_2 "eruptive" release of 2.3 Tg y^{-1}, which is seven times lower than that associated with persistent degassing. Unfortunately, the SO_2/halogen ratio signature of eruptive clouds is poorly constrained because measurements are challenging and, therefore, limited in number. Nevertheless, we tentatively infer the eruptive degassing fluxes as follows: ~0.01–0.14 Tg HCl y^{-1} (with molar HCl/SO_2 = 0.01–0.11); ~0.02–0.18 Tg HF y^{-1} (molar HF/SO_2 = 0.03–0.26); ~0.00003–0.0015 Tg BrO y^{-1} (molar BrO/SO_2 = $8 \times 10^{-6} - 4.4 \times 10^{-4}$); and ~0.00002–0.0003 Tg HI y^{-1} (molar HI/SO_2 = $4 \times 10^{-6} - 6 \times 10^{-5}$) (references for these ratios are given in Supplementary References found at http://elementsmagazine.org/supplements). The "eruptive" Br degassing flux should be considered a minimum estimate because BrO represents only a fraction of total erupted bromine (FIG. 3A). Even if these estimates should be considered preliminary, they do indicate that eruptive halogen emissions are negligeable compared to those associated with persistent (passive) degassing (FIG. 4). This is not surprising, because eruptions are sporadic and short-lived events. Note also that the satellite era is dominated by small- to mid-magnitude eruptions (30% of VEI 2 eruptions, 40% of VEI 3 eruptions) (Carn 2019), and the single VEI 6 eruption of this period (Mount Pinatubo, Philippines, in 1991) was a halogen-poor eruption (<4.5 Tg Cl) (e.g., Brenna et al. 2019). Large-scale (VEI 6–7) historical eruptions of subduction-zone volcanoes were far more substantial halogen sources, releasing tens to several hundred Tg of chlorine (e.g., the 1815 eruption of Tambora in Indonesia; the 1613 BCE Thera eruption in Santorini, Greece; the 1257 eruption of Mount Samalas in Indonesia) (Cadoux et al. 2015; Wade et al. 2020 and references therein), far exceeding the total annual Cl flux from "satellite era" volcanism of ~5 Tg.

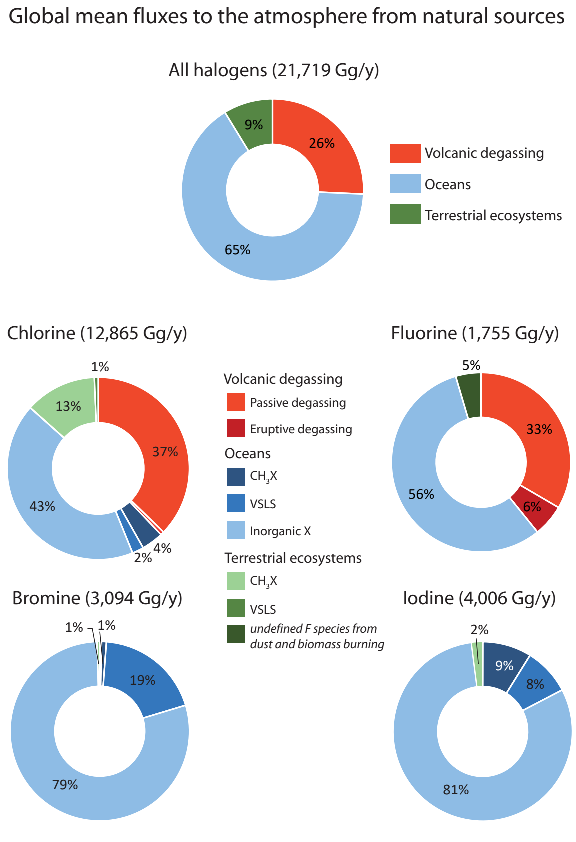

FIGURE 4 Global annual mean fluxes (in %) of halogens from natural sources to the atmosphere. CH_3X and inorganic X, where X = Cl, F, Br, or I. Abbreviation: VSLS = very short-lived substances. Note that the reported fluxes are "source" fluxes, not "net" fluxes, which would be "source" minus "sink" fluxes. Where available, information on sinks (negative fluxes) are provided in the text.

Over geological timescales, the volcanogenic halogen budgets are also likely to have been severely perturbed by the emplacement of large igneous provinces (LIPs). For example, the emplacement of the end-Triassic Siberian Traps (~252–248 Ma) was accompanied by the release of up to 8.7×10^6 Tg HCl and ~$7.1–13.6 \times 10^6$ Tg HF (Mather and Schmidt 2021 and references therein). Because the bulk of the eruption occurred in less than 1 My, this gives annual fluxes of 8.7 Tg HCl and 7–14 Tg HF, which exceeds the "present-day" (i.e., satellite era) annual fluxes, especially that of F (~0.7 Tg y^{-1}).

AN UNDEREXPLORED VOLCANIC SOURCE

One often overlooked source are subaerial-volcanoes that contribute to halogen emissions through the hydrological cycle. The halogens are very water soluble, so only a fraction of the magmatic halogen flux (sustained by stored magma underneath volcanoes) reaches the surface to sustain the atmospheric fluxes, the remaining fraction being trapped by thermal and cold groundwaters (FIG. 3A). This latter component of volcanic halogen emissions is poorly constrained yet may be of central importance, especially at subduction-zone volcanoes where magmas are Cl-rich and develop pervasive hydrothermal circulation during their repose periods (Taran and Kalacheva 2019). Efforts to quantify this halogen flux have been complicated by the sparse knowledge of the fluxes and the compositions of both thermal and cold springs. However, based on data for the well-characterized Japanese arc, Shinohara (2013) calculated that the Cl groundwater output could be ~6 Tg y^{-1}, which is higher than the global persistent volcanic Cl flux (estimated here at ~4.8 Tg y^{-1}).

Fluxes from Terrestrial Ecosystems to the Atmosphere

Fluxes of CH_3Cl and CH_3Br from terrestrial sources (FIG. 4) have been estimated based on a large variety of methods (Carpenter et al. 2014 and references therein). Measurement campaigns, including micrometeorological flux measurements, have been applied at canopy scales to derive the gas fluxes from whole-forest ecosystems. Other studies have derived CH_3Br emissions from litter decay based on estimates of the global distribution and quantity of litter decay and the litter's bromine content. Flux estimates from airborne measurements combined with transport simulations have the advantage of considering the whole ecosystem and providing net fluxes. Finally, inverse-modelling approaches make use of frequent atmospheric observations to derive global flux estimates from different terrestrial sources. Flux estimates of CH_3Cl and CH_3Br amount to emissions from terrestrial ecosystems of 1,636 Gg Cl $y^{-1}$and 15 Gg Br y^{-1} as well as uptake by soil of −744 Gg Cl y^{-1} and −34 Gg Br y^{-1} (i.e., 13% of the total fluxes of natural Cl and 1% of the total fluxes of natural Br) (Fig. 4). Terrestrial CH_3I sources are poorly quantified and estimates range around 81 Gg I y^{-1} (i.e., 2% of the total flux of natural I) (Fig. 4).

Natural F fluxes from terrestrial ecosystems are not well documented. Biomass burning (partly natural) may account for 76 Gg y^{-1} to the atmosphere, while wind-blown soil (dust) may account for 6 Gg y^{-1} of F to the atmosphere (Fuge 2019).

ENVIRONMENTAL IMPACT OF NATURAL HALOGEN EMISSIONS

Local- to Regional-scale Impact

Notable local- to regional-scale impacts have been observed above salt lakes and in the polar boundary layer. Ozone depletion events in the Arctic and Antarctic lower troposphere have been linked to “bromine explosion” events during which extremely high BrO levels of up to 41 ppt have been observed (Saiz-Lopez and von Glasow 2012 and references therein). Changes in ozone, such as the ozone-depletion events, will, in turn, lead to substantial shifts in the atmospheric oxidation pathways. For example, the oxidation of gaseous elemental mercury to reactive mercury is strongly enhanced with increased halogen levels. Because reactive mercury can be rapidly removed from the atmosphere, this potentially increases the deposition of a toxic substance to the polar ecosystems. Strong atmospheric mercury-depletion events can also occur over salt lakes such as the Dead Sea. As in polar regions, the atmospheric mercury-depletion events were found to be highly correlated to increased Br levels and decreased ozone. Similar phenomena (e.g., bromine explosion, ozone destruction) are observed within volcanic clouds.

In addition, passive (quiescent) volcanic degassing in the lower troposphere can produce local (e.g., a few kilometres from the source at most) “natural” halogen pollution of soils, vegetation, and surface or groundwater (e.g., Delmelle 2003). These local impacts reflect the rapid scavenging of hydrogen halides (e.g., HCl and HF) in plumes, leading to their fast wet and dry deposition (Fig. 2A). The resulting impacts can locally be severe, with fumigation by acid gas species leading to visible damage to crops and vegetation (following uptake from leaves and roots), and “volcanic” acid rain developing similar detrimental environmental effects to human-related acid rain (Delmelle 2003). During volcanic eruptions, an additional regional impact (tens to hundreds of kilometres from the source) results from the rapid chemical processing of volcanogenic HCl and HF on ash particle surfaces within eruptive clouds. These heterogeneous reactions lead to effective halogen scavenging and to their deposition on the ground as soluble halides on the surface of ash fragments. These soluble surface coatings (ash leachates) can potentially cause acidification and toxic conditions, especially if their accumulation in topsoil and then in vegetation expose grazing animals and livestock to extreme F exposure (causing fluorosis disease).

Global-Scale Impact

Oceanic halogens are known to impact the chemistry of the marine atmospheric boundary layer and free troposphere via halogen-driven ozone destruction and changed oxidation pathways. Based on Cape Verde measurements and model simulations, a contribution of halogen oxides to chemical O_3 destruction of 30%–50% was identified for the marine atmospheric boundary layer (Read et al. 2008). In the free troposphere, oceanic halogens cause an average reduction in tropospheric ozone of 10%, leading to a contribution of −0.1 Wm^{-2} to the radiative flux at the tropical tropopause. Halogens also contribute to the oxidation of climate-active gases, such as dimethyl sulfide (DMS), methane, and mercury (Saiz-Lopez and von Glasow 2012 and references therein) and can lead to a significant reduction of their atmospheric burden and lifetime.

Oceanic and terrestrial emissions of methyl halides and VSLSs can be transported into the stratosphere, where they contribute to the stratospheric Cl and Br budget and, thus, to stratospheric ozone depletion (Engel et al. 2018). More uncertain is the possible stratospheric injection of inorganic iodine and the potential consequences of that for ozone depletion.

In the context of ongoing decrease in anthropogenic halogen emissions and of global warming, changes in natural halogens fluxes are expected but are difficult to quantify. Note that the ocean emissions of iodine have tripled since 1950, driven by anthropogenic ozone pollution and global warming (Cuevas et al. 2018).

Volcanic halogens that reach high altitudes may also cause reductions in stratospheric ozone levels: this has been observed and simulated by atmospheric chemistry numerical models (e.g., Millard et al. 2006). Several studies have combined petrological data and atmospheric chemistry modelling (e.g., Cadoux et al. 2015; Brenna et al. 2019; Wade et al. 2020) to show that large, halogen-rich, pre-industrial eruptions (e.g., ~1613 BCE Thera, Santorini; 1257 Samalas, Indonesia) caused significant stratospheric ozone depletion (reaching ozone hole conditions), even when a very small fraction of halogens (<2%) reached the stratosphere (Cadoux et al. 2015; Wade et al. 2020). The recovery to pre-eruption ozone levels is estimated to have taken about a decade (Cadoux et al. 2015; Brenna et al. 2019).

Stratospheric ozone depletion induces an increase in harmful ultraviolet (UV) radiation, particularly shortwave UV-B radiation at the Earth’s surface (80% to 400% following past large explosive tropical eruptions) (Brenna et al. 2019), causing damages to ecosystems. Halogen release from the long-lasting, mainly non-explosive, Siberian Traps volcanism (~250 Ma) has been suggested as a possible trigger for the Permian–Triassic boundary mass extinction (Mather and Schmidt 2021 and references therein).

However, it is noteworthy that even relatively small volcanic eruptions can inject significant amounts of halogen compounds in the stratosphere (e.g., Millard et al. 2006) and that this can impact the global atmospheric chemistry. Cadoux et al. (2015) emphasized that if eruptions of similar magnitude to the 1980 eruption of Mount St. Helens (Washington, USA) or the 1991 eruption of Mount Pinatubo (recurrence of a century or less) were to occur in rapid succession, this could affect the environment at the global scale and perturb the ongoing recovery of global and Antarctic ozone.

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GLOSSARY

Bromine explosion: occurrence of extremely high concentrations of reactive bromine species in the troposphere; associated with rapid ozone depletion via autocatalytic reaction cycles.

Degassing: process of volatiles' separation and release from silicate melts during ascent and decompression. "Eruptive" degassing refers to gas release during a volcanic eruption: it may last from days to several years (more or less continuously). According to the Smithsonian Institute's Global Volcanism Program, the median length of time for a single eruption is seven weeks. "Passive" persistent degassing refers to gas release during quiescent phases (no eruption). It most commonly occurs at open-vent basaltic volcanoes and may last for months to years. The periods of passive degassing may be interrupted by large eruptions.

Marine atmospheric boundary layer (MABL): part of the atmosphere that has direct contact with, and hence is directly influenced by, the ocean.

Micrometeorology: refers to atmospheric meteorological phenomena occurring at a spatial scale smaller than about 1 km.

Ozone: highly reactive atmospheric gas composed of three oxygen atoms (O_3) of natural or anthropogenic origin. Most ozone is found in the stratosphere where it protects the Earth from harmful ultraviolet radiation (the ozone layer); smaller amounts of ozone found in the troposphere impact negatively on air quality.

Planetary boundary layer (PBL): the portion of the troposphere that is directly influenced by its contact with a planet's surface. On Earth, the PBL responds in an hour or less to the combined action of mechanical and thermal forcings.

Tropopause: the border between the troposphere and the stratosphere.

Troposphere: the lowest layer of Earth's atmosphere where weather primarily occurs. The average height of the troposphere is 18 km in the tropics, decreases with latitude and reaches 6 km in the polar regions.

Stratosphere: second layer of Earth's atmosphere, just above the troposphere. The stratosphere is stratified (layered) in temperature, with warmer layers higher up and cooler layers closer to the Earth: this increase of temperature with altitude is a result of the absorption of the Sun's ultraviolet radiation (shortened UV) by the ozone layer.

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Toshiko Nagao copied by the pen Hokusai's 1832, "The Big Wave". Note the five new members on the boats.

Experimental and Observational Constraints on Halogen Behavior at Depth

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Halogens are volatile elements present in trace amounts in the Earth's crust, mantle, and core. They show volatile behavior and tend to be incompatible except for fluorine, which makes them key tracers of fluid-mediated and/or melt-mediated chemical transport processes. Even small quantities of halogens can profoundly affect many physicochemical processes such as melt viscosity, the temperature stability of mineral phases, the behavior of trace elements in aqueous fluids, or the composition of the atmosphere through magma degassing. Experiments allow us to simulate deep-Earth conditions. A comparison of experimental results with natural rocks helps us to unravel the role and behavior of halogens in the Earth's interior.

Keywords: element partitioning; volatiles; degassing; subduction; fluid inclusions

INTRODUCTION

Halogens are present in the deep Earth as volatile trace elements. Whereas fluorine is relatively abundant in crustal rocks (~550 ppm), as is chlorine (~240 ppm), bromine and iodine abundances are more than three orders of magnitude lower (<1 ppm). In the Earth's primitive mantle, the halogens are present in low concentrations, ranging from 7 ppb for iodine to 25 ppm for fluorine, with even lower concentrations in the depleted mantle. In contrast, the halogens are relatively enriched in the outer reservoirs of the Earth, e.g., ~2 wt% Cl in seawater and ~28 ppm iodine in marine sediments (Pyle and Mather 2009 and references therein).

The heavy halogens (chlorine, bromine, and iodine) behave incompatibly in most minerals due to their large ionic radius, and they partition preferentially into melts or fluids. Their distribution is influenced by fluid mobility, crystal fractionation, degassing, and partial melting, which makes them excellent tracers for volatile transport processes in the deep Earth. Fluorine, the lightest halogen, shows a more compatible and rather lithophile behavior due to its smaller ionic radius, which is comparable to that of an OH group. As a consequence, F and the heavy halogens decouple during fluid-mediated metamorphic reactions and magmatic differentiation. Knowledge of the behavior, abundance, and distribution of F and the heavy halogens can help us to better understand the mechanisms that control the origin, distribution, and transport of volatiles in the deep Earth and the complex processes during subduction and recycling of oceanic lithosphere.

Here, we discuss the importance of the halogens by examining experimental challenges and by reviewing pioneering studies on halogen abundance, distribution, and behavior. This review will focus on the application of experimental studies to four topics corresponding to different halogen-bearing reservoirs in the deep Earth: (1) the behavior of halogens in magmas; (2) constraints on halogen transport and storage in silicate minerals; (3) halogens in fluids, with implications for their recycling in subduction zone settings; and (4) halogens in metallic phases, including the first constraints on their abundance in the Earth's core.

EXPERIMENTAL CHALLENGES

Microthermometry uses a heating and cooling stage under an optical microscope. This method can characterize fluid inclusions under the assumption that there is a constant volume that will reestablish itself to the original pressure during experimental heating. High-temperature furnaces at atmospheric pressure are used to study silicate melts, the assumption being that the effect of pressure on the studied process (e.g., melt viscosity) may be negligible (Dingwell and Hess 1998).

In contrast, the study of magmatic processes requires reproducing the pressure (P) and temperature (T) conditions relevant to those of magma chambers and conduits. Most of the experiments that study halogen partitioning between fluids, melts, and minerals, and their solubility in these magmatic phases, are performed in a large variety of high-P–high-T apparatuses, such as rapid quench cold-seal pressure vessels (up to a few GPa and up to 1,200 °C; i.e., Bureau et al. 2000) or piston cylinders (0.5–5 GPa, up to 1,600 °C).

These experimental setups come with two major limitations. First, experiments usually last only hours or days, which is orders of magnitude shorter than natural processes. Second, they have to be quenched (cooled down) as fast as possible in order to preserve the volatiles (i.e., the halogens and water) and the silicates that were dissolved in the fluid phases during the experiment. It is often assumed

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that the halogen concentrations in a glass, which represents a quenched melt, reflects the respective equilibrium concentrations at a designated *P* and *T*. Today, we know that this approach is not accurate for the investigation of fluid properties, which requires that volatile species are monitored in situ at high-*P* and high-*T*. A new generation of experiments has been proposed that can associate specific high-*P* tools, such as diamond anvil cells (up to a few GPa and up to 1000 °C) and combine these with in situ characterizations (e.g., Bureau et al. 2016).

Another challenge is the analysis of heavy halogens in small experimental samples. Conventional analytical methods require crystal sizes with a diameter of at least several tenths of micrometers. This can be achieved with the addition of small crystal nuclei to the starting material (Dalou et al. 2012), slow cooling (Beyer et al. 2012), or deliberate temperature-cycling around the target temperature. Potential methods to assess if these crystals were in equilibrium with the surrounding melt are (1) euhedral, monocrystalline, and inclusion-free crystal shapes; (2) a homogeneous major-element distribution between crystals and melts; and/or (3) partition coefficients that are identical at varying crystal growth rates (Joachim et al. 2015).

HALOGENS IN MAGMAS

The Role of Halogens in Crustal Magmatic Systems

Fluorine and chlorine were the first halogens to be analyzed in volcanic glasses and rocks because of their relatively high abundances. They have been the subject of numerous studies since the 1980s. During the last two decades, the role of bromine and iodine in magmatic processes has also been studied thanks to methodological advances, including in situ chemical analyses and satellite monitoring, and databases that can correlate halogen concentration and distribution with depth in the Earth have been established (see Pyle and Mather 2009). Experimental studies of the role of the halogens in magmatic processes include determining their solubilities in melts; their partitioning behavior between fluids, silicate melt, and mineral phases; chemical differentiation during mineralization; and their effects on the physical properties of magmas.

Experimental constraints on halogen properties in silicate melts

The term *solubility* refers to the maximum amount of halogens that can be dissolved in a silicate melt that is saturated with an immiscible aqueous fluid + brine assemblage at a given set of conditions (Carroll 2005) (Fig 1A). Partitioning is defined by the Nernst-type partition coefficient *D* between two phases, for example between an aqueous fluid (f) and a melt (m) ($D_{\text{halogen}}^{\text{f/m}}$). Halogens also fractionate into minerals from melt during crystallization. Vapor–liquid immiscibility processes have been observed at magmatic conditions, mostly for Cl (Fig. 1B). Indeed, depending upon the bulk halogen concentration, a silicate melt can coexist with variable phases: a low-density aqueous phase (vapor); a vapor–liquid mixture; solid salts; and a liquid, also called a high-density hydrous phase or a hydro-saline liquid.

Many studies have measured the solubility of chlorine in hydrous felsic melts at pressures and temperatures relevant for crustal conditions (e.g., Webster 1997; Carroll 2005 and references therein). Both, Cl and F solubilities in magmatic melts depend on the Al content, Na/Si ratio, and on network-modifier alkalis (Fig. 1A). Whereas chlorine is mainly associated with the network-modifying cations Al, Na, and K, fluorine favors complexes with Al and Na. Dissolved water has a strong effect on the silicate melt structure. The solubility of F increases with increasing water content, while the solubility of Cl decreases (Fig. 1B) (Dalou and Mysen 2015).

Solution mechanisms established for Cl are also found for Br (Bureau and Métrich 2003), and their solubilities are comparable in felsic melt compositions (Fig. 1A). Iodine shows a similar solubility despite its larger ionic size (Leroy et al. 2019), which opposes the expectation that the four halogens exhibit a systematic change in solubility in

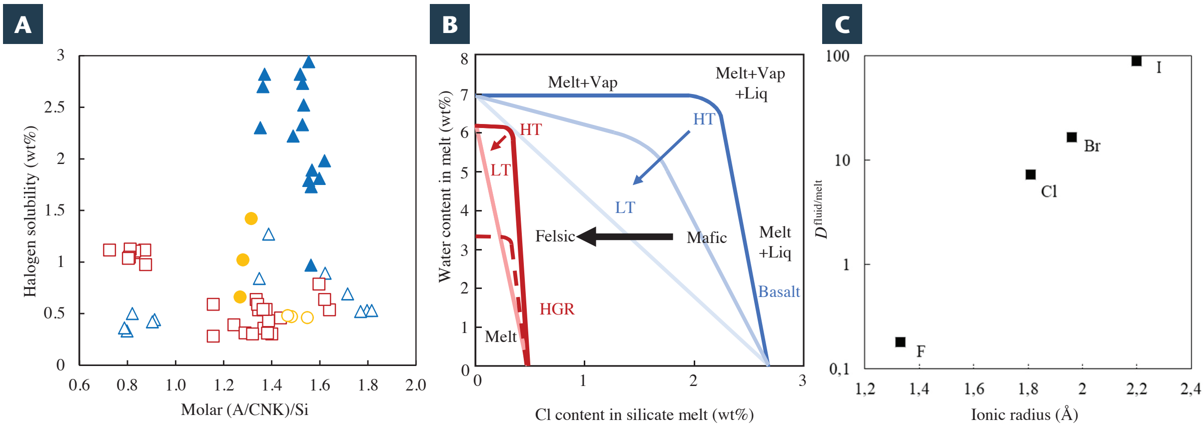

Figure 1 (**A**) Representative solubility data for Cl, Br, and I versus (A/CNK)/Si [molar (Al_2O_3/(CaO + Na_2O + K_2O)/SiO_2] determined using similar experimental protocols at water saturation (except for I): 0.1–0.4 GPa and 900–1,400 °C for felsic (open symbols) and mafic (closed symbols) melts. Blue triangles = Cl; red squares = Br; orange circles = I. Data for Br and I are limited; nevertheless, the diagram illustrates that Cl, Br, and I have a similar solubility mechanism in felsic melts at a comparable range of pressures and temperatures. In mafic melts (i.e., basalts), Cl (closed blue triangles) may have a higher solubility than I (closed orange circles). (**B**) Phase relations in the silicate melt–water–Cl system between 800 °C (low temperature, LT) and 1,700 °C (high temperature, HT). The curves delimit isobaric solubilities of saturated magmatic volatile phases and silicate melts. They show that small quantities of Cl have a dramatic effect on volatile phase exsolution. The curves designate the H_2O and Cl solubilities and delimit the stability of silicate melt, melt-plus-vapor (or low-density gas), melt-plus-liquid (or brine), and melt-plus-vapor-plus-liquid. The light curves express the volatile solubilities and phase relations at comparatively lower temperatures. The H_2O solubility varies only minimally as the melt composition changes from felsic to mafic at constant pressure. The Cl solubility in H_2O-poor melts increases by an order of magnitude. The strong relationship between melt composition and Cl solubility implies that the chemical evolution of magma from mafic to more felsic composition enhances the role of Cl in driving volatile phase exsolution. The dashed red curve represents the Cl in a haplogranite (HGR) solubility curve at lower pressure (0.05 GPa), illustrating the strong pressure effect on Cl solubility. (**C**) Fluid/melt partition coefficients ($D^{\text{f/m}}$, where D = partition [i.e., distribution] coefficient) of halogens versus their ionic radius in the albite–water system at 900 °C and 0.2 GPa. References for data in online Supplement.

chemically identical melts depending on their ionic radii. In fact, the three heavy halogens have the capacity to be incorporated at similar concentrations in hydrous silicate melts (Fig. 1A). Fluorine, the smallest halogen, is the most compatible in silicate melts and has the highest solubility (e.g., Dalou and Mysen 2015 and references therein).

Several experimental observations illustrate the effect of F and Cl in petrogenesis. For example, the presence of ≥1 wt% F in a diopside melt causes a depression of the liquidus temperature that is of similar magnitude to that of dissolved water, and the addition of F to depolymerized liquids increases that liquid's viscosity (Dingwell and Hess 1998). In polymerized peraluminous or peralkaline melts, the extent to which dissolved water decreases viscosity is suppressed due to the presence of dissolved F and Cl (Baasner et al. 2013 and references therein). Small amounts of dissolved chlorine can lower the liquidus temperature of basaltic melts. Chlorine also forms complexes with Fe, and perhaps Mg and Ca, in basaltic melts, which increases silica activity and stabilizes pyroxene against olivine (Filiberto and Treiman 2009).

Experiments also reveal the strong affinity of Cl to form complexes with ore metals and trace elements that preferentially partition into hydrothermal fluids and are responsible for mineralization. Halogen behavior during magma degassing can be controlled either by partitioning into vapor/aqueous fluid phases or by saturation of a halogen-bearing mineral phase. Halogen behavior in immiscible brine is probably controlled by saturation processes alone (see Shinohara 2009 for Cl).

Experimental Constraints on Volcanic Degassing of Halogens

The exsolution of magmatic volatiles is a key process in volcanic systems, because it drives magma differentiation, crystallization, ascent, and eruption. Locally, it also drives hydrothermal alteration and mineralization. Because halogens are lost from magmatic melts through degassing, the best constraints on their initial melt concentrations are through the analysis of melt inclusions trapped in crystals.

The impact of volcanic degassing of halogens on atmospheric chemistry is one important justification for experimental research on halogen behavior in magmas. For example, estimates of halogen fluxes into the oceans and atmosphere are based on measurements from fumaroles and plumes, and mass–balance calculations between melt inclusions and volcanic glasses. However, these calculations require knowledge of the partitioning behavior of halogens between silicate melts and fluids at magmatic conditions. Early experimental studies have shown that Cl partitions strongly into fluids (i.e., large $D_{\mathrm{Cl}}^{\mathrm{f/m}}$) (Webster and Holloway 1988). For example, in the topaz–rhyolite–H_2O ± CO_2 ± F system at 0.5–5 kbar and 725–950 °C, the $D_{\mathrm{Cl}}^{\mathrm{f/m}}$ ranges from 2 to 130. The $D_{\mathrm{halogen}}^{\mathrm{f/m}}$ may approach unity as the miscibility gap is closed–between melt and an aqueous fluid (Bureau et al. 2016). Although F, the most compatible halogen in silicate melts, exhibits late degassing at shallow depths, the heavier halogens experience early degassing, which is enhanced by the presence of water (Bureau et al. 2000, 2016). In felsic melts (e.g., albitic melts), $D_{\mathrm{halogen}}^{\mathrm{f/m}}$ increases with increasing ionic radius at 0.2 GPa and 900 °C: 8.1 ± 0.2 for Cl, 17.5 ± 0.6 for Br, and 107 ± 7 for I (Bureau et al. 2000) (Fig. 1C). Despite their low concentrations in silicate melts, Br and I can be released into the atmosphere, as confirmed by measurements from volcanic plumes.

Combining natural halogen abundances with experimentally derived partition coefficients enables the calculation of volcanic halogen input to the atmosphere. Experimentally combining fluid–melt–mineral phase equilibria at magmatic P–T conditions with in situ characterization (i.e., by synchrotron radiation X-ray fluorescence and/or by Raman and infrared spectroscopy) is a powerful tool to understand halogen behavior in magma chambers and volcanic conduits because it avoids quench modifications (Fig. 2). This experimental approach established the extreme efficiency of water to wash out Br and I from hydrous silicate melts and their significant input to the atmosphere during magma ascent (e.g., Bureau et al. 2016 and references therein), and also applies to the study of recycling processes of volatiles in subduction zones (i.e., slab burial).

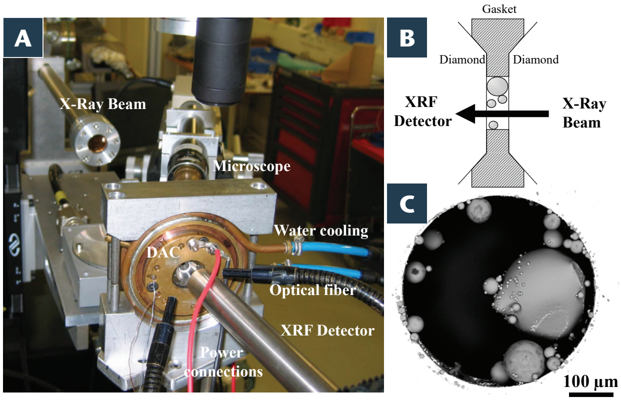

Figure 2 (**A**) Experimental setup of Synchrotron Soleil's DIFFABS ("diffraction/absorption") beamline (France). The hydrothermal diamond anvil cell (DAC) is aligned to the high-energy (17 keV) X-ray beam. Synchrotron radiation X-ray fluorescence (XRF) is detected with a Si-drift detector. The experiment is monitored through an optical microscope. (**B**) Section through the DAC during an experiment at high pressure and temperature. Globules of silicate melt are in equilibrium with an aqueous fluid in the sample chamber. Because the X-ray beam can cross the DAC, the halogen content in the melt and fluid phases can be quantified simultaneously. (**C**) Scanning electron microscope (SEM) image of the sample chamber after quenching.

HALOGENS IN SILICATE MINERALS

Mid-ocean-ridge basalt (MORB) and ocean island basalt (OIB) can provide sources of information for the abundance and distribution of halogens in the Earth's mantle, because they represent partial melts that originate from different mantle sources and depths. Elemental ratios (e.g., Cl/K or F/P) have long been used to determine respective halogen concentrations in different source regions and still offer a reliable and important database (Pyle and Mathers 2009 and references therein). Here, the focus is on recent experimental and analytical developments that allow the investigation of fluorine and chlorine partitioning behavior between silicate melt and residual minerals at the P–T conditions where the mantle partially melts. These provide an independent approach to estimate halogen concentrations in these mantle source regions.

The major residual minerals that remain in the mantle after partial melting are olivine and pyroxene. Temperature strongly affects the partitioning behavior of halogens between olivine (ol) and silicate melt ($D_{\mathrm{halogen}}^{\mathrm{ol/m}}$). As an example, $D_{\mathrm{F}}^{\mathrm{ol/m}}$ increases by about two orders of magnitude from ~0.003 at 1,350 °C (Beyer et al. 2012) to ~0.3 at 1,600 °C (Joachim et al. 2015). The $D_{\mathrm{F}}^{\mathrm{ol/m}}$ also increases linearly with increasing dissolved water in the silicate melt (Joachim et al. 2017), which is not the case for $D_{\mathrm{Cl}}^{\mathrm{ol/m}}$. The effect of pressure on the fluorine and chlorine partitioning behavior seems to be negligible in the upper mantle. Halogen partition coefficients between the pyroxenes and silicate melt are usually greater than those between olivine and a melt. Fluorine partitioning between orthopyroxene and melt seems to be largely independent of the crystal chemistry and correlates positively with increasing melt polymerization, whereas initial results suggest that the increase of a jadeite component ($NaAlSi_2O_6$) in orthopyroxene and the increase of a calcium Tschermak's ($CaAlAlSiO_6$) component in clinopyroxene can promote Cl incorporation (Dalou et al. 2012). These experimentally derived halogen-partitioning data allow the concentrations of halogens in MORB and OIB mantle source regions to be calculated based on a simple batch melting model, which neglects degassing of halogens during ascent and eruption of the basalts because of the relatively low volatile concentrations in MORBs and OIBs (Beyer et al. 2012; Joachim et al. 2015, 2017).

A comparison of the halogen concentrations in the MORB source region with primitive mantle estimates indicates that the upper mantle is degassed and relatively homogeneous with respect to fluorine and chlorine. In contrast, the fluorine and chlorine concentrations in the OIB source region are heterogeneous and show a significant enrichment in fluorine relative to the primitive mantle, which indicates substantial fluorine recycling and partial separation between fluorine and the heavy halogens during the subduction of oceanic lithosphere into deeper mantle regions.

Serpentinization and deserpentinization of peridotite play a crucial role for volatile transport of the heavy halogens in subduction zones. After deserpentinization, most of the heavy halogens are likely to be transported via fluids (and through melts if supersolidus temperatures are reached) to the overriding mantle wedge due to their hydrophilic nature. Fluorine will more likely be transported in mineral phases because of its lithophile behavior. An important fluorine- and water-bearing mineral in subducting oceanic crust is amphibole, which can retain significant quantities of fluorine in the solid residue, thus leading to substantial F/Cl fractionation during partial melting (Van den Bleeken and Koga 2015). Other minerals that may lead to halogen recycling into the mantle through subduction and a partial fluorine–heavy-halogen separation in the subducting slab are olivine, humite group minerals, garnet, apatite, lawsonite, phlogopite, and phengite.

In the Earth's upper mantle, potentially important hosts for the halogens are the hydrous minerals apatite and humite, although their abundance can be limited by available concentrations of phosphorus and titanium, respectively. Nominally anhydrous minerals are another potentially important host due to their large modal abundance. An example is olivine, which is the most abundant mineral in the upper mantle. Experimental results show that olivine may contain hundreds of ppm of Cl (170 ppm) (Dalou et al. 2012). A combination of high *P*–high *T* experiments and first-principles calculations shows that fluorine and water are clumped and associated with Si vacancies in the crystal structure of forsterite, resulting in fluorine solubilities of up to ~1,715 ppm at 2 GPa and 1,250 °C (Crépisson et al. 2014). This implies that significant amounts of associated F and OH have the potential to be stored in the upper mantle and can be recycled into deeper mantle regions in the peridotite layer at the bottom of subducting plates. At depths of the transition zone (410–670 km), which represents the zone between the upper and lower mantle, olivine becomes unstable and is transformed into wadsleyite (Wd) and ringwoodite (Rw), whose fluorine solubilities decrease with increasing water concentrations. These minerals may not only store significant amounts of fluorine but also up to 200 ppm (Wd) and 113 ppm (Rw) chlorine in hydrous systems (Roberge et al. 2017). This implies that the transition zone can be a significant repository for fluorine and the heavy halogens in the Earth's mantle. Bridgmanite (Brg) is another potential host for fluorine in the deep Earth, having a solubility of >8,000 ppm in aluminous and water-bearing systems at 1,800 °C and 25 GPa. However, in Al-free and water-free systems, Brg exhibits fluorine contents below 50 ppm at identical *P*–*T* conditions (Yoshino and Vazhakuttiyakam 2018).

If substantial amounts of halogens are recycled from the surface and stored in the Earth's upper mantle, the transition zone, and perhaps the lower mantle, these may have an effect on physicochemical properties. For example, the presence of fluorine has the potential to increase the stability of mineral phases, such as clinohumite, to higher temperatures (Grützner et al. 2017). Fluorine-rich phlogopite may produce electrical anomalies in the upper mantle, thus challenging the assumption that high electrical conductivity zones are always related to the presence of partial melts, aqueous fluids, saline fluids, graphite, or sulfides (Li et al. 2016).

HALOGENS IN MANTLE FLUIDS

Chlorine is observed in arc volcanic gases as a form of hydrochloric acid, with an abundance that follows water, carbon dioxide, and sulfur dioxide/hydrogen sulfide. The enrichment of alkaline, alkaline earth elements, and Pb is characteristic for subduction-zone basalts compared to MORB and has been attributed to "slab-derived

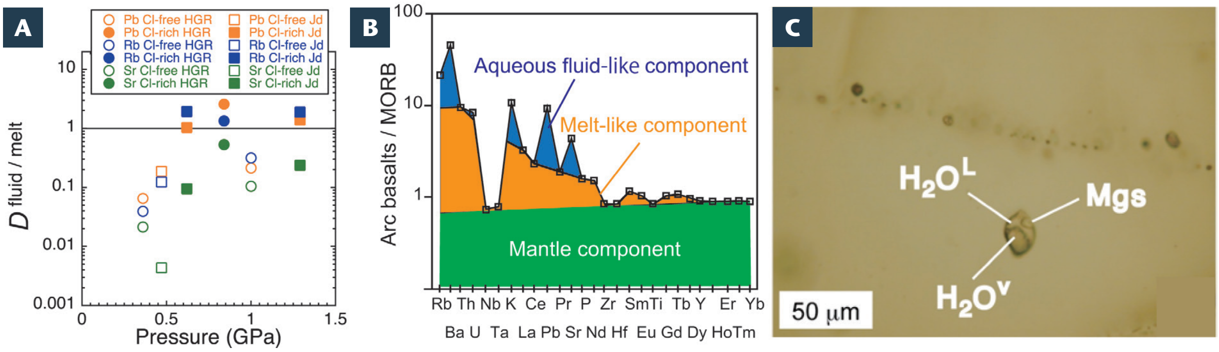

FIGURE 3 (**A**) Partition (distribution) coefficients ($D^{fluid/melt}$) of Pb, Rb, and Sr between aqueous fluids and coexisting haplogranite (HGR) or jadeite (Jd) melts as a function of pressure. Open symbols denote a Cl-free system; filled symbols denote systems with 5 mole (Na, K)Cl/kg. (**B**) Schematic diagram of trace element concentrations in arc basalts normalized to mid-ocean-ridge basalt (MORB). Aqueous fluid- and melt-like components are attributed to aqueous fluids and sediment-derived melts or supercritical fluids from subducted oceanic plate, respectively. (**C**) Fluid inclusion composed of saline solution (H_2O^L), vapor (H_2O^V), and magnesite (Mgs) in an olivine from a tremolite-bearing harzburgite xenolith collected from a pyroclastic flow from the Mount Pinatubo (Philippines) eruption of 1991. REFERENCES FOR DATA IN ONLINE SUPPLEMENT.

components”. Chlorine, present in aqueous fluids in the form of (Na, K)Cl, has a strong effect on the partition coefficient of these enriched elements between aqueous fluid and silicate melt. This was first shown by quench experiments (Keppler 1996) and later verified in situ using an externally heated diamond–anvil cell combined with synchrotron radiation X-ray fluorescence (Fig. 2) (Kawamoto et al. 2014). The partition coefficient of Pb between saline fluid and melt increases by more than one order of magnitude compared to that between pure H_2O fluid and melt (Fig. 3A). A similar effect is observed for alkaline elements (Rb) and the alkaline earth elements (Sr), which show enhanced partitioning into saline fluids. Geochemical systematics suggest that the ingredients of arc magmas are a mantle peridotite component, a slab-derived aqueous fluid component, and a slab-derived melt component (Fig. 3B). Figure 3A and 3B indicate that slab-derived fluids are saline fluids that contain Pb, alkaline, and alkaline earth elements, whereas slab-derived melts contain the fluid-insoluble elements Th, Ta, P, Zr, Hf, Y, and the rare earth elements.

Fluid inclusions are locally observed in mantle peridotite xenoliths and high-pressure metamorphic rocks (Kawamoto et al. 2013, 2018). Raman microscopy shows that the fluid inclusions are composed of aqueous solutions and vapor bubbles. Findings of magnesite-bearing saline fluid inclusions in tremolite-bearing harzburgite xenoliths from Mount Pinatubo Volcano (Philippines) suggest the presence of H_2O-CO_2-NaCl fluids at high-P and high-T conditions. This discovery led to the hypothesis that seawater-like saline fluids are present in the mantle wedge beneath the Philippine volcanic arc (Fig. 3C) (Kawamoto et al. 2013). The presence of tremolite indicates $P–T$ conditions of <830 °C at 0.9 GPa, which is above the temperature stability of serpentine minerals and talc and below the solidus temperature of H_2O-saturated mantle peridotite. Thus, the $P–T$ conditions that stabilize tremolite allow excess H_2O to exist as aqueous fluids in the mantle wedge.

Microthermometry on fluid inclusions in mantle xenoliths and metamorphic rocks from various arcs allows an estimate of the NaCl equivalent concentrations in the entrained rock: 5.1 ± 1 wt% in the harzburgite beneath Mount Pinatubo Volcano; 3.7 ± 1 wt% in lherzolite beneath Ichinomegata Volcano; 4.5 ± 1 wt% in jadeitite and jadeite-bearing rocks in the suprasubduction zone of the Dominican Republic; and 3–7 wt% in the high-pressure metamorphic rocks of the southwest Japan arc (e.g., Kawamoto et al. 2013, 2018) (Fig. 4). This suggests that subduction-zone fluids are slightly more saline than present seawater (3.5 wt% NaCl). Rare-gas and heavy-halogen systematics show that the fluid inclusions in mantle xenoliths from Mount Pinatubo have chemical features similar to sedimentary pore–fluids and to serpentinite, both of which are enriched in iodine through the decomposition of subducted organic materials (Kobayashi et al. 2017). This implies that subduction-zone fluids are probably produced through hydration and dehydration processes during seawater–oceanic plate interactions and inherit their sedimentary signature possibly through the dehydration of serpentinites.

Experimental studies suggest that saline (i.e., halogen-bearing) fluids not only enhance the dissolution of metals but also that of carbonate (Newton and Manning 2002). For example, 10 wt% NaCl-bearing fluids can dissolve more than double the amount of carbonate at 800 °C and 1 GPa. This shows the importance of being salty in subduction-zone fluids for the enhancement of elemental transfer. Experiments and natural observations indicate the presence of H_2O-CO_2-NaCl fluids in the mantle wedge (e.g., Kawamoto et al. 2013), although CO_2 is less common in fluid inclusions in the high-pressure metamorphic rocks that originate from subduction channels, the interplate boundary layers composed of oceanic crust and serpentinites at the base of the mantle wedge (e.g., Kawamoto et al. 2018). Isotopic investigation of the carbon in magnesite found in fluid inclusions within mantle xenoliths may be useful for understanding the transfer of carbon in subduction channels and the mantle wedge.

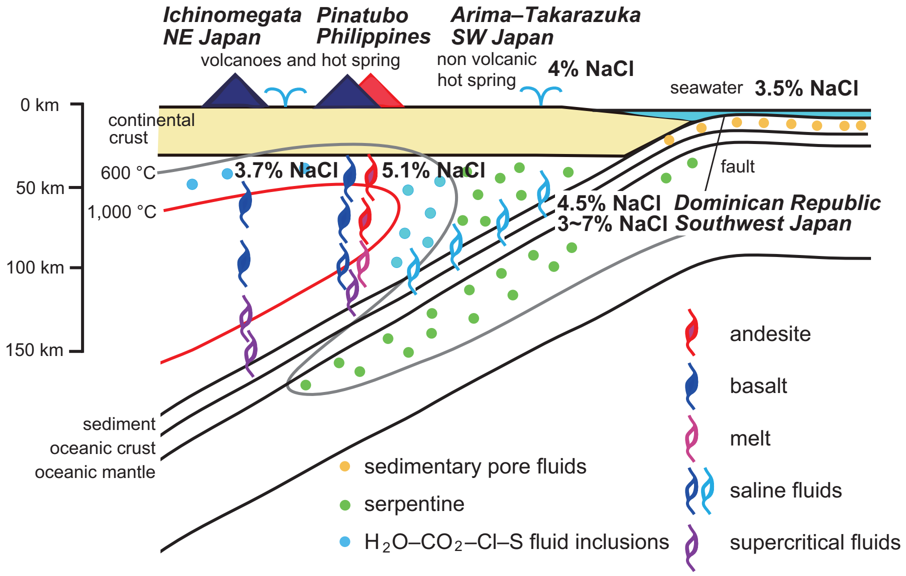

Figure 4 Salinity map of subduction-zone fluids. Symbol: % NaCl = wt% NaCl-equivalent. Arima–Takarazuka (Japan) is a hot spring in the forearc region and is characterized by high $^{3}He/^{4}He$ ratios suggesting its deep mantle origin. Aqueous fluids with 4.5% NaCl and 3%–7% NaCl are observed in jadeite-rich rocks formed in subduction channels of Dominican Republic and Southwest Japan arc, respectively. References for data in online Supplement.

HALOGENS IN METALLIC PHASES

During core formation, which occurred early in Earth’s history during the ~100 My interval after the initial solar nebula processes, the partitioning behavior between Earth’s silicate mantle and the metal core controlled the elemental distribution between these reservoirs. Whereas chlorine seems to be largely lithophile and remains in the silicate melt, iodine exhibits mildly siderophile behavior, indicating that the core could be a significant iodine reservoir containing up to 82% of the bulk Earth’s budget (Armytage et al. 2013 and references therein).

FUTURE PERSPECTIVES

To date, available studies strongly indicate that the transport of water and halogens into the deep Earth is closely linked, either through halogen-bearing aqueous fluids, melts or through the combined incorporation of OH groups and halogens in hydrous or nominally anhydrous minerals. This implies that a better understanding of the halogen behavior and distribution in the solid Earth is of fundamental importance for understanding the deep volatile cycle and its effects on physicochemical processes. This, in turn, will give a deeper insight into the role of halogens during the origin and evolution of our planet.

Carefully designed experiments to identify the key halogen–carrier phases in the crust, subducting slab, and mantle, are needed to better understand the halogen–incorporation mechanisms in minerals and melts, halogen speciation in fluids and melts, and to quantify their distribution, mobility, and release through partitioning or degassing at depth. The unquenchable properties of deep fluids/melts will require the novel use of in situ characterization techniques (i.e., infrared spectroscopies, X-ray characterization) combined with either laser-heated diamond anvil cells or any optical or X-ray-transparent high-pressure devices. These experimental strategies must be associated with new analytical tools, such as synchrotron X-ray fluorescence using nanoscale beams. Conventional setups will remain relevant to investigate processes and properties in the Earth's mantle, such as the solubilities of halogens in mineral phases, and mineral–melt partitioning of the heavy halogens. These will require the development of analytical techniques that allow for the precise analysis of Cl, Br, and I down to the parts-per-billion level with high spatial resolution to analyze them in individual phases.

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Developments in Halogen Abundance and Isotope Measurements

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The four stable halogens (F, Cl, Br, and I) are low-abundance elements that are widely distributed in nature. Two of the halogens, Cl and Br, each have two stable isotopes showing a range in natural isotope variation of up to a few parts per thousand. A variety of analytical techniques have been developed to determine the abundance and isotopic ratios of the halogens: these include in situ techniques for high spatial resolution studies and bulk determinations, and they have been applied to a range of materials, including whole rocks, minerals, glasses, and fluid inclusions. Here, we summarise some of the established methods for determining halogen abundances and isotopes and highlight key advances.

KEYWORDS: halogens; neutron activation analysis; ion chromatography; X-ray spectrometry; halogen stable isotopes; mass spectrometry

INTRODUCTION

The four halogens that are relevant to understanding Earth systems (F, Cl, Br, I) are key elements for constraining Earth's volatile processes and play an important role in geodynamic cycles. Progress on understanding halogen behaviour has been impeded by analytical challenges in measuring their low abundances in Earth's materials. Natural abundances span several orders of magnitude: they can reach mg/g (m = 10^{-3}) but more often are at µg/g (µ = 10^{-6}) to ng/g (n = 10^{-9}) levels, with Br and I usually showing 2–3 orders of magnitude lower abundance than F and Cl. To measure the abundances of all four halogens in a sample may require using two or more analytical techniques with different sample preparation procedures. Methods based on X-ray spectrometry, ion chromatography, neutron activation analysis, and mass spectrometry provide the foundation for the quantitative analysis of halogens (and their isotopes) in geological samples. In this article, we summarise some of the well-established and newer techniques for quantitative analyses of halogen abundances and for determining their isotopic ratios. Our aim is to highlight that routine analysis of these interesting elements is possible and remains an area of active development. The range and level of detail presented in this review is not exhaustive and the reader is referred to Hanley and Koga (2018) for more in-depth coverage of specific techniques. The relationships between the different analytical techniques covered in this article are summarised in FIGURE 1 and the approximate levels of detection and precision are given in TABLE 1.

X-RAY SPECTROMETRY

The X-ray spectrometry techniques provide a powerful tool to determine halogen abundance and distribution at a range of spatial scales. They require minimal sample preparation, are non-destructive, analytically fast, and the instrumentation is readily accessible. Detection is based on the principle that excited elements emit X-rays. The X-ray spectrum contains lines characteristic for a particular element, which can be identified according to their wavelength or photon energy. By comparing the intensity of the lines that are obtained from an unknown sample with those from a standard material of independently determined composition, a quantitative measure of the elements' concentration in the unknown can be obtained. The basic set-up for all spectrometers is a radiation source, a sample, and a detection system. For halogens, detection of F and Cl is hampered by their characteristic X-rays being of relatively low energy and by spectral interferences from Fe on F, Al on Br, and Ca on I. Recent developments in X-ray sources, optics, and detectors have improved analytical performance, and the analysis of synthetic halogen-free glasses (containing Fe, Al, and Ca) enables calibration of spectral interferences (Zhang et al. 2016, 2017; Flemetakis et al. 2020). Quantitative measurements are facilitated by analysing halogen-bearing experimental glasses and well-known reference materials (Marks et al. 2016; Cadoux et al. 2017; Flemetakis et al. 2020). The following are some important X-ray spectrometry techniques used to quantify halogen abundances.

X-Ray Fluorescence Spectrometry (XRF)

In X-ray fluorescence (XRF) spectrometers, an X-ray tube acts as a source that irradiates a sample directly, and the fluorescence emanating from the sample is measured with a wavelength- or energy- dispersive detection system. Sample preparation involves forming pressed pellets of several grams of powdered sample. The use of fused beads is best avoided because halogens are volatile elements that may experience loss during heating. Wavelength dispersive XRF has a superior spectral resolution at medium-to-low energies and allows lower detection limits and minimal matrix effects. This technique has been used to determine all four halogens in bulk sediment samples and has detection levels of 0.5 (Br) to 500 (F) µg/g (Li et al. 2015) (TABLE 1).

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Synchrotron Radiation XRF (SR-XRF)

Synchrotron radiation is employed as a tunable and high spectral brightness source of X-rays. It has the advantage that tuning of the X-ray beam exploits the strong energy dependence of inner shell electron excitations to increase element specificity and reduce background radiation. The highly energetic X-rays penetrate below the sample surface, enabling both imaging and chemical mapping at the micrometre scale. The detection limits for SR-XRF are less than 1 µg/g and can be coupled with X-ray absorption near-edge spectroscopy (XANES), a technique used to identify chemical species in samples. The SR-XRF technique has been applied to studies of Br in fluid inclusions, melt inclusions, and matrix glasses. Cadoux et al. (2017) prepared synthetic glass standards to quantify Br abundances in natural glasses using SR-XRF. Bromine contents of >10 µg/g were determined with a precision of <10% (Table 1).

Electron Probe Microanalysis (EPMA)

The electron microprobe uses a focussed beam of electrons to excite X-rays from a sample. It can be focussed to a small spot size of 5–10 microns for high spatial resolution analyses. Analytical protocols developed by Zhang et al. (2016, 2017) have improved the ability to measure halogens by lessening the problems that arise from low count rates and spectral interferences. To quantify the Fe, Al, and Ca interferences on F, Br, and I peaks, halogen-free glasses are used to subtract the amount of "apparent" halogen arising from spectral interference. Using this approach, Flemetakis et al. (2020) obtained detection limits of 30–160 µg/g for halogens (Table 1). The EPMA technique is suitable for measuring natural abundances of F and Cl in a broad range of geological samples; however, only particularly Br- and I-rich minerals and natural glasses are accessible using this technique.

DETERMINATION OF HALIDE CONCENTRATIONS BY ION CHROMATOGRAPHY

Ion chromatography (Weiss 2016) is a technique in which a liquid sample is mixed with an eluent (liquid solvent) that behaves like the carrier gas in gas chromatography. This mixture is injected into an ion-chromatography column where ions are separated based on their mass and their interaction with the column material and the eluent. To measure halogens by ion chromatography, the column material (stationary phase) is often polyvinyl alcohol with tertiary ammonium groups, while the eluent is often a carbonate/bicarbonate solution. The components in the solution are measured with a conductivity detector. When a sample peak arrives at the detector, the conductivity changes and this change is related to the concentration, with different ions separated in the column according to their retention time. The area of a sample peak is compared to the areas of reference-material peaks measured under the

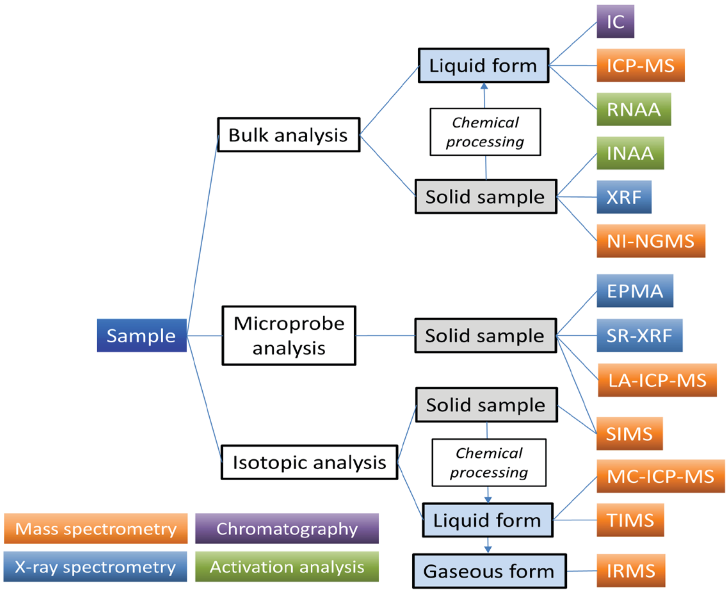

Figure 1 Relationships between sample type and analytical techniques for halogen abundance and isotope determinations considered in this article. Note that the term "liquid form" indicates that samples are chemically processed to concentrate halogens in the liquid state: for some techniques there may be a further stage to precipitate solids (e.g., RNAA) or to form a gas (e.g., IRMS) from this liquid prior to analysis. Abbreviations: IC = ion chromatography; ICP-MS = inductively coupled plasma mass spectrometry; RNAA = radiochemical neutron activation analysis; INAA = instrumental neutron activation analysis; XRF = X-ray fluorescence; NI-NGMS = neutron irradiation noble gas mass spectrometry; EPMA = electron probe microanalysis; SR-XRF = synchrotron radiation X-ray fluorescence; LA-ICP-MS = laser ablation inductively coupled plasma mass spectrometry; SIMS = secondary ion mass spectrometry; MC-ICP-MS = multicollector inductively coupled plasma mass spectrometry; TIMS = thermal ionisation mass spectrometry; IRMS = isotope ratio mass spectrometry.

Table 1 Detection limits and relative standard deviations (RSDs, 1σ) for analytical techniques (see text for description) used for halogen abundances. For many techniques, detection limits have been reported over a wide range. Values shown here are indicative and may not be practical limits for many samples. The most important index for evaluating an analytical method is the accuracy of the data obtained.

Technique	Sample size	Detection level (RSD %, 1σ)			
		F (µg/g)	Cl (µg/g)	Br (ng/g)	I (ng/g)
EPMA	µg	90 (1)	30 (0.5)	155 × 10^3 (3)	75 × 10^3 (1)
SR-XRF	micro	na	na	10 × 10^3 (10)	na
ICP-MS	g	na	3 (2)	0.4 (5)	0.13 (5)
NI-NGMS	mg	100 (5)	1 (5)	4 (5)	0.5 (7)
IC	mg	45 (<1)	20 (<1)	150 (1)	250 (3)
XRF	g	100 (5)	5 (5)	500 (5)	10 × 10^3 (5)
INAA (PGAA)	mg–g	na	5 (5)	na	na
RNAA	mg	na	3 (5)	30 (5)	30 (10)
SIMS	micro	0.1 (3.5)	0.2 (3.5)	10 × 10^3 (10)	100 × 10^3 (10)

Abbreviations: EPMA = electron probe microanalysis; SR-XRF = synchrotron radiation X-ray fluorescence; ICP-MS = inductively coupled plasma mass spectrometry; NI-NGMS = neutron irradiation noble gas mass spectrometry; IC = ion chromatography; XRF = X-ray fluorescence; INAA (PGAA) = instrumental neutron activation analysis (prompt gamma-ray activation analysis); RNAA = radiochemical neutron activation analysis; SIMS = secondary ion mass spectrometry; na = halogen element not usually analysed by this technique; RSD = relative standard deviation same conditions, enabling the concentration in a sample to be calculated from a calibration curve.

In the case of solid material, halogens must be extracted into aqueous solution. The commonly used method is pyrohydrolysis combustion. With this technique, a solid sample is mixed with a flux, generally V_2O_5 or WO_3, and heated in a water vapour flow to a temperature of between 1,000 °C and 1,500 °C. Volatile elements, such as the halogens, are evaporated during this process, trapped in the water flow, and transferred to a collecting flask. The solution in this flask can, in principle, be measured by ion chromatography as described above (e.g., Shimizu at al. 2015).

For automated analysis of solid samples there are systems available that integrate combustion with ion chromatography. For example, Metrohm AG has developed an absorber unit that automatically collects the solution from a combustion unit, absorbs this solution into a H_2O_2 solution to oxidise reduced species, and transfers the sample to the ion chromatograph in one go. Although originally developed for metal and plastic, this technique suits solid geological samples very well (Epp et al. 2019). With its simplicity, low detection limits (µg/g), good precision (TABLE 1), and relatively rapid procedures, ion chromatography can be widely used for the routine analysis of all four halogens in many geological materials.

DETERMINATION OF HALOGENS BY ACTIVATION ANALYSIS

Activation analysis is based on using nuclear reactions on stable nuclides of halogens to "activate" them through a transformation to unstable (radioactive) nuclides. Radioactive nuclides then decay back to stable nuclides, with a number of particles and/or photons being emitted (FIG. 2). The parent halogen identity is determined by measuring decay properties, such as half-life and radiation energy for radioactive nuclides (i.e., qualitative analysis), while the measurement of radiation rates yields quantitative information. Among nuclear reactions used in activation analysis, a neutron-capturing reaction expressed as (n,γ) is the most common (neutron activation analysis, NAA), followed by a reaction induced by photon irradiation (photon activation analysis, PAA).

Instrumental Neutron Activation Analysis (INAA)

In principle, the concentrations of all four stable halogens (F, Cl, Br, and I) in solids can be quantitatively determined by instrumental NAA (INAA), using a research reactor as a neutron source. TABLE 2 summarises nuclear and some related data for INAA of the four halogens, and FIGURE 2 shows a schematic of the relationship with the related technique of radiochemical NAA (RNAA) discussed later. The most advantageous feature of INAA is that chemical processing of an activated sample is not required. Samples are homogenised by turning them to powder and then the powder is irradiated with neutrons for a few minutes to several hours, depending on the half-lives of the radioactive halogen nuclides produced. After an appropriate cooling interval, the irradiated samples are measured for their emitting gamma- rays. Reference samples that contain known amounts of halogens, prepared using chemical reagents of individual halogen compounds, are processed simultaneously in the same manner as the samples.

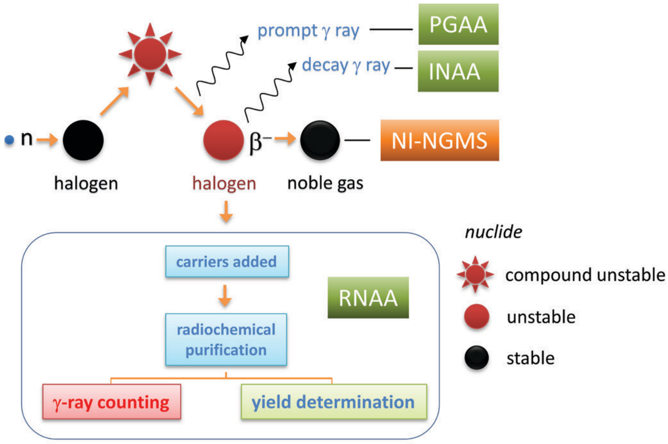

FIGURE 2 Schematic of neutron activation analysis and flow of RNAA (radiochemical neutron activation analysis) procedures. A stable halogen nuclide captures a neutron and a compound nuclide is formed, emitting prompt gamma- rays (within 10^{-14} s). These gamma- rays are measured for elemental quantification by PGAA (prompt gamma-ray activation analysis). The compound nuclide decays to a stable nuclide by a beta-minus decay mode. A nuclide just after decay is in an excited state of nuclear energy and transitions to a ground state by emitting decay gamma- rays, which are used in INAA (instrumental neutron activation analysis).

Among the four halogens, F is the most difficult to determine by the conventional INAA procedure described above because of the very short half-life (11.1 s) of the neutron-capturing nuclide ^{20}F. For INAA of F, a sophisticated analytical procedure, named cyclic activation analysis, needs to be applied; however, it is not commonly used because of limited facilities. For the remaining halogens, INAA may be routinely applied. However, because precision is dependent on concentrations of halogens and coexisting (matrix) elements, INAA has limited application in many terrestrial samples. Nevertheless, INAA is a practical method for determining Cl and Br in some types of chondrites, where abundances for Cl are on the order of several hundred µg/g, whereas for Br this is a few µg/g. Iodine can scarcely be quantified for most terrestrial and extraterrestrial samples by conventional INAA. Because ^{127}I has a relatively large neutron capture cross section for epithermal neutrons (TABLE 2), the detection of ^{128}I can be improved by irradiating samples while shielded with a

TABLE 2 NEUTRON REACTIONS USED IN NEUTRON ACTIVATION ANALYSIS AND NOBLE GAS MASS SPECTROMETRY FOR DETERMINING HALOGEN ABUNDANCES.

Parent	Abundance	Reaction	Cross-section[a]	Decay mode[b]	Half-life	Product	INAA	RNAA	PGAA	NI-NGMS
^{19}F	1	(n,γ)^{20}F	0.0095, 0.018	β^-	11.07 s	^{20}Ne	✓			✓
^{35}Cl	0.7576	(n,γ)^{36}Cl	43.6, 17.9	β^-	3.013×10^5 y	^{36}Ar				
^{37}Cl	0.2424	(n,γ)^{38}Cl	0.433, 0.3	β^- (98.1%)	37.23 min	^{38}Ar	✓	✓	✓	✓
^{79}Br	0.5069	(n,γ)^{80}Br	10.32, 120.2	β^- (91.7%)	17.68 min	^{80}Kr				✓
^{81}Br	0.4931	(n,γ)^{82}Br	2.36, 46	β^-	35.282 h	^{82}Kr	✓	✓		✓
^{127}I	1	(n,γ)^{128}I	6.15, 162	β^- (93.1%)	24.99 min	^{128}Xe	✓	✓		✓

[a] Thermal neutron cross-sections and resonance integrals given in barns (10^{-24} cm^2).

[b] β^- = beta decay by spontaneous emission of an electron; 100% decay route unless otherwise stated.

ABBREVIATIONS: INAA = instrumental neutron activation analysis; RNAA = radiochemical neutron activation analysis; PGAA = prompt gamma activation analysis; NI-NGMS = neutron irradiation noble gas mass spectrometry.

✓ = a technique with relatively low detection limits.

Cd or B_4C filter: this effectively absorbs thermal neutrons, and I contents of <1 μg/g can be determined for relatively I-rich sedimentary rocks.

When capturing neutrons, a target nuclide emits prompt gamma- rays in addition to decay gamma- rays, which are used for conventional INAA (Fig. 2). During prompt gamma activation analysis (PGAA), neutrons are guided with a neutron guide tube out of a reactor core and gamma-ray measurements are conducted as in-beam spectrometry. As an analytical method, PGAA has the great merit of being non-destructive, and it has a high sensitivity for several major elements of geological samples, including Si, and does not induce radioactivity above safety regulation levels applied to non-radioactive materials. The PGAA technique has a relatively high sensitivity for Cl (Table 1) and can be used to determine the abundance of this element in most samples (Islam et al. 2011). In PGAA, a large bulky sample (in chunks) can be quantitatively analysed with the use of an internal standard calibration method (Latif 2013), which is an additional advantage of this technique.

Radiochemical Neutron Activation Analysis (RNAA)

Radiochemical neutron activation analysis (RNAA) is applicable for Cl, Br, and I (Ebihara et al. 1997) and is considered "destructive" because samples undergo a stage of chemical processing, unlike INAA, which utilises powdered samples. In RNAA, the sample is first irradiated with neutrons (e.g., for 5 to 10 minutes), followed by cooling for several minutes, then radiochemical procedures for purification of halogens are carried out. Normally, samples are fused with an alkaline flux and fusion cakes are digested with H_2O. From the supernatant liquid, the halogens are successively precipitated, with Cl and Br as silver halides and I as PdI_2. These precipitates are collected on disk filters and subjected to gamma-ray spectrometry. Because the half-lives of neutron-capturing halogen nuclides (^{38}Cl, ^{82}Br, and ^{128}I) are relatively short, especially for ^{38}Cl and ^{128}I (Table 2), the radiochemical separation needs to be completed within an hour of irradiation. The RNAA technique has a unique feature among quantitative analysis methods: it suffers neither errors due to contamination nor errors caused by analyte loss. Therefore, RNAA can yield the most reliable (accurate) analytical values. Figure 2 illustrates a flow of RNAA procedures. In RNAA, the addition of carriers to the irradiated samples help to optimise chemical separation procedures. Once an isotopic equilibrium between the stable nuclides in the carriers and the radioactive nuclides in the neutron-irradiated samples is established, neither contamination nor analyte loss affects the accuracy of the analytical data (Sekimoto and Ebihara 2013). It is particularly important that great care is taken in the proper preparation of such reference samples in RNAA, especially for I. Application of a k_0-standardisation method (Ozaki and Ebihara 2007) is an alternative choice for quantification of halogens by RNAA, and also by INAA, which enables an absolute analysis and reduces the number of reference materials, thus simplifying the sample preparation procedures and the gamma spectrometry. Therefore, methodologically, RNAA can yield very accurate (reliable) quantitative values.

MASS SPECTROMETRIC TECHNIQUES

Mass spectrometry is used for determining halogen abundances in samples and for measuring the variations in isotopic ratios of Cl and Br. A mass spectrometer is an instrument in which particles are separated based on mass and charge differences. It consists of the following essential three components: (i) an ion source, where a beam of charged particles (ions) is produced; (ii) an analyser, basically an evacuated tube with a flattened bend in the middle over which a large magnet is placed and where the beam is separated into different mass components; and (iii) a detector system that records the different ion beams. Mass spectrometers were originally developed during the 1930s and optimised by Nier (1947) and at Harold Urey's laboratory (McKinney et al. 1950). Figure 3, taken from Nier's classic 1947 paper, shows that the overall design of mass spectrometers has not changed significantly since then. The main differences between different mass spectrometer types concern the inlet systems and the preparation methods to obtain pure, uncontaminated, ion beams, because the best results are obtained when ion beams consist of only those particles that are measured.

Neutron Irradiation Noble Gas Mass Spectrometry (NI-NGMS)

Halogen isotopes formed by neutron activation are unstable and decay to stable noble gas isotopes with short half-lives (Fig. 2; Table 2). By controlling the neutron fluence that a sample receives, and assuming natural abundance levels, a rate of conversion of about 1:10^5 halogen atoms provides sufficient noble gas isotopes to be generated for measurement in a noble gas mass spectrometer. Neutron-induced noble gas isotopes are released from an irradiated sample either by heating, using a furnace or laser for solid minerals, or by laser ablation, or by in vacuo crushing for fluid inclusions. By including standard minerals of known halogen composition, together with the samples that are irradiated, quantitative estimates of parent halogen abundances are achieved (Kendrick 2012). The NI-NGMS technique is often considered an extension of ^{40}Ar/^{39}Ar dating, as it relies on similar sample preparation methods and instrumentation. The main advantage is the extremely low detection limit (Table 1) and the ability to measure F, Cl, Br, and I in a single extraction step (Kobayashi et al. 2021). Together with information obtained on halogens, other proxy noble gases are formed from neutron reactions on isotopes of Ca, K, Ba, and U, and some natural noble gas isotopes can also be measured. Because the required neutron fluxes are relatively high, the main disadvantages are the need to access a high-powered research reactor for irradiation purposes, and the hazards and controls associated with handling radioactive materials.

Inductively Coupled Plasma Mass Spectrometry (ICP-MS)

In ICP-MS, the halogens are present in an aqueous solution that has usually been produced using a previous sample preparation step, e.g., by combustion, extraction, or digestion. The solution is sucked into the inlet system where it is heated in an argon plasma where it is ionised, and then analysed by the mass spectrometer. This technique provides rapid sample throughput and the capability to determine all four halogens at excellent detection levels (Table 1). Direct analysis of a solid sample is also possible using laser ablation microanalysis (laser ablation inductively coupled plasma mass spectrometry, LA-ICP-MS). With its high first ionisation potential, F is only very slightly ionised in the plasma and is rarely determined by ICP-MS. Other limitations arise from memory effects in the mass spectrometer, spectral interferences formed in the plasma, matrix effects from the multi-element sample solution, and the potential loss of halogen elements during the sample preparation step (Flores et al. 2020).

Secondary Ion Mass Spectrometry (SIMS)

Secondary ion mass spectrometry (SIMS) is an in situ technique where the sample is introduced to the ion source as a polished gold-plated thin section. This is bombarded with a beam of Cs^+ ions, which produces a beam of negatively charged secondary ions from a small spot of a few microns in diameter. However, the ion yield of halogens in SIMS is strongly sensitive to matrix effects (dependent on the chemical composition of the material being measured), and the accuracy of the measurements depends on the availability of appropriate standard materials. For this reason, it is most often used for halogens in silicate glasses (including melt inclusions) and mineral phases, where it is relatively simple to either manufacture or find suitable natural samples as standards (Cadoux et al. 2017). The superior detection levels of SIMS relative to EPMA for F and Cl means it is a preferable method for in situ determination of these elements in relatively low-abundance samples (Table 1). Both Br and I determinations are limited by detection levels and from partially overlapping interferences on the halide ion beams, which become more acute at low ion beam intensities. However, procedures have been developed that indicate in situ determinations of iodine contents <1 µg/g are feasible in meteorites (Goswami et al. 1998).

STABLE ISOTOPE RATIO ANALYSES OF CHLORINE AND BROMINE

Of the four geologically relevant halogens, only Cl and Br have two stable isotopes so that isotope ratio variations can be determined. Isotope ratio variations are defined as the variations between the stable isotope ratio of a sample relative to that of an international reference material.

In stable isotope geochemistry, small variations in the range of a few parts per thousand ("per mil") are measured between stable isotope ratios. The two stable Cl isotopes are ^{35}Cl and ^{37}Cl, and the two Br isotopes are ^{79}Br and ^{81}Br. Isotope variations are reported as δ^{37}Cl or δ^{81}Br, the delta notation being one originally defined by McKinney et al. (1950):

$$\delta = \left(\frac{R_{\text{sample}}}{R_{\text{standard}}} - 1 \right) \cdot 1000$$

In the equation above, δ translates to the per mil (‰) difference between the stable isotope ratios (R) of the sample and of the standard. For Cl and Br, δ values in most geochemical samples differ by no more than a few ‰ from the standard. It has been shown that the isotope variation of ocean water is less than the error of measurement (which is about 0.05‰ for both Cl and Br isotopes) and this is used as the international reference material (Kaufmann 1984; Godon et al. 2004; Du et al. 2013).

Natural Cl and Br isotope variations are significantly smaller than those for other light elements, as both elements are normally found in oxidation state −1 and (inorganic) redox variations are uncommon on Earth. It was only in 1984 that natural Cl isotope variations were confirmed (Kaufmann 1984), whereas for Br this had to wait until 2000 (Eggenkamp and Coleman 2000).

Depending on the amount and type of sample available for measurement, and whether one wants to measure Cl or Br isotope variations, the four most common mass spectrometric techniques used for isotopic measurements are as follows: (i) isotope ratio mass spectrometry (IRMS); (ii) thermal ionisation mass spectrometry (TIMS); (iii) multi-collector inductively coupled plasma mass spectrometry (MC-ICP-MS); and (iv) secondary ion mass spectrometry (SIMS). The different techniques need different sample quantities for optimal use. In general, IRMS requires the largest amount of sample (≥20 µmol) but is the most accurate (better than 0.05‰). The TIMS and MC-ICP-MS methods use significantly smaller sample amounts (≥300 nmol), with analytical errors on the order of 0.1‰–0.2‰. The SIMS method has a similar accuracy and is particularly applicable to solid samples. The technique of choice for Cl is IRMS, for Br it is MC-ICP-MS. The use of TIMS as a technique to measure Cl (or Br) isotopes has declined since 2010: prior to this it was used extensively.

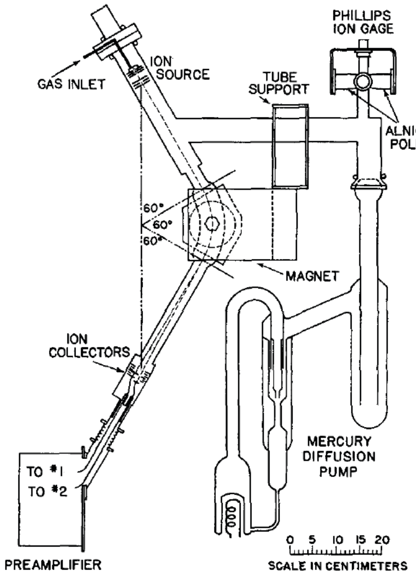

Figure 3 Schematic drawing of a Nier-type mass spectrometer showing the mass spectrometer tube, magnet, pressure gauge, and pumping system. Reproduced with permission of AIP Publishing from Nier (1947).

In IRMS, the sample is introduced as a gas into the inlet system where it is ionised at the filament. To prepare a gaseous Cl or Br compound, chloride or bromide in a sample is converted to gaseous CH_3Cl or CH_3Br. This is done by precipitating the halide ion with silver nitrate and then reacting the solid silver halide with CH_3I to give halomethane as the product. This can be separated from excess iodomethane by gas chromatography, resulting in very pure halomethane that can be introduced into the mass spectrometer and measured.

In natural samples, Cl is always present in large excess compared to Br (in seawater the Cl/Br molar ratio is about 660). Because their chemical behaviour is very similar, they need to be separated prior to Br isotope analysis using IRMS, TIMS, and MC-ICP-MS. This can be done by either ion-exchange techniques or by the oxidative distillation of Br from Cl. This last technique oxidises Br^- in a sample, using either $K_2Cr_2O_7$ or HNO_3 to produce Br_2 (these oxidation agents do not oxidise Cl^-), and then one distils the produced Br_2 to a reducing trap that reduces the Br_2 back to Br^-, which can be treated like chloride.

In TIMS, the sample is introduced as a slurry onto the filament in the ion source, which is subsequently dried and evacuated. When the filament is heated, it releases ions into the analyser. Prior to their introduction to the filament, the cations in the sample solution are exchanged with caesium, and graphite powder is added to this solution. This caesium halide/graphite sludge is added to the filament and gently dried, leading to the evaporation of Cs_2X^+ ions (where X = Cl or Br), which are measured.

In MC-ICP-MS, the sample preparation involves purification using ion exchange techniques so that primarily halide anions and ammonium cations are present. The solution is sucked into the inlet system where it is heated in an argon plasma and ionised. Due to the use of an argon plasma, this method is not well suited for Cl isotopes because the ion $^{36}ArH^+$ that forms in the plasma has almost the same mass as ^{37}Cl, and interference is so large that measuring Cl isotopes by IRMS is almost always more convenient. Although $^{40}Ar_2H^+$ with mass 81 is formed during Br isotope measurements and interferes with ^{81}Br, the effect is not as large and Br isotopes can be measured successfully, especially when it is realised that in most cases not enough bromine is available to be measured by IRMS.

The SIMS method is less suited for Br because of the mass interference from CaCl ions formed in the process when Ca is present, and because Cl is always present in excess compared to Br.

Apart from the above-mentioned techniques, many other approaches have been developed to measure Cl and Br stable isotope ratios. Most are described in detail in Eggenkamp (2014), except for recent MC-ICP-MS techniques, which are described in Louvat et al. (2016) and Eggenkamp and Louvat (2018).

SUMMARY AND OUTLOOK

Although there are a range of well-established techniques for analysing halogens in geological samples, none readily meet the requirements of being non-destructive and capable of quantitatively analysing all four halogens at natural levels, whilst being environmentally friendly. Particular challenges surround detection levels, and although larger sample masses can help, they are not always available, in particular for precious extraterrestrial samples. Another critical point is that some of the methods require access to highly specialised facilities, including nuclear reactors, synchrotron radiation sources, and ion microprobes. These are scarce resources, demanding high levels of expertise, and are not readily accessible to many laboratories worldwide. In spite of these challenges, the important role of halogens in geochemical studies has stimulated progress, in particular in the use of higher-sensitivity detectors and improved X-ray and ion-optical designs to enhance resolution. Improvements aimed at minimising sample preparation, matching detection limits to natural abundances, and simultaneous measurement of all four halogens in a sample, remain important targets for the future.

ACKNOWLEDGMENTS

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The Clay Minerals Society

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THE PRESIDENT’S CORNER

How many of you have Facebook or Twitter accounts? Did you know that The Clay Minerals Society (CMS) has a presence on both, as well as a YouTube channel? No account is required to access these sites. Search for TheClayMineralsSociety (**Facebook**), ClayMinSociety (**Twitter**), “The Clay Minerals Society” (**YouTube**). In addition to society announcements, these pages are full of useful and interesting tidbits. Recent posts include seminar announcements, student and postdoc openings, and a picture of a dress whose pattern was based on the X-ray fluorescence map of a shale!

We have three times as many followers on social media as we have CMS members. Let’s all try to recruit new members, particularly those that already follow our social media pages. To boost our member recruiting effort, the CMS is making content available online through our **YouTube** channel, starting with our 2020 annual meeting webinar. But as CMS members we can identify potential new members from our own professional affiliates. These could be colleagues, students, or postdocs. Please join me in recruiting new CMS members.

I encourage all CMS members to get more involved, whether you are a student, postdoc, career professional, or retired. Volunteer societies like the CMS depend on the efforts of its members, working toward the society’s objective of the advancement of clay mineral science. Here are some ways that you can participate:

- attend our annual meeting (or better yet, present!)
- participate in annual meeting programming
- serve on CMS committees
- serve on CMS Council

Please visit the CMS website (https://www.clays.org) for more information.

Jeffery Greathouse, CMS President

CMS PROFESSIONAL AWARD 2022 SPOTLIGHT

Lynda B. Williams is the recipient of the 2022 George W. Brindley Clay Science Lecture. She is a Research Professor at Arizona State University (USA) where she enjoys research on a variety of clay science topics related to geochemical interactions of fluids, minerals, microbes, and organic compounds. Her most recent research focuses on Li and B isotopes in clays to trace paleofluid sources. Additionally, more than a decade of her research was devoted to understanding the geochemical mechanisms of antibacterial clays. For 35 years, she has been entirely funded by US federal grants (National Science Foundation, National Institute of Health, Department of Energy).

Lynda received an Bachelor of Arts (AB) in geology from Smith College (Massachusetts, USA) in 1980. After working in mineral exploration, she completed an MS at Dartmouth College (New Hampshire, USA) with Half Zantop and Robert Reynolds (1984). She worked in the Basin Research Institute at Louisiana State University (USA) and raised two children with her husband Stanley N. Williams, then moved to Arizona State University in 1991. In 2000, she received a PhD in geochemistry at the University of Calgary (Alberta, Canada), supervised by Ian Hutcheon. At Arizona State University she manages the National Science Foundation supported Secondary Ion Mass Spectrometry (SIMS) Facility and studies light stable isotopes of nanometric clay size fractions that record paleo-fluid changes during crystal growth.

Her most cited research is on antibacterial clays, as she discovered that certain reduced-iron clays have a chemistry that causes destruction of antibiotic-resistant human pathogens. Identification of the mineralogical and geochemical conditions that produce such clays, and applications toward human health is ongoing.

Michael F. Hochella, Jr. is the recipient of the 2022 Pioneer in Clay Science Lecture. He is currently a University Distinguished Professor (Emeritus) at Virginia Tech (USA) and a Laboratory Fellow and Senior Advisor at the Pacific Northwest National Laboratory (Washington, USA). His interests are nanogeoscience, minerals, geochemistry, and biogeochemistry at local, regional, and global scales. His research is supported by laboratory, field, theory, and computational work. Michael has won many honors, medals, and awards for both research and teaching, including the Dana Medal of the Mineralogical Society of America, the Clair C. Patterson Medal of the Geochemical Society, the Geochemistry Division Medal of the American Chemical Society, and the Virginia Outstanding Faculty Award, the highest honor for faculty in the Commonwealth of Virginia. He is a fellow of the American Geophysical Union, American Association for the Advancement of Science, Royal Society of Chemistry, Geochemical Society, European Association of Geochemistry, Mineralogical Society of America, International Association of GeoChemistry, and the Geological Society of America. He is a former president of both the Geochemical Society and the Mineralogical Society of America. He is also the founder and former director of NanoEarth (https://www.nanoearth.ictas.vt.edu/), a node of the National Nanotechnology Coordinated Infrastructure (NNCI), a National Science Foundation funded network of 16 centers spread throughout the United States serving as user facilities for cutting edge nanotechnology research. NanoEarth is part of Virginia Tech’s Institute for Critical Technology and Applied Science (ICTAS), and headquartered in Blacksburg, Virginia.

JOURNAL’S ISSUE UPDATE

Clays and Clay Minerals has new articles after issue 6 of 2021. A few include:

“A FIB-SEM Study of Illite Morphology in Aeolian Rotliegend Sandstones: Implications for Understanding the Petrophysical Properties of Reservoir Rocks” by Markus Peltz, Arne Jacob, Georg G. Grathoff, Frieder Enzmann, Michael Kersten, and Laurence N. Warr.

“Modifying a Smectite using Organic Nutrients to Enhance its Efficacy at Removing Aflatoxin B1 from Corn Fermentation Solution” by Sabrina Sharmeen Alam and Youjun Deng.

“Development of Kinetic Parameters for Nitric Acid Leaching of Phlogopite and the Characterization of Solid Products” by Cheri M. Favel and Barend J. du Plessis.

“Adsorption Behavior of Asphaltene on Clay Minerals and Quartz in a Heavy Oil Sandstone Reservoir with Thermal Damage”” by Yanlong He, Weizhe Niu, Zhanwu Gao, Hao Dong, Shizi An, Chunchun Han, and Liang Zhao.

Read more of these papers and others at the journal homepage: https://www.springer.com/journal/42860

CMS MEMBERSHIP RENEWAL

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W.K. FLETCHER – AAG GOLD MEDAL AWARD FOR 2021

The Association of Applied Geochemists is pleased to announce that the 2021 Gold Medal for outstanding contributions to exploration geochemistry is awarded to **Dr. W. K. Fletcher**, Professor of Geological Sciences (retired) at The University of British Columbia (Vancouver, Canada).

William Kenneth ('K') Fletcher was born in England and received both his BSc in geology and his PhD in applied geochemistry from the Imperial College of Science and Technology, University of London (UK), where he was a student of the pioneering exploration geochemist John Webb. Shortly afterwards, in 1968, he moved to The University of British Columbia (UBC), where he would spend his entire professional career. From 1968 till 1971, he was a postdoctoral fellow with Harry Warren working on the application of geochemistry to agricultural and public health issues as well as to mineral exploration. Upon Warren's retirement, K was appointed assistant professor in the Department of Geology in 1971, and later appointed associate professor in 1979 and professor in 1987. He served as Acting Head of the Department of Geological Sciences in 1992–1993. From 1999 until his retirement in 2003, K occupied the Norman B. Keevil Chair in Mineral Exploration.

In all, K spent 35 productive years at UBC as a researcher and teacher, continuing and expanding on UBC's leadership in exploration geochemistry training and research, which Harry Warren began many years before. During that time, he published over 100 scientific papers on exploration geochemistry and related topics, including 76 in refereed journals. He also authored, co-authored or edited three books, most notably his 1981 textbook *Analytical Methods in Geochemical Prospecting*.

K's most significant research at UBC centred on the fluvial transport of heavy minerals, including gold and cassiterite, in temperate and tropical regions; on the development of effective methods of sampling and analysis of stream sediments for mineral exploration; and on the statistical evaluation of the results of regional geochemical exploration surveys. His work in stream sediment transport in various climatic regions remains a foundation of regional geochemical programs in the mineral exploration industry. He also made important contributions to our understanding of the distribution and behaviour of base and precious metals in soil, till, and organic sediments in glaciated terrain. K conducted field investigations, delivered invited lectures, and gave short courses in many parts of the world, most notably in Canada, US, Brazil, Africa, and Southeast Asia.

K was also fully engaged with the mineral industry outside the university environment and, during leaves of absence from UBC, was the Chief Geochemist to MINDECO in Zambia (1975–1978) and the United Nations Geochemist and Team Leader at the Southeast Asian Tin Research and Development Centre in Malaysia (1982–1984). He was active in the Association of Exploration Geochemists (AEG) throughout his career, serving as president in 1991–1992, and was AEG distinguished lecturer in 1988–1989, with his lecture tour including several cities in Europe, Australia, and Brazil. He was, at various times, an AEG councillor and served as chairman of both the Short Course Committee and the Regional Geochemical Committee. K also served as co-editor of the *Journal of Geochemical Exploration* in 1998–1999, was a member of the Canadian Geoscience Council, and represented the discipline of geochemistry on the Geoscience Committee of the Association of Professional Engineers and Geoscientists of British Columbia.

Perhaps K's greatest contribution to the discipline of applied geochemistry, however, has been as a teacher and mentor, in training many young scientists at the MSc and PhD level. He supervised 23 graduate students, many of whom went on to important leadership roles as exploration geochemists in industry, academia, and government. He was very generous with both his time and ideas, and no less than six of his graduate students were awarded the AEG Student Paper Prize for papers co-authored with K. With his energy, enthusiasm, and many years of leadership in geochemical research and in teaching students, he played no small role in helping to make Vancouver the important global centre of exploration geochemistry, which it has become.

K Fletcher retired from UBC in 2003, after which he and his wife Donna were able to devote themselves full-time to their avocation of wildlife photography. His exemplary record as a researcher, teacher, and global ambassador for exploration geochemistry makes him a worthy recipient of the AAG's Gold Medal. The medal presentation will take place in October 2022 at the upcoming 29th International Applied Geochemistry Symposium in Viña del Mar, Chile.

DR. PAUL MORRIS – AAG SILVER MEDAL AWARD FOR 2021

The Association of Applied Geochemists Silver Medal is awarded for dedicated service to the association, to those individuals who voluntarily devote extraordinary time and energy to advancing the affairs of the AAG. For 2021, the AAG is pleased to announce that the Silver Medal is awarded to Dr. Paul Morris, Chief Geochemist (retired) of the Geological Survey of Western Australia.

Paul completed his BSc (Hon) in geology at the University of Otago (New Zealand) in 1976 and his PhD at the Victoria University of Wellington (New Zealand) in 1981. He held various teaching positions at the University of Sydney (Australia) and Shimane University (Japan). In 1987, he joined the Geological Survey of Western Australia, becoming the Chief Geochemist in 1997. He retired in 2018 after a 30-year career at the Geological Survey of Western Australia, including 22 years as Chief Geochemist.

The award of the Silver Medal to Paul honours his long-standing and continuing service to the AAG, on the Executive Council, on no less than six AAG committees, and through many other AAG activities over the course of his long and distinguished career. He served as president during 2010–2011, served five terms as an ordinary councillor, and notably was co-chair of the very successful 2005 International Applied Geochemistry Symposium in Perth (Australia). He has been a tireless contributor to the AAG's journals over the years and has reviewed numerous technical articles in the *EXPLORE* newsletter. His committee service has been marked by a record of thoughtful evaluation and improvements. He is a most worthy recipient of the 2021 Silver Medal.

This is the first award of the Silver Medal since 2016. More information on this and other awards of the association is available on the AAG website at https://www.appliedgeochemists.org/association/awards.

Formal presentation of the medal to Dr. Paul Morris will take place at the 29th International Applied Geochemistry Symposium in Chile in October 2022.

Stephen Cook
AAG Past President
Chair, Awards & Medals Committee

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DMG PARTICIPATION IN IMA

With great pleasure Priv.-Doz. Dr. **Melanie Kaliwoda** has accepted the position as German representative of the International Mineralogical Association (IMA) in December 2021. She follows Prof. Dr. Gerhard Brey, who held this position for more than seven years and performed his work in the IMA always conscientiously and with enthusiasm. In addition to her role as the new IMA speaker of the German group, Melanie has also been the German speaker of the IMA Commission on Museums (IMA CM) since 2017 and in this function has participated, among other things, in the 2018 IMA meeting in Melbourne (Australia) and in 2021 the 9th International Conference Mineralogy and Museums (MM9) meeting in Sophia (Bulgaria). The IMA CM is currently in the process of revising its homepage and also meeting more often in online meetings to better connect international and national projects of researchers and museum curators. Scientifically, Melanie works on ophiolites, mantle rocks, and meteorites. She supervises her own Raman spectroscopy group, which supported her in establishing a new Raman database. In addition, she is the vice director of the Mineralogische Staatssammlung München (Mineralogical State Collection Munich, Germany) and the associated Museum Mineralogia Munich (Germany).

Dr. **Malte Junge** followed Dr. Hans-Jürgen Bernhardt as the German representative in the IMA Commission of Ore Minerals (IMA COM). Since January 2022, he has been temporarily serving as chairman of the IMA COM. In 2021, he had established new monthly online meetings for scientific exchange and promotion of ore mineralogy as a first initiative. Malte primarily studies ore minerals and ore deposits but also ophiolites. Since June 2020, Malte has been employed as a scientist and curator at the Mineralogische Staatssammlung München. He also curates mineralogical exhibitions within the Museum Mineralogia Munich.

DMG WORKING GROUP ON MINERALOGICAL MUSEUMS AND COLLECTIONS

Annual Meeting 2021 – Report

The 17th meeting of the DMG Working Group on Mineralogical Museums and Collections took place on 26–27 July 2021 in the Zwickau Art Collections in the Max Pechstein Museum (Germany). In addition to talks by the members of the working group on scientific issues and on specific developments of the individual museums and collections, there was also plenty of time for mutual exchange. The meetings of the working group enable insights into the current exhibitions of the mineralogical museums and the development of the collections. The working group thus serves the purpose of scientific exchange, but also allows important discussions to be held (e.g., regarding current conservational changes and guidelines). Sven Neuhaus, the curator of the Mineralogical Department of the Max Pechstein Museum, gave a tour through the Mineralogical and Geological Collections in Zwickau and guided an excursion to the Cainsdorf Bridge. The excursion provided an opportunity for material from the carbon outcrop in Zwickau to be directly sampled for collections. After seven years, Dr. Birgit Kreher-Hartmann (Mineralogical Collection of the Friedrich Schiller University, Germany) has handed over the office of spokeswoman for the working group to Dr. Dorothée Kleinschrot (Mineralogical Collection of the University of Würzburg, Germany). Christin Kehrer (Mineralogical Collection in Freiberg, Germany) is the new deputy spokeswoman for the working group. We would like to thank Birgit for her many years of professional work as spokeswoman. We look forward to working together with Dorothée and Christin. Special thanks go to Sven Neuhaus for the hospitality and interesting insights into the mineralogical and geological collections in Zwickau, as well as the information on regional geology. The working group will next meet at the 100th annual DMG meeting in Cologne.

Treasuries of the Earth collection on display at the Max Pechstein Museum Zwickau (Germany).

Malte Junge
(Mineralogische Staatssammlung München, Germany)

GeoMinKöln 2022 –
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Onsite participation planned at the 100th Annual Conference of the DMG

WELCOME

Register now for the GeoMinKöln 2022 – the Annual Conference of the Deutsche Mineralogische Gesellschaft (DMG – The German Mineralogical Society) and the Deutsche Geologische Gesellschaft – Geologische Vereinigung (DGGV – The German Geological Society) to be held 11–15 September 2022 at the University of Cologne, Germany.

The DMG Annual Meeting will celebrate its 100th anniversary in 2022 and will return to Cologne, the city where the first DMG Annual Meeting was held in 1908.

We are very much looking forward to celebrating this special anniversary together with you in September 2022!

Cordially,

Sandro Jahn, Carsten Münker, Patrick Grunert, Reiner Kleinschrodt
(Cologne University)

Friedhelm von Blanckenburg (DMG) & *Martin Meschede* (DGGV)
Organizing committee

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CHANGES IN THE EAG COUNCIL

The European Association of Geochemistry (EAG) members elected three new councillors in the autumn 2021 elections. The new councillors will each serve for three years.

Lena Alakangas is a professor of applied geochemistry at the Department of Social, Environmental and Natural Resource Engineering at Luleå University of Technology (Sweden). She is an environmental geochemist with research that focuses on the understanding of geochemical processes in natural environments and in environments that have been affected by human activities such as mining. Her research also includes evaluation and development of preventive methods to reduce environmental impact. She is currently the head of the research subject Applied Geochemistry, which includes research in analytical chemistry, isotope geochemistry, and environmental forensics to trace the source of pollutants and geochemical processes. She works closely with the extractive industry and infrastructure companies.

Ernest Chi Fru is a geomicrobiologist/biogeochemist interested in the biogeochemical evolution of the geobiosphere through Earth history. He was born in anglophone Cameroon and later moved to Sweden where he earned a PhD in geomicrobiology at Gothenburg University in 2006. Subsequent postdoctoral stints took Ernest to the University of East Anglia (UK), Newcastle University (UK), and the University of Windsor (Canada). In 2011, Ernest took up an Intra-European Marie Curie Fellowship position at the Swedish Museum of Natural History (Stockholm). He later relocated to Stockholm University with an European Research Council starting grant in 2013. Since 2016, Ernest has been a senior lecturer in geomicrobiology/biogeochemistry in the School of Earth and Environmental Sciences at Cardiff University (UK).

Johanna Marin-Carbonne is an assistant professor in stable isotope geochemistry at the University of Lausanne (Switzerland). Her research interests rely on better constraining the environmental conditions of the early Earth—especially the redox conditions—as well as the link between the environmental conditions and the evolution of microbial life. Her research uses the high spatial resolution methods of stable isotope geochemistry associated with mineralogical and petrographic tools to better understand what kind of metabolic biosignatures can be preserved in the geological rock record.

The EAG Council has also elected former EAG councillor **Kate Kiseeva** to serve as Secretary for a term of three years.

Kate Kiseeva is a lecturer in geochemistry at the University College Cork (Ireland). Her research interests focus on two topics: the behaviour of chalcophile elements in mantle processes and during the Earth's accretion and differentiation, and high-pressure mantle geochemistry, metasomatism in the cratonic mantle, and upper- and lower-mantle inclusions in diamonds.

We would also like to take this opportunity to thank departing councillor **Alberto Vitale Brovarone** and secretary **Mihály Pósfai** and for their important contributions to the growth and success of the EAG during their respective terms.

2022 EAG COUNCIL

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Olivier Namur (University of Leuven, Belgium)
Carmen Sanchez-Valle (University of Münster, Germany)
Jill Sutton (University of Brest, France)

EAG CO-SPONSORED EVENTS IN 2022

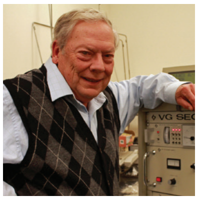
We are pleased to announce that two events will be co-sponsored as part of the 2022 **EAG Short Course and Conference Sponsorship Program.** See https://www.eag.eu.com/outreach/event-sponsorship/ for more information.

- **12th International Symposium Geochemistry of the Earth's Surface**
  Zurich, Switzerland; 24–29 July.
  http://ges12.com/
- **Forming and Exploring Habitable Worlds**
  Edinburgh, UK, and online; 7–13 November.
  https://www.habitableworlds.co.uk/

2022 EAG AWARDS

We are pleased to announce the three recipients of the 2022 European Association of Geochemistry awards. The medallists will present their award lectures at the Goldschmidt2022 conference in July.

H.C. Urey Award to William White



The recipient of the 2022 H. C. Urey Award is William 'Bill' White (Cornell University, New York, USA). White is a pioneer who shaped our understanding of chemical geodynamics of the deep Earth. He has made several fundamental contributions in many areas of geochemistry, but especially to our understanding of the geochemical architecture of the mantle, the nature of crustal recycling into the mantle, and the evolution of the mantle-crust system. White is also well known for authoring the two most widely used textbooks on geochemistry and isotope geochemistry. Through the generous sharing of his ideas, his influence goes far beyond his publications and permeates all of geochemistry and Earth science.

Heinz Lowenstam Science Innovation Award to Lenny Winkel

The recipient of the 2022 Science Innovation Award, named in honour of Heinz Lowenstam for his work in biogeochemistry, is Lenny Winkel (ETH Zürich, Switzerland). Winkel has made major contributions to the understanding of selenium occurrence in soils and arsenic occurrence in groundwater. She integrates global-scale mapping and data analysis based on chemical modelling and machine learning with geochemical experimentation based on molecular-scale interrogation of biogeochemical processes.

F.G. Houtermans Award to Raffaella Demichelis

The recipient of the 2022 F. G. Houtermans Award is Raffaella Demichelis (Curtin University, Australia), who is recognized for her important contributions to fundamental geochemistry by applying both ab initio quantum mechanical techniques and force-field based molecular dynamics to understanding the nucleation and surface geochemistry of biominerals, such as calcium carbonate and calcium phosphate. Demichelis has emerged as a world leader in the application of computational methods to such challenging problems.

SIX QUESTIONS TO ANDY RIDGWELL

Dr. Andy Ridgwell (University of California, Riverside) writes computer models – numerical representations of the primary interactions of climate with atmospheric CO_2, including the cycling of carbon, oxygen, and nutrients between land, ocean, and marine sediments. He applies these models to diverse questions, ranging from geological episodes of extreme glaciation and warming, and global-scale ocean anoxia,through understanding global biogeochemical cycling in the modern Earth system, to quantifying future marine impacts of fossil fuel CO_2 emissions and the effectiveness (or otherwise) of geoengineering. His current interests revolve around simulating the co-evolution of marine plankton and their environment, and their ecological sensitivities to past climate perturbations and global environmental catastrophe. He never sets foot in the lab.

1. What or who inspired you to become a geochemist?

Assuming that you can even call me a card-carrying 'geochemist' ;)

My inspirations go back to James Lovelock and Andrew Watson (the latter being my PhD thesis advisor) and the concept of 'planetary homeostasis', which was originally framed in terms of physical climate and surface albedo (in fact, 'Daisy World' was my very first computer program/model). However, the primary importance of greenhouse gases in climate regulation quickly leads you down the rabbit hole of aqueous carbonate chemistry, trace metal speciation and cycles, isotope systems and ... worse ... In summary: understanding what makes the system 'tick' in its messy totality inspired me.

2. How do you think the field has changed since you were a student?

In a sense it was easier to build a model of the Earth system when we understood only the very basics of marine biogeochemical cycling (co-limitation of marine productivity by dissolved iron was a 'new' thing at the time). It was also possible to have and read *all* of the relevant literature! Conversely, you had to try much harder to devise meaningful process representations in models, be creative in making use of sparse data, and somehow pull the numerical rabbit out of the hat of no data whatsoever.

3. Which career choices were the most important?

Given that my first degree steered off in an unfortunate solid state (mineral) physics direction; taking a Masters degree (Environmental Science, University of Nottingham, UK) was critical to reorient my qualifications. This proved to be a great tour through ... (trying to cast my mind back to the mid-1990s – a time even before COVID) ... air and water pollution and geochemistry, plant physiology and soil structure, and of particular use: numerical methods and programming (although I had previously spent time whilst unemployed, teaching myself to code).

4. What has been your greatest obstacle?

Non-parallelized computer code? I guess you mean ... e.g. finding myself stuck with a poor grade in a less-than irrelevant first degree (see above).

5. What inspires or motivates you?

Cats and elegant computer code?

I guess you mean ... understanding how the Earth system 'works'. I attempt this through constructing with computer models and develop learning and insights – treating them as games and 'playing' – exploring scenarios, testing sensitivity to parameters or perturbations, asking 'what if' questions of the model. Even doing real work (specific scenarios associated with specific questions) sometimes. These days I find myself particularly driven by questions surrounding biological evolution and extinctions and what the dynamical relationship is between geochemical and ecological changes on Earth through geological time.

I am also inspired by people who have worked hard to create numerical codes and tools for the community and have been so open and generous with their time in providing and supporting these tools (David Archer, and his sediment diagenesis models was an important influence early on; and e.g. the work of Reiner Schlitzer – Ocean Data View has become a foundational tool in marine geochemistry, although for my sins, I prefer to hack things myself in MATLAB).

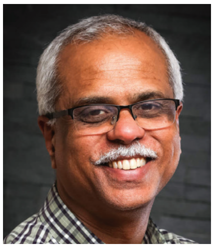
6. What qualities do you look for in a potential PhD student?

Motivation, independence, numerical and programming skills, and a deep appreciation of how superior cats are to dogs. I see my role as facilitating and encouraging scientific exploration rather than prescribing specific directions and steps.

Geochemical Society

www.geochemsoc.org

FROM THE PRESIDENT



Sumit Chakraborty

I am honored to begin my term as President of the Geochemical Society. As Vice President, the period of which pretty much coincided with that of the pandemic, I was witness to the stewardship provided in very difficult times by Vickie Bennett as President and Roberta Rudnick as past President. I learned of the untiring work of Kevin Johnson and Mattie Burris that keeps the wheels of the society turning. They deserve a collective vote of thanks from all of us. As Roberta leaves the GS executive after six years, Vickie continues as past President and Liz Sikes joins as Vice President – I look forward to working with them, the GS Board and office, and all of you.

It seems it was just the other day that I was at my first ever conference, seeing some of the people I had known only through print, getting to realize that these were real persons with highs and lows that shaped the topography of the social landscape of our community. And there I was in early 2020, all of a sudden in the position of helping to not only organize one of these, but pivoting quickly to shape what would become one of the first online conferences in our field – Goldschmidt 2020. A measure of the slope of that learning curve is perhaps this: the point of departure was learning new words and concepts such as “Zoom”. The conference did succeed, but the mixed feedback raised many questions that have become better defined as we have had to deal with many more online events in the last two years of the pandemic. Now, as I begin my term as President, one of the main thoughts that occupies all our minds is the question: What are conferences of the future going to look like? This is certainly a topic that will occupy not just geochemists, but all academics, for the next few years to come.

My personal opinion is that hybrid conferences have come to stay. The fact that one can participate in a conference (or any other event) online when time and/or funds are tough to come by is a benefit for many that we are not going to do away with. Even if time and money were no constraints, carbon footprint is, and all of us need to act responsibly. At the same time, the limitations of online modes have also become apparent – the chance encounters that germinate new ideas, or just getting to know a person beyond a talk or a poster to understand their point of view better, are aspects that need to be sustained through in-person interactions. The cultural canvas does not transmit as well across computer screens. Going forward, each person would have to find the right balance of these for themselves. In doing so, I hope geochemists would act in awareness of their roles as global science citizens and ambassadors – in these times of political polarization that role is more significant than ever, discourses across geographic and cultural boundaries have never been as important in our lifetimes.

As a geochemist-petrologist, I find myself currently trying to locate my comfort zone in the ternary diagram with the apices “CO_2 footprint concerns” – “the benefits of face-to-face interactions across different scientific cultures, disciplines and upbringings” – “the need and opportunity to see different geological settings”. It is a tough balancing act.

What occupies all of our minds right now of course is Goldschmidt 2022 in Honolulu. In that ternary diagram, CO_2 footprint stands out as a major component for a conference on an island. Since dabbling in numerical modeling is one of the things I do, I had to run some crude models – just looking up the carbon costs of direct flights along great circles on the globe for the typical Goldschmidt attendee demography. The outcome was interesting. Carbon costs for Honolulu are on the higher end, but are not much different from costs on any other West coast US location (recall that we have many attendees from east Asia)*. If that were to be the only consideration, then one could optimize it for the attendee address profile and settle on a location, and stick with that every year. That is the pattern for many conferences, but it would mean a shift for Goldschmidts – this is something we, as a community, would have to consider in the coming years. Do we want people from certain parts of the world to always be traveling long distances if they want to have the benefit of in-person interactions? But then the other factors weigh in as well – Hawai‘i offers an incredible array of opportunities for seeing features from volcanoes through coral reefs, and a trip where one combines that experience and education with a conference could be an optimized effort (a note: many field trips are on offer at the Honolulu conference). Coming out of a couple of years where we dissected the quality of indoor air circulation in different settings, I personally feel somewhat reassured that the conference is at the Hawai‘i Convention Center with its many outdoor facilities where one can sit, have a coffee or a beer, and chat. While I would be delighted to see many of you there – after many months of confinement it would be nice to meet people off screen - if you are unable / unwilling to travel, efforts are on to make the online experience as complete as possible. One way or the other, I hope you will participate and carry on the discussion about the future form of our conferences. I look forward to hearing from you at president@geochemsoc.org.

Sumit Chakraborty
President, Geochemical Society 2022-23

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* A full-blown calculation of carbon costs takes into account many more factors – from nature of air conditioning at the conference centers to catering, actual travel routes and means of travel and so on.

GS OFFERS FREE GOLDSCHMIDT CONFERENCE REGISTRATION FOR SCIENTISTS IN LOW-INCOME COUNTRIES

GOLDSCHMIDT® Hawai‘i 2022

Virtual and hybrid conferences present an opportunity to expand access to scientific meetings. This year, the Geochemical Society is pleased to offer free remote registration to the Goldschmidt Conference for scientists in countries with low and lower-middle-income economies. Without travel and registration expenses as a potential barrier, we hope that this will allow more delegates in these countries to participate. Remote registration provides full access to oral sessions and posters via the conference website. This offer is open to both professionals and students in qualifying countries. For more information, visit https://2022.goldschmidt.info.

NEW MEMBERS JOIN GS BOARD OF DIRECTORS

Five new members joined the Geochemical Society's (GS) Board of Directors in January 2022. They represent the diverse fields of study and geographic distribution of the society's membership. Meet the entire board of directors at www.geochemsoc.org/board

Elisabeth (Liz) Sikes was elected to a two-year term as vice president. She is a professor of oceanography at Rutgers University (New Jersey, USA). She is a paleoceanographer and paleoclimatologist whose research seeks to understand the ocean's influence on the carbon cycle and climate. Her research interests range from investigating the Southern Ocean's multiple roles in controlling glacial climate cycles to modern carbon cycling in estuaries. She previously served the GS as a board member, chair of the Organic Geochemistry Division, and as the founding chair of the Ethics Committee. She serves as co-chair of the Southern Ocean Regional Panel of CLIVAR (Climate and Ocean Variability, Predictability, and Change) and CliC (Climate and Cryosphere), which is a core program of the World Climate Research Programme. She is a member of the Southern Ocean Task Force for the United Nations Decade of Ocean Science for Sustainable Development. Following her term as vice president. Dr. Sikes will serve as president and then as past president.

Christopher Junium joined the board as the new chair of the Organic Geochemistry Division. He is an associate professor of geobiology, astrobiology, paleoclimate, paleoceanography at Syracuse University (New York, USA). A sedimentary and organic geochemist, he focuses on the redox evolution of the Earth, specializing in biogeochemical cycling. Dr. Junium uses a range of geochemical tools, but focuses on the stable isotopes of nitrogen, carbon, and sulfur, with a particular interest in compound-specific, stable isotope techniques. His research interests span the spectrum of geologic time from the Archean to modern systems. Currently he is working primarily on the Cretaceous and Neoproterozoic with an eye toward understanding future global change.

Alexis Templeton was elected to a three-year term as a director from Region 1 (Canada and USA). She is a geochemist and geomicrobiologist at the University of Colorado at Boulder (USA). She utilizes spectroscopic, isotopic, and molecular tools to characterize the chemical and biological states of systems undergoing active water−rock interactions. Her research focuses on defining the role of microorganisms in transforming the aqueous and mineral chemistry of rock-hosted ecosystems. She has previously been a member of the Geochemical Society Patterson Award and Endowed Biogeochemistry Lecture committees.

Marly Babinski was elected to a three-year term as a director from Region 3 (Africa, Asia, Australia, and Central/South America). She is an associate professor at the Department of Mineralogy and Geotectonics, Institute of Geosciences, University of São Paulo (Brazil). She uses traditional and non-traditional isotopes to determine the age of the rocks and unravel seawater changes along the Earth's evolution to track major changes in the atmosphere, hydrosphere, and lithosphere, and impacts on life evolution. More recently, she has explored the atmosphere pollution in megacities using isotope geochemistry, mainly applying Pb, Zn, and Cu isotopes. She is on the scientific committee of the Brazilian Geochemistry Society and member of the Brazilian Geology Society.

Allison Greaney was elected to a two-year term as an early career board member. She is a radiogeochemist at Oak Ridge National Laboratory (Tennessee, USA). She is involved in a variety of projects related to the nuclear fuel cycle and non-destructive assay of nuclear materials for safeguards purposes. She received her PhD in geochemistry in 2018 from the University of California at Santa Barbara (USA). Her doctoral research revolved around molybdenum and other questionably chalcophile elements and their use as geochemical proxies for understanding how the composition of the continental crust and atmosphere have evolved over time. Dr. Greaney is the first person to hold the newly created early career board position.

VOLUNTEER SERVICE OPPORTUNITIES

The society's programs are driven by the efforts of hundreds of volunteers. Serving on a board, committee, or working group is a way to give back to the community and meet new colleagues. There are opportunities for scientists at every career stage, including students. Go to www.geochemsoc.org/get-involved to learn more.

Association Internationale pour l’Étude des Argiles

www.aipea.org

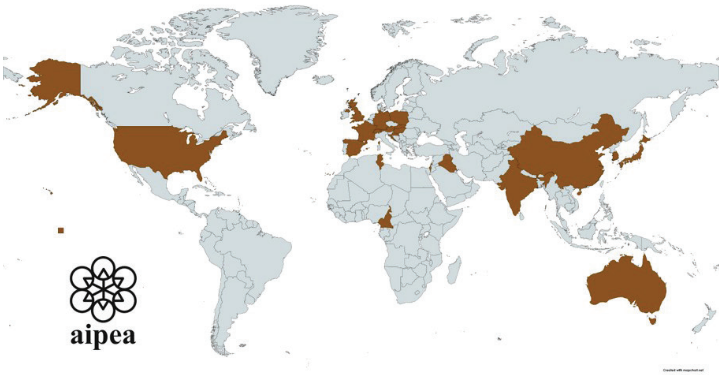
Reiner Dohrmann, President of AIPEA

The Association Internationale pour l’Étude des Argiles (AIPEA) has established an Early Career Clay Scientists (ECCS) network for scientists within 5 years of completion of their PhD. The aim of the ECCS is to create meaningful networking opportunities for early career clay scientists to foster international collaboration, to exchange cutting-edge research achievements, and to contribute to intergenerational knowledge transfer in the field of clay sciences.

Liva Dzene, Chair of the AIPEA Early Career Clay Scientists Committee

One of the first activities of the ECCS Committee was to establish Early Career Research Grant and Travel Grant guidelines. The Early Career Travel Grant provides funding for ECCS to attend the 17th International Clay Conference (ICC), which will be held July 2022 in Istanbul (Turkey). The Early Career Research Grant provides financial support in the form of seed money to assist early career researchers (post-doc, assistant professor, or lecturer) of clay science and technology to explore a proof of concept or to fund areas of an ongoing project that were not included in the original project scope. It should allow recipients to support future applications to national or regional research funding bodies. The AIPEA will award two grants in a period of 4 years (i.e., from one ICC to the next ICC). Application guidelines and application forms of both new grants are available at the aipea.org website.

On 3 December 2021, the first National Clay Group ECCS representative meeting was held to launch the network. The ongoing work focuses on preparing activities specifically tailored for ECCS during the ICC in Istanbul. In the future, the ECCS network plans to focus on developing a strategy for the effective communication of new research achievements using social networks.



We all invite you to come to the 17th International Clay Conference in Istanbul in July 2022, with >30 thematic sessions. Along with field trips, this ICC also offers three workshops: an AIPEA School of Young Scientists workshop focused on kaolin, a CMS workshop on bentonite characterization, and an AIPEA workshop on clay mineral catalysis of organic reactions.

Prepared by **Liva Dzene** and **Reiner Dohrmann**

Japan Association of Mineralogical Sciences

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

INVITATION TO THE JAPAN GEOSCIENCE UNION MEETING 2022

We are pleased to inform you that the 2022 Japan Geoscience Union (JpGU) meeting was held 22 May – 3 June 2022 at Makuhari Messe in Chiba (Japan). A hybrid format (in person and online) was used for oral presentations held at the Makuhari Messe (Chiba, Japan) 22–27 May 2022. This was followed by an online poster session 29 May–3 June 2022. The JpGU has recently grown to embrace over 51 members of academic societies and has over 10,000 individual members. By taking advantage of the new format, the 2022 meeting provided a forum for free and vigorous discussion and interaction among participants from the fields of Earth and planetary science and the public. More information is available at http://www.jpgu.org/meeting_e2022/.

JOURNAL OF MINERALOGICAL AND PETROLOGICAL SCIENCES

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Original Articles

Structure changes of nanocrystalline mackinawite under hydrothermal conditions: formation of greigite and its structural properties – Yoshinari SANO and Atsushi KYONO

Raman spectroscopic study of pressure-induced phase transitions in tridymite modifications – Masami KANZAKI

Modulated structure of hemimorphite associated with pressure-induced phase transition – Keitaro OKAMOTO, Takahiro KURIBAYASHI, and Toshiro NAGASE

Au(Ag)-Sn-Sb-Pb minerals in association with placer gold from Rumoi province of Hokkaido, Japan: a description of two new minerals (rumoiite and shosanbetsuite) – Daisuke NISHIO–HAMANE and Katsuyuki SAITO

Technical Note

Structure refinement of prehnite from Passaic County, New Jersey, USA – Kazumasa SUGIYAMA, Toru KAWAMATA, and Takahiro KURIBAYASHI

The annual meeting of the JAMS was held at Hiroshima University (online) on September 16–18, 2021. On the following day, a public lecture "HAYABUSA 2: Six Years of Exploration of Asteroid Ryuguu, and Ground Sample Analysis and New Journey" was held by our society for the general public. Three members involved in HAYABUSA2 gave lectures on the project's past achievements and future expectations, and two MCs gave mini-lectures. With more than 400 participants, these lectures were a great success.

1) Prof. Yuichi Tsuda (Institute of Space and Astronautical Science, JAXA, Hayabusa2 Project Manager)

Technologies and Achievements of Hayabusa2, which Achieved a Round-Trip Interplanetary Flight

2) Prof. Seiichiro Watanabe (Nagoya University, Hayabusa2 Project Scientist)

The Mysterious Island (Ryuguu Castle), which Hayabusa2 Watches

3) Prof. Shogo Tachibana, (University of Tokyo/Specially Appointed Professor, Institute of Space and Astronautical Science, JAXA, Head of Hayabusa2 Initial Analysis Team)

Stories from Once Upon a Time Leading from the Treasure Casket of Ryugyu

4) Prof. Hikaru Yabuta (Hiroshima University, Leader of Solid Organic Matter Analysis Team, Hayabusa2 Initial Analysis Team)

5) Prof. Masaaki Miyahara (Hiroshima University, Member of Sand Material Analysis Team, Hayabusa2 Initial Analysis Team)

Mineralogical Society of Poland

www.ptmin.pl

MOROZEWICZ MEDALS AWARDED

Morozewicz medal, (**A**) front and (**B**) back.

The Morozewicz Medal is awarded annually by the Polish Mineralogical Society to recognize fundamental contributions to mineralogical sciences in Poland. The medal is named after Józef Morozewicz (1865–1941). He was an outstanding Polish petrographer and mineralogist, organizer of scientific institutions, and academic teacher.

The 2020 medal recipient is Prof. Andrzej Manecki from AGH University of Science and Technology (Kraków, Poland), and the 2021 medal recipient is Prof. Jan Środoń from the Polish Academy of Sciences.

Professor **Andrzej Manecki** has widely contributed to many fields of geological sciences with his scientific interests focused on both terrestrial and cosmic matters. The scientific research of Prof. Manecki has resulted in a series of scientific papers on feldspars, meteorites, and atmospheric dust. He introduced the concept of aeromineralogy and created the first research school in Poland that was focused on the mineralogical studies of atmospheric dusts. He was the head of three polar expeditions to Spitsbergen (1984, 1985, and 1988), which led to the 1993 publication of the map, "Geological Map of the SW Part of Wedel Jarlsberg Land". His work inspired many of his students to become polar researchers. Prof. Manecki authored (or coauthored) many excellent and widely read academic textbooks, encyclopedic publications, and popular science books in the fields of mineralogy and meteorites. For 30 years, he represented Polish mineralogy by serving on the International Mineralogical Association's Commission on New Minerals, Nomenclature and Classification.

Jan Środoń in the steppes of Donbas (Ukraine) in 2008. Photo: M. Paszkowski.

Professor **Jan Środoń** has made many fundamental contributions to the mineralogical sciences by developing methods for studying clay minerals. These contributions include developing a widely used X-ray method for measuring the illitization degree of smectites and using the illitization degree as a measure of maximum palaeotherms. Prof. Środoń also developed a method of clay fraction separation for geochronological measurements that significantly increased the applicability of the K–Ar method for thermal history studies. In collaboration with Victor A. Drits and Dennis D. Eberl, he developed two methods to measure the thickness of illite crystallites. These two methods are much more precise than the Kübler method and are now widely used in research on low-temperature metamorphism of sedimentary rocks. At the beginning of this century, the Laureate, while working in the Chevron laboratories in Houston (Texas, USA), he created an X-ray method for quantifying the mineral composition of sedimentary rocks, which is currently used by Chevron to study drill cores. More recently, Prof. Środoń, together with a large international team, has been conducting comprehensive studies of the Proterozoic sedimentary cover of the East European Craton. This research is funded by a MAESTRO grant (National Science Center, Poland).

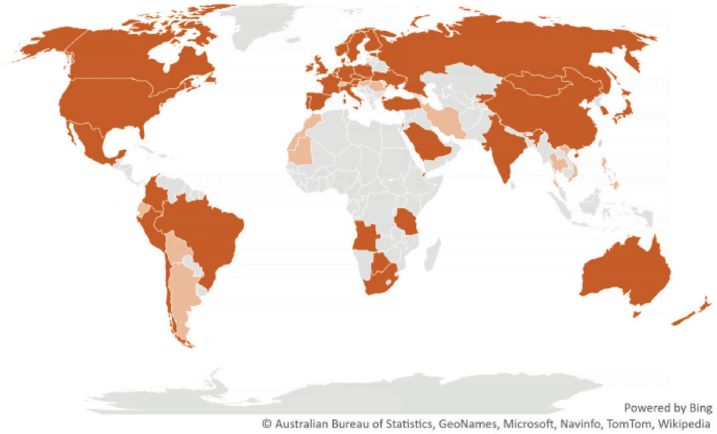
International Association of Geoanalysts

http://geoanalyst.org

GEO*PT* WORKSHOP

In September 2021, we hosted a workshop to celebrate 25+ years of Geo*PT*, our flagship proficiency testing scheme. It was a pleasure to welcome over 60 participants from locations ranging from Canada to Mongolia, despite some significant differences in local time. In the past, we have held Geo*PT* workshops in conjunction with our Geoanalysis conferences but video conferencing made it possible for a wider range of participants to join in and to put faces to the people who currently organise Geo*PT*.

The success of the Geo*PT* programme has surpassed our wildest dreams when we first set up the scheme over 25 years ago. We now have well over 100 labs participating from many different types of organisations located all over the world! So, it was very appropriate for Phil Potts, one of the masterminds behind the launch of the scheme, to start proceedings by describing a little of its early history. The Geo*PT* programme started in the early days of the World Wide Web and an important step forward was the introduction of a web-based management scheme. Peter Webb, who manages the website, provided background to these developments. Originally, all the sample preparation and distribution were organised through The Open University (Milton Keynes, UK). The British Geological Survey now provides this vital support role and Charles Gowing gave us a glimpse into what this involves.



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Geo*PT* participants 2021: 123 participants from 44 countries (58 countries since 1996)

There followed presentations of some strategic issues that affect the performance of the Geo*PT* scheme, including an introduction by Thomas Meisel to the capabilities of the Shiny App for the interpretation of Geo*PT* data distributions. Participants were asked to complete a poll to indicate what test materials they would like to see in the scheme and there was an opportunity to pose questions to members of the Geo*PT* Steering Group. We were very pleased with the feedback from this workshop, and we plan to run similar workshops for our other proficiency testing schemes.

GOLDSCHMIDT QUALITY ASSURANCE WORKSHOP

The International Association of Geoanalysts (IAG) organised an online workshop on quality assurance as part of the Goldschmidt 2021 virtual conference in June. To maximise attendance, the workshop was presented twice, with the morning session targeting Australasian participants and the afternoon session (CEST) for some European and many scientists from the Americas. Under its title of *Reliability of Geochemical Data: How Do We Know?* there was a lot to cover in just under four hours! The first part of the workshop provided an overview of the current understanding of metrological traceability and the proper use of reference materials. The role of measurement uncertainty and how it is affected by such issues as sample preparation, sample heterogeneity, and data acquisition was highlighted. A breakout session was held to identify problems surrounding various definitions. After a short break, the main emphasis turned to proficiency testing (PT) with examples from the IAG's three PT schemes, Geo*PT*, G-Probe, and G-Chron. Feedback from participants was very positive and we aim to run an additional workshop during Goldschmidt 2022.

IAG HONORARY FELLOWSHIP

On 29 September 2021, we held an official ceremony at which we presented Dr Klaus Peter Jochum with an Honorary IAG Fellowship. Professional colleagues joined him at the Max Planck Institute (Mainz, Germany) and by video link to celebrate his scientific achievements and support for the IAG over many years. In the words of the IAG President, Prof Jacinta Enzweiler, "Dr Jochum's many years of research in the field of geoanalytical method development and reference materials, as well as his commitment to the promotion of junior scientists, aligns perfectly with the tasks and goals of the IAG".

Honorary IAG Fellowship awardee Klaus Peter Jochum (RIGHT) pictured with IAG Vice President Regina Mertz (LEFT).

You can read more about this splendid occasion in a Max Planck Institute press release at https://www.mpic.de/5042527/honorary-fellowship-jochum.

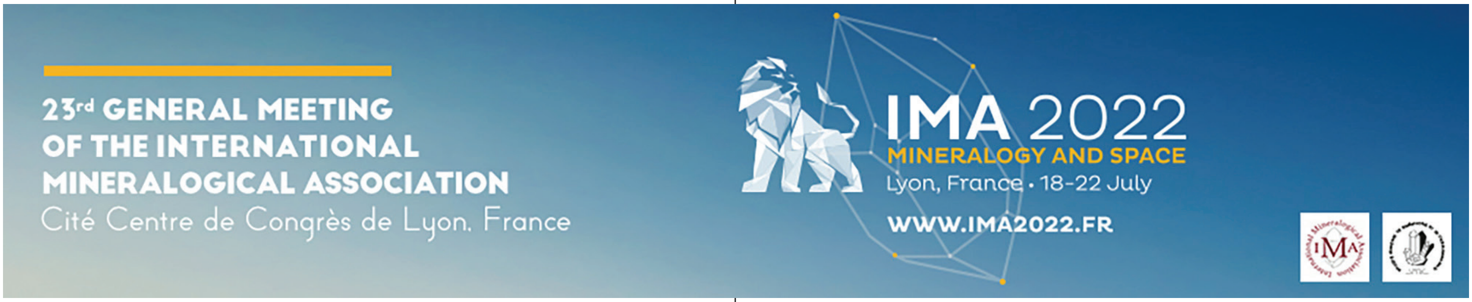
If everything goes according to plan, Dr Jochum will present some of his work in a plenary lecture during Geoanalysis 2022, to be held 6–12 August 2022 in Freiberg, Germany.

GEOANALYSIS 2022

The 11th International Conference on the Analysis of Geological and Environmental Materials (Geoanalysis 2022) will be held 6–12 August 2022 in Freiberg, Germany. Registration and abstract submission begin 3 January 2022. Full details can be found at the website geoanalysis2022.de.

International Mineralogical Association

www.ima-mineralogy.org



Following the tradition of quadrennial general meetings of the International Mineralogical Association (IMA) organized by national societies, the French Society for Mineralogy and Crystallography will host the 23rd General Meeting of the IMA in Lyon, France during 18–22 July 2022.

2022 is the year to celebrate mineralogy. It marks the bicentennial of the death of René Just Haüy (born 1743), who is the father of modern mineralogy and crystallography. Two centuries ago, Haüy published his seminal works *Traité de minéralogy* and *Traité de cristallographie*. Fast-forward to 2022, the two most recent Mars exploration programs, *Perseverance* (Mars2020) and *Huoxing 1*, are flooding us with amazing data and remarkable results. With the return of a sample capsule from *Hayabusa2*, fragments of a primitive carbonaceous asteroid have now been analysed for the first time.

The 23rd Meeting of the IMA will celebrate these momentous occasions. We, the organizers, would like to paint IMA 2022 with the colours of space exploration. Alongside the more traditional mineralogists, we want to inspire the emerging next generation of scientists and take a step closer toward the final frontier. The meeting will bring together all the new facets of modern mineralogy. It will be a playground, where traditional research rooted in Haüy's careful experiments with rocks and crystals will meet planetary exploration of the 21st century, and it will be the place to celebrate two centuries of mineral sciences.

This General Meeting will offer stimulating plenary lectures by the world's leading scholars, society events, short courses, award ceremonies, presentations from funding agencies, national business meetings, and about 60 scientific sessions grouped under several overarching themes:

T1 – Extraterrestrial mineralogy

T2 – Planetary interiors

T3 – Mineral systematics, gems, collections

T4 – The dynamic world of minerals

T5 – Environmental mineralogy and biomineralogy

T6 – Applied, ore, and industrial mineralogy

T7 – Mineralogy and petrology

With such a diversified technical program, everyone will be sure to find a session in their area of expertise, or venture outside their familiar territory to learn about new discoveries, techniques, and ideas of modern mineralogy. Particular emphasis will be placed on societal issues by facilitating discussions, cross-field symposia, and sessions to address the current challenges in ore and raw materials supply, energy and environmental sustainability, health, and cultural heritage.

Lyon is well known for its remarkable historical and architectural landmarks that earned it the status of UNESCO World Heritage Site. The city was recognized as an important area for the production and weaving of silk from the late 1400s and through the Industrial Revolution. Unsurprisingly, the first programmable loom was invented here by the Lyonnaise weaver Jean Marie Charles – two centuries ago, as well! It is also the city, where Auguste and Louis Lumière invented the cinematograph at the end of the 1880s. Today, Lyon is a major hub for the chemical, pharmaceutical, and biotech industries. And let's not forget its reputation as the gastronomic capital of France (some even say the world)! In the heart of Europe, this city can be easily reached from anywhere in the world, and serves as a gateway to Languedoc, Dauphiné, Burgundy, and the Western Alps with the iconic Mont Blanc. The venue is the Lyon Convention Centre, an impressive state-of-the-art facility featuring 25,000 m² of innovative interior architecture and situated between the Rhône River and Tête d'Or Park. The venue is ideally situated close to the historic center and public transportation routes.

To stay updated, please regularly visit the official conference website (https://ima2022.fr) and follow us on Facebook (https://www.facebook.com/IMA2022/) and Twitter (@CongressIma).

We look forward to seeing you in France this summer!

Mineralogy is one of the oldest branches of science, and it has played a key role in the deciphering of the structure of matter and in the development of science and technology. To commemorate the bicentennial of the death of René Just Haüy, the International Mineralogical Association declared 2022 the YEAR OF MINERALOGY.

MINERALOGY
2022

IYBSSD2022
International Year
of Basic Sciences
for Sustainable Development

Mineralogy 2022 is a global initiative intended to highlight the importance of mineral sciences in our everyday lives. Mineralogy 2022 will consist of coordinated activities on the regional, national, and international levels. These activities will underscore the significance of mineralogy as a basic science. As such, all Mineralogy 2022 activities will take place under the patronage of the International Year of Basic Science for Sustainable Development declared by UNESCO (https://www.iybssd2022.org/en/).

While the Year of Mineralogy 2022 will be launched during the 23rd General Meeting in Lyon, outreach, promotional, and other activities are already in full swing and will continue beyond July 2022.

Société Française de Minéralogie et de Cristallographie

www.sfmc-fr.org

SFMC ELECTION RESULTS FOR 2022–2023

SFMC members have elected a new council for 2022–2023 (see SMFC officers: https://sfmc-fr.org/?p=2413&lang=en for details):

BOARD: Michel Grégoire (president), Nathalie Bolfan-Casanova (vice president), Fabrice Gaillard (2nd vice president), Marc Blanchard (secretary), Pierre Lanari (vice secretary), Christian Chopin (treasurer), Benoît Dubacq (vice treasurer), Mary-Alix Kaczmarek (bulletin editor)

COUNCILORS: Emilie Bruand, Mathieu Chassé, Guillaume Delpech, Benjamin Malvoisin, Jean-Marc Montel (2022–2025); Laura Airaghi, Muriel Andreani, Hervé Cardon, Camille Cartier, Laura Creon, (2020–2023).

AUDITORS: Jannick Ingrin, Celine Rommevaux.

For their dedicated service, the SFMC thanks the outgoing vice presidents Jean-Marc Montel and Armand Masion, the assistant secretary Etienne Balan, the vice treasurer Pierre Lanari, the councilors Hélène Bureau, Sylvie Demouchy, Benoît Dubacq, Alexandre Mussi, Benjamin Rondeau, and auditor, Catherine Mevel.

2022 YEAR OF THE MINERALOGY

MINERALOGY
2022

2022 is the year to celebrate mineralogy

Mineralogy 2022 is a global initiative to highlight the importance of mineralogy in our everyday lives. Mineralogy 2022 will consist of coordinated activities of the regional, national, and international levels. These activities will emphasise the importance of mineralogy as basic fundamental science.

This Year of Mineralogy will take place under the patronage of the International Year of Basic Science for Sustainable Development, which has been approved by UNESCO.

The SFMC dedicated a website where all the events supported by the SFMC are listed (https://min2022.sfmc-fr.org/). Don't hesitate to promote your manifestation using this website!

23rd GENERAL MEETING OF THE INTERNATIONAL MINERALOGY ASSOCIATION

IMA 2022
MINERALOGY AND SPACE
Lyon, 18-22 July

The French Society of Mineralogy will host the IMA in Lyon, France, 18–22 July, 2022

In 2022, we honour the bicentennial of the death of the most famous French mineralogist René Just Haüy. The French Society for Mineralogy and Crystallography wishes to associate the International Mineralogical Association in this celebration by hosting the 23rd IMA General Meeting in France. The French Association of Micromineralogy (AFM), which is the major discoverer of new minerals in France, joins us in this effort to offer a memorable happening.

In 2022, Mars2020 (the rover Perseverance) will be on Mars for more than a year, it will just have had enough time for science return and post-processing. The ongoing missions will also have had time to reveal mineralogical secrets of small bodies (e.g. Hayabusa) or outer solar system bodies (i.e. New Horizon). This will be a ripe year for assessing the advances that mineralogy has made as science in planetary exploration.

The 23rd meeting of the IMA will mark these celebrations. In Lyon, we want to paint IMA 2022 with the colours of space exploration. Alongside the more traditional mineralogist we want to inspire the new generation and make a step closer toward the final frontier. The meeting will bring together all the new facets of modern mineralogy; it will be the ground play where mineralogy as we know it will meet exploratory planetology, all to celebrate two centuries of mineralogy.

As part of its efforts to make a general meeting that is as broad and inclusive as possible, IMA2022 themes are:

- Mineral systematics
- Applied, ore, and industrial mineralogy
- Mineralogy and petrology
- Extraterrestrial mineralogy
- Planetary interiors
- Environmental mineralogy, biomineralogy
- The dynamical world of minerals

To stay updated visit regularly the official conference website: www.ima2022.fr and follow us on Facebook and twitter. The venue is the Lyon Convention Centre, a state-of-the-art, impressive convention centre featuring 25,000 m² of innovative architecture and situated between the Rhône river and the Tête d'Or Park.

On behalf of the French Society for Mineralogy and Crystallography, the leading committee is formed of:

- Razvan Caracas – President of the IMA2022
- Herve Cardon – Executive director
- Cathy Quantin-Nataf – Vice-President

We are looking forward to seeing you in Lyon in July!

Mineralogical Society of the UK and Ireland

www.minersoc.org

OUTREACH AND MINERALOGY

James Byrne, PRO

One of the main goals of the Mineralogical Society (MinSoc) is to support the study, promotion, and application of mineralogy and to share that information with the wider public. As such, we often ask ourselves how best to engage with different communities. Fortunately, we are associated with several fantastic special-interest groups who find creative ways in which to educate about minerals. This has been especially evident over the past 18 months with a range of fascinating activities organised to appeal to a wide audience. In early 2021, the Applied Mineralogy and Mineral Deposits Studies groups arranged a workshop on "Science Communication" given by Rowena Fletcher-Wood. Over the course of five sessions, 120 attendees learned about the different ways to tailor their science to targeted audiences. Recently, the Geochemistry Group hosted a series of talks entitled "Out of Academia", which were aimed at helping participants consider alternative careers outside of the university sector. The series attracted speakers from a number of different industries. We look forward to seeing further events. Looking more at how to attract others to the world of mineralogy, the Environmental Mineralogy Group just closed their video competition in which anyone from school children to emeritus professors were invited to submit a 3-minute video showcasing a mineral of their choice. The Metamorphic Studies Group also just launched a video competition seeking stories about "why metamorphic geology rocks". Beyond MinSoc, we are also pleased to see other activities such as the annual Mineral Cup on twitter (@MineralCup). This annual event regularly attracts more than 2,000 people voting between a range of minerals in order to crown a mineral champion (Quetzalcoatlite won the 2021 title). All in all, as we approach 2022, which has been designated the Year of Mineralogy, it is refreshing to see the creativity of so many of our colleagues to get the message out about the importance of mineralogy!

SOCIETY MEDALLISTS FOR 2022

Neumann Medal 2022: Lidunka Vočadlo

Professor Lidunka Vočadlo has been a professor of mineral physics at University College London (UCL) (UK) since 2009. She has a significant and impactful publication history and plays a leading role in the UK Earth Sciences equity, diversity, and inclusivity community. In 1994, Lidunka was the first to use atomistic simulations as a way of obtaining accurate melting temperatures of mantle minerals at high pressures. This research paved the way for many other groups around the world to replicate and enhance her methods. For example, the melting temperature of MgO that she obtained showed that the experimental melting curve of Zerr and Boehler (1994, *Nature* 371: 506-508) was far too low. This finding has been verified repeatedly since. Remarkably, her predicted MgO melting temperature of 8,000 K at the core–mantle boundary is within the uncertainty of estimates from ab initio calculations that were made a decade later. This temperature is still considered to be accurate. At about the same time, Lidunka was using computational minerals physics methods to calculate, for the first time, the diffusion properties of mantle minerals. Not only did this provide the first high-pressure diffusion properties of MgO, but it also led the way for many such studies from groups around the world.

A few years later, Lidunka turned her hand to working on the Earth's core, something she has continued working on with enormous success. She has provided groundbreaking results on the viscosity, melting temperatures, phase relations, equations of state, seismic properties, light elements, and other fundamental properties of the core. Almost all of these findings have stood the test of time. Some of these are particularly difficult problems. For instance, the ongoing discussion as to what the stable crystal phase of iron is in the core—which is of essential importance when interpreting seismic data from the core—is something Lidunka has led for a number of years. This is a particularly tricky problem because the free-energy curves of bcc iron and hcp iron are very similar. As such, small concentrations of light elements may have an inordinately large effect on the free energies and so change the stable phase of iron. Through a number of papers, Lidunka has concluded that the hcp phase of iron is indeed the stable one throughout the core. Little by little, this has become the accepted view, but not without considerable careful and detailed work.

One of Lidunka's great strengths is to recognise the power of combining theoretical modelling with experimentation. Many of her papers present the results of this sort of collaboration. This is exemplified by her work on planetary ices—for which she developed a small but highly effective group at UCL—and has seen her to put in overnight sessions at various synchrotrons around the world to complement her theoretical calculations.

Finally, Lidunka is and has been engaged in outreach for many years; her curriculum vitae has a long list of outreach activities, including a leading role in the London-GeoBus, a highly successful outreach programme reaching ~10,000 school children a year.

Hey Medal 2022: Sophie Nixon

Sophie Nixon's career, to date, has been highly multidisciplinary. Her research sits at the interface between mineralogy, geochemistry, and the biosciences and links both fundamental and applied sciences. She started her career with an MSci (first class in geographical sciences) during which she focused on life in subglacial and supraglacial environments. This led her to a PhD in astrobiology at the University of Edinburgh (UK), after which she moved to the geomicrobiology group within the University of Manchester (UK). She began working with Rawwater Engineering Company Ltd to assess the potential for organic additives in hydraulic fracturing fluids in order to stimulate microbial souring of shale gas. She demonstrated that guar gum, a widely used fracturing fluid additive in shale gas extraction, stimulates biogenic sulfide production under relevant subsurface pressures by a sulfate-reducing enrichment culture. Continuing her research into the links between microbial carbon cycling and biogeochemical cycling in the subsurface, she worked on the EU Horizon2020 Microbiology in Nuclear Waste Disposal (MIND) consortium project. She demonstrated that PVC additives are a bioavailable source of organic carbon and electron donors to fuel microbial nitrate reduction at the high-pH conditions anticipated in a geodisposal facility. From there, Sophie went on to be awarded a NERC Industrial Innovation Research Fellowship for unearthing the role of microbiology in shale gas extraction using a bioreactor approach.

Throughout her research career, Sophie has strived to develop new collaborations whilst strengthening existing ones. This has resulted in an impressive collaboration network, spanning academia and industry, for an early career scientist. For example, the most recent international collaboration with Douglas Bartlett at Scripps Institution of Oceanography (USA) was financially supported by a competitive Deep Carbon Observatory (DCO) Cultivation Internship. Outside of academia, she developed a collaboration with Cuadrilla Resources, the only oil and gas exploration company to exploit the UK's onshore shale gas reserves.

Her potential to become a future leader in the field was recognised by the DCO through an invitation to their 3rd DCO Science Meeting in 2017. This meeting brought together leading international scientists and emerging leaders from across all aspects of deep carbon science in order to map out the future direction of the DCO and its underpinning science, including deep subsurface microbiology. She was subsequently invited to deliver a keynote talk at the 2019 DCO early careers meeting at the Geological Society of London (UK), and later that year delivered a keynote at the Molecular Microbial Ecology Group meeting at the Open University (UK).

Sophie has shown strong support for the MinSoc's Geomicrobiology Network where she has played a key role in building the social media presence for the group and has presented during its online seminar series.

Collins Medal 2022: Hilary Downes

Hilary Downes is an outstanding scientist who, during her long career, has made several remarkable contributions to both pure and applied mineral sciences. Her track record is exceptionally strong and wide-ranging. Her research mainly covers the petrology of igneous rocks on Earth and in space, but also addresses important topics such as the origin and evolution of the Earth's crust, the importance of xenoliths in understanding the evolution of the upper mantle, the formation and destruction of early planetesimals, the links between volcanism and plate tectonics, and the characteristics of important ore-bearing igneous rocks such as carbonatites. In terms of published work her outputs are exceptional: since 1985 she has accumulated 6,402 citations, an average of 35.97 citations per publication, and an h-index of 51 (Web of Science). She is, without question, one of the premier authorities on the petrology of the Earth's lower crust and upper mantle.

Hilary is a committed and excellent educationalist. At Birkbeck, she has taught a wide range of modules on igneous petrology, planetary science, volcanism, geochemistry, and field techniques.

She was president of the Mineralogical Society of Great Britain and Ireland from 2017 to 2019 and was also Head of the Department of Geology (afterwards Department of Earth and Planetary Sciences) at Birkbeck from 1997 to 2005, a total of nine years. She was a highly effective department head, overseeing growth in student numbers and in distance learning, bringing planetary science into the curriculum and hiring new staff in key areas. In all of her academic leadership roles, Hilary has been a superb mentor. She has helped countless young staff to develop their teaching and research portfolios by providing advice, course materials, and opportunities in and outside of the university. This has been particularly true for her colleagues in Eastern Europe, shown by the large numbers of joint research papers that she has participated in, and giving opportunities for them to travel to the UK to learn new techniques and develop new collaborations.

Hilary Downes is undoubtedly a polymath: a very knowledgeable, personable, helpful, and interesting geologist, geochemist, and mineralogist.

SOCIETY MEDALS 2023

Nominations are now sought for the 2022 medals (closing date: 15 April 2022). Go to https://www.minersoc.org/awards.html for information about how to make a nomination. Membership of the Society is not necessary to make or receive an award.

STUDENT AWARD WINNERS 2021

The following is our latest list of Student Award winners for 2021. This award is given to: the second-year student (or student in the penultimate year of their undergraduate degree course) with the highest ranking marks in Mineralogy and Petrology, or an equivalent exam.

Congratulations to them all and welcome! Each will now receive two years of membership of the Society along with a certificate and a book.

Oxford University	Clare	Ballantyne
University of Liverpool	Robert	Clarke
University of East Anglia	Phoebe	Cleary
University of Portsmouth	Andreia	Costa
University of Plymouth	Cadogan	Dethick
University of Leicester	Evie	Fawcett
University of Portsmouth (2)	James	Gardiner
University of Manchester	Joshua	Hollowood
Imperial College	Alexander	Jones
University College London	Bethany	Neilson
Newcastle University	Tom	Onslow
University of Cardiff	Maxwell	Porter
University of Brighton	Millie	Reed
University of Derby	Thi Mai Khanh	Tranova
National University of Ireland, Galway	Ciara	Wall
Trinity College Dublin	Rebecca	Payling
University of Birmingham	Amelia	Smith
Durham University	Simon	Cocks
University of Hull	Jessica	Ince
Keele University	Adam	Hope
University College Dublin	Conor	Farrell
University of Cambridge	Tom	Metherell
University of Edinburgh	Julius	Pesola
University of Exeter	William	Parker
University of Aberdeen	Benjamin	Medley
Bristol University	James	Simpson
University of Glasgow	Elena	Zanni
Birkbeck College	Mary	Kitchen
Open University	Rebecca	Spain
University College Cork	Hilary	Balding
University of Leeds	Isobel	Nash
Royal Holloway University of London	Isaac	Chapman-Drake

WHAT'S IN A NAME?

In 1876, the Mineralogical Society was founded and given the name "Mineralogical Society of Great Britain and Ireland". In 1921 (100 years ago at the time of writing), an agreement was signed between the British and Irish authorities, which ultimately led to separation of the two states. The term Great Britain includes England, Scotland, and Wales. So, during a major revision of our byelaws, of which more to come in the next issue of *Elements*, we decided to tackle the question of our name. From 2022 onwards, we will be known as the Mineralogical Society of the UK and Ireland. This includes Ireland and Northern Ireland as well as the countries listed above.

Mineralogical Society

Mineralogical Society of America

web

www.minsocam.org

PRESIDENT'S LETTER

Pamela Burnley

Free Stuff from MSA!

The Mineralogical Society of America has a wide variety of multi-media resources that are available to members and non-members alike. These are all freely available online, and can provide information and tools for scientists, mineral collectors, teachers, students, parents, and anyone with a keen interest in minerals and rocks. These resources include the following:

Communications

MSA-Talk: MSA hosts a listserv to which anyone can subscribe. The list is moderated by the MSA Business Office and is an excellent source of information about meetings, job postings, research opportunities, and general queries about mineralogy, petrology, and geochemistry topics. Postings are archived and subscribers are able to access these. Information on how to subscribe to MSA-Talk is here: http://www.minsocam.org/msa/MSA_Talk.html.

MSA YouTube Channel: The MSA YouTube Channel contains a number of videos that were a result of MSA events (Centennial Symposium, Awards Ceremonies, Minerals Day), as well as the most recent Short Course on Triple Oxygen Isotope Geochemistry. Topics covered by the videos are as wide-ranging as Gems and Gemology, Mineralogy of Mars, Archaeology and Mineralogy, Forensic Geology, Mineral Museum Curation, Wire Gold and Wire Silver, The Social Relevance of Apatite, and much more. The link to MSA's YouTube Channel is https://www.youtube.com/channel/UC43D1PLrmBkChtrsNi2y7YQ.

MSA Social Media Outlets: In addition to its YouTube Channel, MSA also has a presence on Facebook, Twitter, and Instagram. MSA thanks its Social Media Liaison, Dr. Andrea Koziol, for oversight of these outlets.

Publications and Support Materials

American Mineralogist: MSA publishes American Mineralogist, a peer-reviewed journal first published in 1916. The preprints of Papers in Press are available on the MSA website at http://www.minsocam.org/msa/Ammin/AM_Preprints.html. In addition, pdf versions of articles from 1916 through 1999 are also on the website for free at http://www.minsocam.org/msa/ammin/toc/.

Handbook of Mineralogy: The Handbook of Mineralogy, a five-volume set, is now available on the MSA website at http://www.handbookofmineralogy.org/. The Handbook devotes one page to each mineral, and now contains 5082 pdf pages.

Mineralogy and Optical Mineralogy: This 24-chapter textbook (Dyar, Gunter and Tasa, 2020) is available for purchase through MSA, but is accompanied by a large collection of free videos, images, and animations. These are on the MSA website at http://www.minsocam.org/msa/DGT_Figures/

Open Access Publications: MSA has a set of Open Access publications on its website that include two Reviews in Mineralogy and Geochemistry volumes (Vol. 75 – Carbon in Earth, Hazen, Jones, and Baross, Eds, 2013; and Vol. 80 – Pore-Scale Geochemical Processes, Steefel, Emmanuel, Anovitz, Eds, 2015). Also included in the collection are monographs, guides, and newsletters. These publications can be found on the MSA website at this link: http://www.minsocam.org/msa/openaccess_publications/.

Mineralogy4Kids

Mineralogy4Kids is one of MSA's most visited websites. Designed for children, their parents, and teachers, the engaging and easy-to-use site contains activities, content, and games covering such topics as mineral groups, properties and identification, minerals in your house, crystals, and the rock cycle. The site was recently reconstructed and has a new URL: https://min4kids.org/

Minerals Day

MSA, in partnership with the Earth Science Week celebration hosted by the American Geosciences Institute, launched the first Minerals Day in 2020. This event, which takes place on the Monday of Earth Science Week (second full week in October), gave rise to the Minerals Day website. This site, which is managed by MSA, contains educational resources, downloadable posters, and links to the Minerals Day webinars. The link for the Minerals Day website is www.mineralsday.org.

Online Teaching Resources

During the pandemic lockdown, subscribers to MSA-Talk put out a call for online teaching resources. Other MSA-Talk members rose to the occasion, suggesting a very wide variety of excellent teaching tools. These included videos, free online textbooks, illustrations, interactive programs, 3-D models, databases, quizzes, keys, thin section images, virtual microscopes and more. MSA organized these resources, and made the links available on their website here: http://www.minsocam.org/msa/Teaching_Resources.html If you have additional resources to recommend, please email them to the MSA Business Office at business@minsocam.org.

Crystal Structure Database

The crystal structure database includes every structure published in the American Mineralogist, The Canadian Mineralogist, European Journal of Mineralogy, and Physics and Chemistry of Minerals, as well as selected datasets from other journals. The database is maintained under the care of the Mineralogical Society of America and the Mineralogical Association of Canada and was financed by the National Science Foundation (text from the database website). The database can be found at this link: http://rruff.geo.arizona.edu/AMS/amcsd.php

Collector's Corner

Collector's Corner is a section of the MSA website containing a collection of links to guides, keys, mineral localities, virtual field trips, articles, and other resources of use to the collector community. The link to the Corner is http://www.minsocam.org/msa/collectors_corner/index.htm.

Pegmatite Interest Group

MSA's Pegmatite Interest Group (PIGs) has a section of the MSA website containing essays, articles, events, images, videos, and links to other sites with interesting information on pegmatites. The PIG site, overseen by Dr. David London, is at this link: http://www.minsocam.org/msa/Special/Pig/.

Mineral-Related Links

MSA has reserved one portion of its website for links to mineral-related resources that don't fit easily into any other category. These links include those to databases, software, other societies and their publications, laboratory facilities, spatial data of mineral resources, virtual petrographic microscopes, and much more. These links can be accessed from the top menu of MSA's home page: www.minsocam.org

Pamela Burnley
2022 MSA President

NOTES FROM CHANTILLY

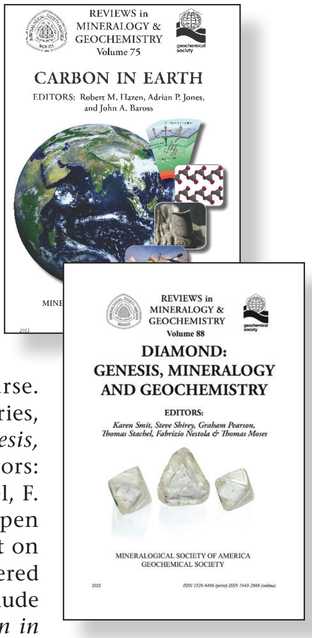
- The MSA 2022 membership renewals continue. Please renew today using the link on the MSA home page (www.minsocam.org) if you have not already done so.
- Members and fellows who are in the senior, honorary, and life categories are sent renewal notices. They need not pay dues. Rather, they are sent notices as the best way to prompt an update of membership information, particularly mail and e-mail addresses.

CONTRIBUTIONS

Many members contribute to MSA by including a contribution with their annual dues and/or by responding to special appeals. Depending on the wishes of the member, the money is deposited in 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. The income of these funds is 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 contributing at the next opportunity.

REVIEWS IN MINERALOGY AND GEOCHEMISTRY

The Reviews in Mineralogy and Geochemistry (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 content of each volume consists of fully developed text, which can be used for self-study, research, or as a textbook for graduate-level courses. The RiMG volumes are typically produced in conjunction with a short course. However, volumes can also be published without a short course. There are currently 88 volumes in the series, the last of which was *Diamond: Genesis, Mineralogy & Geochemistry* (2022, Editors: K. Smit, S. Shirey, G. Pearson, T. Stachel, F. Nestola, and T. Moses). Volume 88 is open access and is available in digital format on the MSA website. Print copies can be ordered from the MSA Bookstore. Other titles include *Carbon in Earth* (open access), *Diffusion in Minerals and Melts*, *Oxygen in the Solar System*, *New Views of the Moon*, *Pore-Scale Geochemical Processes*, and many more. 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



REVIEWS in MINERALOGY & GEOCHEMISTRY
Volume 75

CARBON IN EARTH

EDITORS: Robert M. Hazen, Adrian P. Jones, and John A. Baross

REVIEWS in MINERALOGY & GEOCHEMISTRY
Volume 88

DIAMOND: GENESIS, MINERALOGY AND GEOCHEMISTRY

EDITORS:
Karen Smit, Steve Shirey, Graham Pearson, Thomas Stachel, Fabrizio Nestola & Thomas Moses

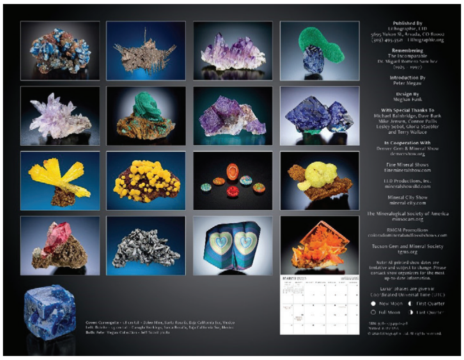
MINERALOGICAL SOCIETY OF AMERICA
GEOCHEMICAL SOCIETY

MSA 2022 DEADLINES

15 August 2022: This is the deadline to vote in the 2022 election for MSA Officers and Councilors. Members can vote via the MSA website (www.minsocam.org) or by requesting a paper ballot from the MSA Business Office (business@minsocam.org). Ballots must be returned by midnight EDT to be counted.

2022 CALENDAR

The theme for this year's calendar from Lithographie is *Minerals of Mexico.* The 16-month calendar, published by Lithographie, Ltd., is available through the MSA Bookstore for $12.



EVENTS

MSA will have a booth at the Annual Meeting of the Geological Society of America, Oct. 9-12, 2022 in Denver, CO, USA. There will also be an Awards Luncheon honoring the 2022 MSA Awardees on Tuesday, 10 October, 2022.

DID YOU KNOW?

The Mineralogy4Kids website is now back up and running (https://min4kids.org). The free site has content and activities for grade-school children, their parents, and their teachers grouped into these categories:

- Mineral Properties
- Mineral Groups
- Mineral Identification
- Minerals in Your House
- All About Crystals
- Rock Cycle
- Mineral Games

Please encourage elementary teachers and students you know to visit the site. Any feedback or suggestions are welcome and can be emailed to business@minsocam.org.

Meteoritical Society

http://meteoriticalsociety.org

IN MEMORIAM: EDWARD ROBERT DALTON SCOTT

Edward Robert Dalton Scott (74) passed away unexpectedly on 7 October 2021 at his home in San Rafael (California, USA). Scott was a distinguished meteoriticist, former President of the Meteoritical Society, and Emeritus Professor at the School of Ocean and Earth Science and Technology at the Hawai‘i Institute of Geophysics and Planetology (HIGP).

Born in Heswall (England), Ed earned his BA and MA degrees from the University of Cambridge’s Churchill College (UK), majoring in mineralogy and crystallography with a minor in physics and materials science. In 1972, he received his PhD from the University of Cambridge with a thesis on the geochemistry, mineralogy, and petrology of iron meteorites. After completing his PhD, Ed took postdoctoral positions at the University of California, Los Angeles, with John Wasson, and then at the University of Cambridge with Stuart Agrell. He also held a position as a Senior Fellow in the Department of Terrestrial Magnetism at Carnegie Institution of Sciences in Washington (USA) and spent 10 years as a Research Scientist and then Senior Research Scientist at the University of New Mexico (USA) before joining the staff at HIGP, where he remained until his retirement in 2015.

Ed was a superb scientist with deep curiosity about the Solar System and its origin. Throughout his career, he did innovative research into the nature and origin of all types of meteorites, from iron meteorites to the origins of primitive components in chondritic meteorites, to the nature of processes operating in the cloud of gas and dust surrounding the Sun as it was still forming, and the accretion of nebular dust into asteroids and planetesimals. He was a big thinker who liked complicated problems.

Ed’s accomplishments were recognized by his receiving the Leonard Medal from the Meteoritical Society, an international organization founded in 1933 to promote the study of extraterrestrial materials and planetary science. The Leonard Medal recognizes outstanding contributions to the science of meteoritics and closely allied fields. Besides receiving this award, Ed was also recognized by having asteroid 4854 named “Edscott” in 2000 and by having the first natural occurrence of the iron carbide Fe_5C_2 named after him: edscottite. Over the years, he held numerous positions with the Meteoritical Society, including serving as its president. He also served as an associate editor for both the *Journal of Geophysical Research* and *Meteoritics & Planetary Science*.

Ed was a devoted educator, teaching courses at both the undergraduate and graduate levels. For many years he was Associate Director of the Hawai‘i Space Grant Consortium, managing the undergraduate fellowship program, which links University of Hawai‘i (UH) undergraduate students with faculty members to do research on projects in space science and engineering. Ed was a beloved member of not only the UH faculty but the planetary science community as a whole. In the words of one of his HIGP colleagues, Ed was a “a science friend to all.” He certainly was that and much more. Ed was also instrumental in the Meteoritical Society’s joining of the *Elements* magazine family. He will be greatly missed.

— Portions of text courtesy of G. Jeffrey Taylor, University of Hawai‘i (modified from https://www.lpi.usra.edu/planetary_news/2021/10/11/in-memoriam-edward-r-d-scott-1947-2021/) along with Gary Huss, Klaus Keil, Sasha Krot, and Ian Sanders.

IN MEMORIAM: SANDRA PIZZARELLO

It is with great sadness that we announce that Sandra Pizzarello passed away on 24 October 2021. Sandra was born in Venice, Italy, in 1933. She obtained a PhD in biological sciences at Universitá degli Studi di Padova (Italy) in 1955. She was a research associate with Farmitalia Research Laboratories, Neuropharmacology Department (Milan, Italy) from 1957 to 1960. She started her research at the Department of Chemistry and Biochemistry, Arizona State University (ASU) (USA) in 1977. She was a research professor and an emeritus professor at ASU until she passed away.

Sandra was a pioneering scientist. While collaborating with the late Prof. John R. Cronin (1937–2010) for over 30 years, she identified and greatly expanded our knowledge of a suite of soluble compounds in carbonaceous chondrites including amino acids, monocarboxylic acids, dicarboxylic acids, hydroxyl acids, hydroxydicarboxylic acids, aliphatic hydrocarbons, ammonia, amines, polar hydrocarbons, as well as insoluble organic matter. Sandra concentrated her efforts on the development of the analytical techniques for these compounds, in particular, a diverse suite of over 80 amino acids, which are different from the distribution of terrestrial amino acids. They carried out the first isotopic analysis of amino acids in meteorites and revealed enrichments in D, ^{13}C, and ^{15}N. These results provided the first evidence that suggested a direct relationship between meteoritic organic compounds and interstellar chemistry. Later, Sandra worked on the compound-specific C, H, and N isotopic analyses of soluble organic compounds in meteorites. Her results demonstrated the diverse synthetic pathways of these compounds in the early Solar System. One of the highly laudable achievements in Sandra’s works, in collaboration with Cronin, was their discovery of L-enantiomeric excesses (ee) in a suite of rare (non-biological) extraterrestrial amino acids from carbonaceous chondrites in 1997.

Sandra’s significant contributions to the research fields of meteoritics, astronomy, astrobiology, and origins of life have influenced the next generation of scientists. She was an effective mentor for younger scientists and a role model for women in science. She served as president of ISSOL (International Society for the Study of the Origin of Life – The International Astrobiology Society) from 2014 to 2017. She is survived by her husband, Tony, and three children and their families.

Modified from full obituary written by: Hikaru Yabuta (Hiroshima University, Japan), George Cooper (NASA Ames Research Center, USA), Lynda Williams (Arizona State University, USA), Kenso Soai (Tokyo University of Science, Japan), Maitrayee Bose (Arizona State University). For the full version please see the society’s website.

Cont’d on page 65

European Mineralogical Union

www.eurominunion.org

EMU RESEARCH EXCELLENCE MEDALS 2021

The 2021 Research Excellence Medal of the European Mineralogical Union (EMU) has been awarded jointly to Dr. Sylvain Bernard and Prof. Matteo Alvaro. They are excellent scientists, who have developed new methodologies for their fields of study and who have come up with new ideas, which can be used by the scientific community.

Both are mentors and role models to a generation of young scientists, carry out highly innovative and inspiring research, and have developed an impressive network of worldwide connections and projects.

They were both scored with very high ratings (32 vs. 30) by the 2021 EMU Medal Committee during the evaluation of their nominations. For these reasons, the committee agreed that they both deserve to be recipients of the 2021 EMU Research Excellence Medal.

Sylvain Bernard

One of the recipients of the 2021 Research Excellence Medal of the European Mineralogical Union is Dr. Sylvain Bernard from the Institute of Mineralogy, Materials Physics, and Cosmochemistry (IMPMC-CNRS, France).

Dr. Bernard's highly innovative and inspiring research at the frontiers of mineralogy, paleontology, biogeochemistry, and mineral physics has provided significant contributions to a number of fields including the weathering and aqueous alteration of minerals, mineral–mineral and mineral–microbe interactions in sedimentary environments, and the processes that influence the preservation of organic matter in carbonaceous meteorites. His cutting-edge studies constitute an important step towards better constraining hydrocarbon generation and retention processes that occur within unconventional gas shale systems. Additionally, he has developed original experimental and analytical approaches to capture the interactions of biomarker molecules and minerals at a near atomic scale. Despite his young age, he has already manifested himself as a major personality on the international scientific stage, as a geochemist of exceptional capabilities, very high productivity, and true creativity.

The esteem in which his peers, nationally and internationally, hold him is reflected in his roles as a member of the ESA-Roscomos ExoMars mission team and a member of the international SuperCam team of the NASA Mars2020 Rover mission. The innovative and productive cutting-edge science should not hide another aspect of Bernard's personality, namely his engagement for the promotion of science and for other outreach activities.

For his highly innovative and inspiring research at the frontiers of mineralogy and geochemistry and his international collaborative research, Sylvain Bernard is a highly deserving recipient of the 2021 EMU Research Excellence Medal.

Matteo Alvaro

The second recipient of the 2021 EMU Research Excellence Medal is Prof. Matteo Alvaro from the University of Pavia (Italy).

Prof. Alvaro is a mineralogist and crystallographer whose activities range across material science, mineral physics, and petrology. His research is, among others, dedicated to the understanding of the properties of minerals and materials at non-ambient conditions and the application of these property changes to understanding geological processes. His new assessment of elastic geobarometry aimed at constraining the "true depth" of the equilibration of rocks by combining mineralogy, mineral physics, and metamorphic petrology is particularly remarkable. He has renewed the old concept of geobarometry and brought it to a decidedly sounder level, hence opening up new and exciting applications.

His research is, and will continue to prove, truly transformative by providing fundamental contributions to our understanding of globally important geological processes using innovative ideas and approaches that are pushing crystallography and mineralogy to the leading role they deserve in Earth sciences. In addition to the successful implementation of exciting mineralogical research and the distribution of scientific results in the form of publications, he has also proved to be an enthusiastic and competent teacher. Prof. Alvaro is currently at the centre of a network of worldwide—but mostly European—connections and projects, offering training and acting as a mentor to a generation of young scientists.

The 2021 Research Excellence Medal of the European Mineralogical Union was awarded to Matteo Alvaro for his impressively significant contributions to research and teaching in mineralogy, and for his international collaborative research.

Cont'd from page 64

THE BARRINGER FAMILY FUND FOR METEORITE IMPACT RESEARCH

The Barringer Crater Company has established a special fund to support field work by eligible students interested in the study of impact cratering processes. The Barringer Family Fund for Meteorite Impact Research will provide a number of competitive grants in the range of $2,500 to $5,000 for support of field research at known or suspected impact sites worldwide. Grant funds may be used to assist with travel and subsistence costs, as well as laboratory and computer analysis of research samples and findings. Masters, doctoral, and post-doctoral students enrolled in formal university programs are eligible. Application to the fund will be due by 8 April 2022, with notification of grant awards by 10 June 2022.

Additional details about the fund and its application process can be found at: http:/www.lpi.usra.edu/science/kring/Awards/Barringer_Fund

ANNUAL MEETING SCHEDULE

2022	(85th Annual Meeting) August 14–19, Glasgow (UK)
2023	(86th Annual Meeting) August TBD, Los Angeles (California, USA)
2024	(87th Annual Meeting) July/August TBD, Brussels (Belgium)
2025	(88th Annual Meeting) July TBD, Perth (Australia)
2026	(89th Annual Meeting) July/August TBD, Frankfurt (Germany)

Mineralogical Association of Canada

www.mineralogicalassociation.ca

SUDBURY 2023 GAC-MAC-SGA JOINT ANNUAL MEETING

May 24–27, 2023

Laurentian University, in Sudbury,
Ontario, Canada

Discovering Ancient to Modern Earth
– Découvrir la Terre Ancienne à Moderne

REQUEST FOR PROPOSALS SYMPOSIA, SPECIAL SESSIONS, SHORT COURSES, WORKSHOPS, AND FIELD TRIPS

The 2023 Joint Annual Meeting of the **Geological Association of Canada** (GAC), **Mineralogical Association of Canada** (MAC), and **Society for Geology Applied to Ore Deposits** (SGA) will be held on **24-27 May 2023** at Laurentian University in Sudbury, Ontario, Canada.

The theme of the meeting is **Discovering Ancient to Modern Earth**, reflecting the location of the Sudbury at the intersection of the Archean Superior Province, Proterozoic Southern and Grenville Provinces, and Paleozoic-Quaternary cover sequences. The conference will include an diverse program of **Symposia**, **Special Sessions**, **General Sessions**, **Field Trips**, **Short Courses** and **Workshops** covering the complete spectrum of geoscience disciplines. The meeting will be delivered in hybrid format with both in-person and virtual components. Abstracts, talks, and posters can be given in French or English.

Symposia are 1-2 day thematic sessions. **Special Sessions** are ½ to 1-day that cover "hot" topics. **Short Courses** are 1-2 days, pre- or post-meeting, with notes printed by the Sponsor. **Workshops** are 1-2 days, pre- or post-meeting, often hands-on, with notes provided as PDFs. **Field Trips** are ½ to several days, pre- or post-meeting, with guidebooks published by Ontario Geological Survey.

Proposal templates for Field Trips and Short Courses can be downloaded from the meeting website at http://event.fourwaves.com/Sudbury2023. The deadline for submission is **15 August 2022**. Please contact Cathy Nadjiwon at cnadjiwon@laurentian.ca if you have any questions.

MAC AWARDS – CALL FOR NOMINATIONS

Pinch Medal

The Pinch medal is awarded every other year since 2001 to recognize major and sustained contributions to the advancement of mineralogy by members of the collector-dealer community.

This medal is named for William Wallace Pinch of Rochester, New York, in recognition of his enormous and selfless contributions to mineralogy through the identification of ideal specimens for study and through his generosity in making them available to the academic community.

Each nomination should consist of a letter describing in detail the contributions of the nominee and a list of publications resulting from the nominee's contributions (the nominee is not required to be an author of these publications); additional supporting letters are welcome.

Nominations for the 2023 medal are to be submitted to **Andrew Conly (**Department of Geology, Lakehead University, 955 Oliver Road, Thunder Bay, ON P7B 5E1, CANADA); E-mail: aconly@lakeheadu.ca

Please submit your nominations by **10 October 2022**.

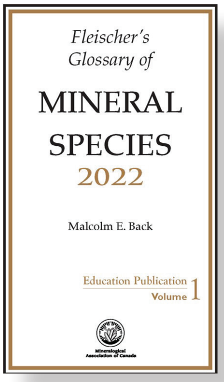
NEW PUBLICATIONS IN OUR 'EDUCATION PUBLICATIONS' SERIES

Fleischer's Glossary of MINERAL SPECIES, 2022 Edition

Education Publications Series Volume 1

Authored by: Malcolm E. Back, Departmental Associate, Royal Ontario Museum. Toronto, Ontario, Canada

ISSN 2564-498X – ISBN 978-0-921294-64-1 – EP 01, 2022. 448 pages



Fleischer's
Glossary of
MINERAL
SPECIES
2022
Malcolm E. Back
Education Publication
Volume 1
Mineralogical Association of Canada

We are taking over the publishing of the Glossary, with the blessing of The Mineralogical Record Inc., which has been published since 1971 when the first Glossary was introduced by Mike Fleischer, 52 years ago. This 2022 Thirteenth Edition of the Glossary, will supersede the 2018 edition.

The Fleischer's Glossary of Mineral Species has been prepared as an alphabetical summary of mineral names for ready reference. This a list, as of October 31, 2021, of the names, symmetry, and chemical -compositions of mineral species. Synonyms and discarded names will not be included. Diacritical marks will be included. All mineral species listed are approved by the International Mineralogical Association.

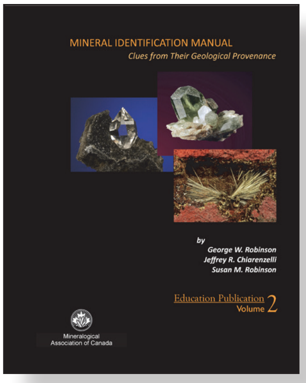
Most mineral classifications are based primarily on chemical grounds (grouping by chemical classes such as oxides, halides, carbonates, silicates, etc.) and secondarily on crystal structure. Accordingly, in this Glossary emphasis is on the chemical composition, polymorphism, and relationships to other minerals. For each mineral, there is given its chemical formula, crystal system and, in most cases, a statement of its relations to other minerals.

MINERAL IDENTIFICATION MANUAL
Clues from Their Geological Provenance

Education Publications Series Volume 2

Authored by: George W. Robinson, Jeffrey R. Chiarenzelli (St. Lawrence University) & Susan M. Robinson

ISSN 2564-498X - ISBN 978-0-921294-65-8 - EP 02, 2022. 208 pages



MINERAL IDENTIFICATION MANUAL
Clues from Their Geological Provenance
by
George W. Robinson
Jeffrey R. Chiarenzelli
Susan M. Robinson
Education Publication
Volume 2
Mineralogical Association of Canada

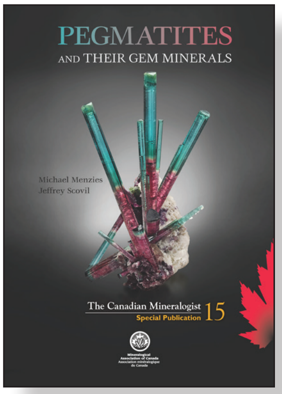
This book is arranged in 15 chapters, each one of which contains an explanation of their geological formation. This assumes the person who collected the mineral sample knows the geological environment in which it was found, e. g., a limestone quarry versus a massive sulfide deposit or a pegmatite, etc. Once the appropriate table for that specimen has been determined, the physical properties of the mineral, beginning with its luster (metallic or non -metallic), is noted, followed by its hardness, density, cleavage, or other discernible physical properties. This is usually sufficient information to identify most common mineral species, since each step eliminates a considerable number of possibilities. As a confirmation, the photographs provide reassurance that the un-known mineral physically resembles the one chosen through the table. The volume includes more than 475 color photos, 3 colour diagrams, along with tables of the minerals' physical properties used for identification in the field and lab.

This book is intended for anyone who is charged with identifying minerals, without having to use sophisticated equipment to do so. This includes geologists in the field, mineral collectors as well as students and professors in the lab. Many similar determinative tables have been used in the past for this purpose, but never arranged by geological environments and modes of genesis.

"HOT FROM THE PRESS" NEW PUBLICATION IN OUR SPECIAL PUBLICATIONS SERIES

Pegmatites and Their Gem Minerals

Special Publications Series Volume 15



Authored by: Michael Menzies and Jeffrey Scovil

Series Editor: Robert F. Martin

ISBN 978-0-921294-66-5 - SP 15, 616 pages, 2022

Pegmatite enthusiasts will be happy to know that a new book, "Pegmatites and their Gem Minerals", is set to appear in mid-August. Michael Menzies and Jeffrey Scovil have teamed up to provide a systematic coverage of the topic. The volume provides a comprehensive description of the geology, worldwide occurrence and formation of gemstone-bearing pegmatites and their gem minerals. It features 40+ worldwide localities, and 40+ gem minerals and other important pegmatite species. The 600 pages are lavishly illustrated with more than 600 maps, diagrams, locality photos and photos of mineral specimens and gems.

Special Publication 15 of *The Canadian Mineralogist* builds on the fundamental concepts of pegmatite formation provided in SP10, *Pegmatites*, by David London (2008). The two volumes are complementary. Pegmatites are here described with a greater emphasis on mineralogy, presented at an intermediate level. There is a strong emphasis on locality descriptions, which make up more than half of the volume. The localities chosen are well known for their miarolitic pegmatites, from which gemstones have been recovered. There is thus a bias in this volume in favor of Paleozoic, Mesozoic and Cenozoic pegmatites that crystallized in the upper crust, where cavities are more likely to form. All continents are represented. Included also are localities where the body of pegmatite has been desilicated by interaction with wallrock or has formed from a silica-undersaturated magma, producing nepheline syenite pegmatite. In every case, there is a strong focus on mineral specimens, gem crystals and gems. The intent is to broaden the readership to include mineral and gem enthusiasts and collectors, museum professionals, and others interested in nature's treasures, as well as earth-science students and graduate students.

You may order any of the above publications from our online store, under the 'Special Publications' category at: https://www.mineralogicalassociation.ca/devOnline/index.php

THE CANADIAN MINERALOGIST: NEW, IMPROVED AND READY FOR THE 21st CENTURY!

While renowned for the publication of high-quality papers with a mineralogical focus, our journal publishes on a broad range of topics: petrology, economic geology and geochemistry. We welcome submissions in any area that involves mineralogy as means to solving a geological research question.

Dealing with an ever-changing landscape means the journal must adapt. To this end, important changes are coming, including:

- Two new principle Editors, Andy McDonald & Steve Prevec, to decrease decision times;
- Reduction in the editorial handling of new mineral characterizations (single reviewer, two-week review, etc.);
- Introduction of Short Communications to provide a forum for cutting-edge techniques or new approaches;
- Enhancing the Associate Editor team (broader range of knowledge, increasing the number).

Our average time-to-decision is two months and our page charges are the most reasonable out there. Be bold, be daring: Submit your manuscript to a journal with an established national and international reputation, The Canadian Mineralogist!

Instructions for Authors are available from https://www.mineralogicalassociation.ca/submission/

Submissions can be made at https://www.editorialmanager.com/canmin

The Editorial Team

UNDERGRADUATE AWARDS 2021–2022

The Mineralogical Association of Canada Undergraduate Student Awards are given annually to undergraduate students (2nd year of study or higher) at a recognized Canadian university or institute of higher education for excellence in one of the specialties supported by the society: mineralogy, crystallography, geochemistry, petrology, and mineral deposits. Congratulations to the following students who received this award in 2021–2022:

Bianca Angheluta, University of Waterloo
Ben J. Bates, Trent University
Jared Scott Brown, University of British Columbia, Okanagan
Kathleen L. Clark, Dalhousie University
Teela Clouthier, Lakehead University
Hayley P. Dill, St. Francis Xavier University
Katharine Emma Gilchrist, University of Calgary
Cameron D'Arcy Greaves, Acadia University
Emily J. Harrison, University of Saskatchewan
Caleb Isaac, University of British Columbia, Vancouver
Jean-Kristof Lapierre, Université Laval
Max Aaron Laxer, Western University
Jenna B. T. Maccagno, University of Alberta
Taylor Mugford, Memorial University of Newfoundland
Madelaine Norman, Laurentian University
Annaliese Paczynski, Brock University
Aboni T. Quabbo, University of Regina
Breanna Marie Stamcoff, University of Windsor
Savanna Yamamoto, University of Victoria

Italian Society of Mineralogy and Petrology

www.socminpet.it

FROM THE SIMP PRESIDENT

On behalf of the Council of the Italian Society of Mineralogy and Petrology (SIMP), I would like to express our gratitude and appreciation to former president Daniele Castelli for serving the SIMP. I am confident that he will continue to support our community as the other former presidents have done. I also trust in his support and assistance during my tenure.

Special thanks also go to the president's office staff. To Sabrina Nazzareni who ends her role as secretary after several years and to the current treasurer Nadia Malaspina who will continue as the secretary of the SIMP.

Welcome to the new members of the SIMP Council. Paolo Mazzoleni is the new vice president. Donato Belmonte is the new treasurer. We also have three newly elected councilors: Paolo Lotti, Mara Murri, and Rosalda Punturo. These individuals—along with Matteo Alvaro, Omar Bartoli and Pietro Marescotti—form the SIMP Council together with the presidents of the SIMP informal groups: Fernando Camara (National Group of Mineralogy; GNM), Elisabetta Rampone (National Group of Petrography; GNP), and Elena Belluso (National Group for Georesources, Environment, and Cultural Heritage; GABEC). Thanks to the auditors Lorenzo Fedele, Alberto Renzulli, and Alessio Langella and to our former councillors Alessandra Montanini, Giovanni Andreozzi, and Mariano Mercurio.

With its new management, the SIMP will continue to pursue and support scientific activities in Italy and abroad through conferences, schools, and seminars and through the activities of its committees. Among the many initiatives, I want to highlight the distinguished lectures, which see brilliant researchers from the SIMP and the Italian Geological Society (SGI) engaged in the dissemination of geological sciences. The SIMP also promotes outreach and educational activities such as schools, workshops, and seminars, which are listed on the SIMP website (www.socminpet.it) and Facebook (@socminpet.it). Together with other Italian scientific societies, the SIMP also supports the "#IOGEOLOGO" campaign (www.iogeologo.it) that is aimed at promoting the geosciences to families and high school students in order to stimulate and encourage enrollment in university geoscience degree programs. I also bring to your attention the SIMP–AIC joint publication "The Crystals Issue", a *Comics&Science* special issue. Notably, 2022 is the International Year of Mineralogy. This is a perfect time to promote our science to our students, colleagues, and the broader community.

The last two years have been particularly challenging due to the COVID-19 pandemic, which forced most of us to minimize contact in person and take refuge in online meetings. However, the activities of the SIMP have not stopped! For example, several schools and conferences, such as our SIMP conference associated with EMC2020 held 29 August to 3 September 2021, were successfully held online and many SIMP members participated. Hopefully, the next joint SIMP–SGI conference ("Geosciences for a Sustainable Future"; https://www.geoscienze.org/torino2022/) will be held in person in Turin (Italy) on 19–21 September 2022.

GEOSCIENCES FOR
A SUSTAINABLE FUTURE
Torino 19-21 September 2022

Finally, I would like to thank all members for giving me the opportunity to serve the SIMP and I trust that their support will be essential in the further growth of our Society.

Francesco Princivalle (University of Trieste)

MINEWA: MINERALS AND WASTE, AN ANTHROPOCENE TALE

Bardonecchia (Torino, Italy), 20–24 June 2022

An international EMU–SIMP school on mineral constituents of wastes, their characterization, recovery, and management.

http://minewa2021.it/index.php/

Registration begins 1 February 2022

Contact

Mario Tribaudino	mario.tribaudino@unito.it
Daniel Vollprecht	daniel.vollprecht@unileoben.ac.at
Alessandro Pavese	alessandro.pavese@unito.it

Topics

1. "Waste and Minerals, an Overlooked Connection"
2. "What is Waste, and How We Manage It"
3. "Thermodynamics and Kinetics of *HT* Processes"
4. "Mineralogy of Industrial Processes at High Temperature"
5. "Low-Temperature Geochemistry"
6. "The Geological Significance of Novel Anthropogenic Materials: Deposits of Industrial Waste and By-Products"
7. "Bio-Mineral Interactions"
8. "Urban Metabolism"
9. "Bottom Ash from Incineration: Production, Characterisation, and Potential for Recycling"
10. "Metal Recycling"
11. "Metallurgical Slags"
12. "Construction and Demolition Waste Description and Recovery"
13. "Waste Recycling in Silicate Ceramics: Feasibility and Effects"
14. "Mineral Tailings"
15. "Waste, Incineration, Environment and Sanitary Issues: Are Really at Odds?"
16. "A Global Strategy for Waste Management"

INTERNATIONAL PHD SCHOOL – "MELTING AND FLUID/MELT-ROCK REACTIONS IN THE MANTLE – MEREMA"

The second edition of the International School: "Melting and fluid/melt-rock reactions in the mantle – **MEREMA**" was organized by the Italian Society of Mineralogy and Petrology (SIMP) in collaboration with the PhD programs of the Universities of Ferrara, Genova, Milano, Modena – Reggio Emilia, Pavia, and Torino. The European Geosciences Union (EGU) and European Mineralogical Union (EMU) acted in partnership and co-sponsored the event.

The school was held in Sestri Levante (FIG. 1), a small pearl of the splendid Tigullio Gulf in the Ligurian Sea (northwestern Italy) on 24–28 October 2021, four years after the first edition (12–17 February 2017). In between, the COVID-19 pandemic definitely changed our way of relating to people and communicating science, and transferring knowledge between different generations of researchers. In such a frame of mind, it has been a real challenge to propose to the scientific community and partnership our intention to have students and lectures in person only, trying to overcome all of the fears to meet *vis à vis*.

FIGURE 1 Panoramic view of Sestri Levante and the Tigullio Gulf from the school venue (PHOTO: HOTEL VIS À VIS)

"Vis à Vis" is also the name of the main venue of the School, the congress centre in Sestri Levante that helped us to arrange the activities in full compliance with the Italian health rules imposed by the COVID-19 pandemic. The audience, including lectures and organisers, was fixed to 60 participants with certification of complete COVID-19 vaccination.

FIGURE 2 MEREMA-2 participants group

The school was attended by a select group of 38 PhD students and early researchers from nine countries, gathering broad interest in Earth and planetary mantle processes (FIG. 3). The students and young researchers shared four days of full lectures and discussion sessions with top level scientists, which offered an overview of the Earth's entire mantle system, covering topics such as:

- Chemical differentiation and internal structure of the Earth (W. McDonough, A.W. Hofmann, G. Caro)
- Mineralogy of the lower mantle and nature of the core-mantle boundary (D. Andrault)

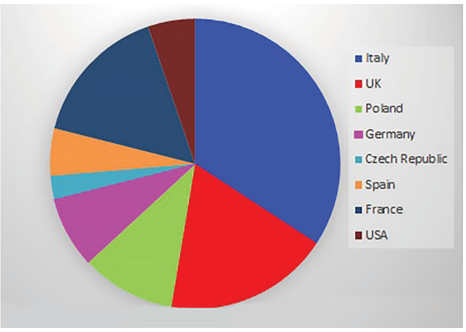


FIGURE 3 Country distribution of student participants

- Geophysical probing of mantle heterogeneities: insights on mantle dynamics from seismic tomography (B. Romanowicz, C. Farnetani)
- Mantle reservoirs: origin and length scale of chemical/isotopic mantle heterogeneities (A.W. Hofmann, A. Stracke)
- Transfer of heterogeneities from the deep mantle to the melting mantle sources and finally to the extruded melt regions (R. Katz, Y. Ricard, S. Lambart)
- Geochemical processes of the lithospheric mantle (M. Godard, M. Gregoire).

An interesting and cutting edge overview of the new frontiers in trace elements and isotopic analyses using QQQ-ICP-MS was provided by the team of Agilent Technologies© (L. Mounier). Each day, the students had the opportunity to present their researcher with "flash talks" that strongly contributed to enrich the school program. Despite the critical period, the entire week saw significant interaction and passionate conversation among all participants that also continued during the various convivial moments (FIG. 5), in full compliance with rules imposed by the COVID-19 pandemic. Very positive feedback from the students, as well as the invited lectures, has stimulated the Scientific Committee to continue this experience and consider a third edition MEREMA School.

FIGURE 4 (**A**) Elisabetta Rampone (University of Genova, Italy) presents to the audience the MEREMA School – second edition. (**B**) Cinzia Farnetani (Institut de Physique du Globe de Paris, France. (**C**) Denis Andrault – Université Clermont Auvergne, France.

We hope to meet the *Elements'* readers at the third edition of the MEREMA School!

The Merema School

Scientific Committee

Elisabetta Rampone, Costanza Bonadiman, Daniele Castelli, Cinzia Farnetani, Patrizia Fumagalli, Nadia Malaspina, Alessandra Montanini, Maurizio Mazzucchelli, Andreas Stracke, Al Hofmann, Riccardo Tribuzio, Alberto Zanetti

See the full Merema report at https://www.socminpet.it/Merema/

TECTONIC PETRAMETER

By Esther Posner

Geologists study the Earth
to learn our planet's natural history.
But the reason behind the planet's birth
still remains a mystery.
Won't you join me
on a very special journey through
geologic time?
Four billion, six hundred million years
have passed
so please don't mind me if I move
somewhat fast through the story.
Rocks are the geologist's inventory
of information.
They give us clues to their formation. Ever
since its creation, the Earth has been
dynamic and constantly changing.
All of our panoramic views are always
rearranging themselves ever so slowly
over time.

The oldest slice of time is called the
Precambrian
which is broken into three, beginning with
Hadean, and as you can see, our Earth
is thought to have been covered by a sea
of magma!
Could you have handled it?
A bombardment of meteorites also hit and
continue to hit our planet.

The Archean came next and it was a blast.
Tectonic plates were smaller and they moved
pretty fast.
In an enthusiastic flash of ash, volcanic islands
smashed together.
I don't know whether it'll bring you to tears
to know that in just a few hundred million
years,
we had our first continents appear
and our oceans and atmosphere evolved.
Acidic iron, which used to dissolve, reacted with
oxygen that stromatolites resolved to release.
Say *that* six times fast – or six hundred million
times slow! TIME is what matters as through
geologic time we go.

The last third of the Precambrian is called the
Proterozoic, which means "before life", but
now we know it is not true because early
Earth creatures occupied the ocean blue.
But there was no life on land, no plants or trees,
so the brisk breezes and bleak rains
drained the land of its debris.
And although it may seem ironic, tectonic forces
broke apart and set micro-continents onto
separate courses
that would collide and divide again and again.
Our friend, the Earth, is always changing and
rearranging its crust.

It must have been a strange sensation
for the Earth to experience a global glaciation.
A planet of ice! A real snowball Earth!
But it may have been this climate catastrophe
that eventually gave birth to complex
critters who began to grow once the snow
began to go away. After three billion years of
single-cellular life,
multi-cellular life was here to stay! Sometimes
more than other times...

The author performing her poetic timescale in Centennial Hall at the University of Arizona. Photo Credit: Marty Pepper

KABOOM!!!
Did you hear that?!
It sounded like an explosion!
Life in the Cambrian was filled with multi-
cellular motion.
We now enter the notion of time
that is called the Paleozoic – and what a stoic
time.
Shelly sea life occupied the oceans and
trilobites were in their prime.
In came the seas and drowned up lots of land
and even Michigan was underwater
and didn't look much like a hand.

In the Ordovician, the seas may have seemed
interesting for fishing, but the most
important event that began to expand
was the emergence of plants and mold on
the land.
Life still flourished in the serene waters
and marine parents probably cautioned their
sons and their daughters, "Kids, stay away
from the squids."
Quite forbidding were the cephalopods,
ancestors of octopi, who terrorized the
trilobites who were living nearby.
And all I can say, with a heavy sigh, about the
end of the Ordovician day is that almost
everything would die.

Although somewhat covered by frost, all life
was not lost.
And without too much grief, the Silurian
boomed with reefs.
Corals like colonies spread throughout the seas
including our friendly *Hexagonaria,*
commonly called Petoskey.
A topical reference
for Earth's geographic change
is this coral's tropical preference,
which means that Michigan was latitudinally
rearranged! Warm waters flowing below the
equator,
in paradise if you please,
while the land was slowly filling with trees.
This was new!

Vascular plants made their biologic debut
and fish with jaws joined the sea life stew.

Now if you visit the Smithsonian stage,
you'll see fish fossils of Devonian age for
the Devonian was the Age of Fish.
Don't you wish you could have a dish of
that fish?!
Some had vertebras the size of flagpoles
while sharp-toothed sharks patrolled.
Coal was just beginning to form on land
as plant life continued to expand
and even the fish began to stand!
Amphibians appeared queerly and in
their growth roamed both the sea and the
land.*

Now it's time to get down with the Coal
Swamp Stomp!
Tap your feet to the beat of the formation
of peat like a plant plantation soaking up
the bright heat. Earth's two massive
continents began to creep their massive way
into each other
to form what today we say was Pangaea.
An important idea to keep in mind
is that Earth's crust, climate, and chemistry
change slowly over long periods of time.
This is what rocks tell us—and sometimes
in rhyme.

The Permian Period is the final chapter
in the myriad of curious details from the
Paleozoic—and what a stoic time.
Pangaea was in full form
and environments were transforming,
informing its living inhabitants
of an upcoming storm.
Ninety-six percent of all life ended up
succumbing to it—but don't be too forlorn.
Life would certainly be reborn in a brand
new form.

Following the distinctly disturbing extinction
of Permian life, the rebirth of the Triassic
seemed enthusiastically fantastic.
In fact, the Mesozoic was quite heroic for all the
reptile fans as dinosaurs began to span the
grand land mass.
But alas, Pangaea would break and move some
more and brand new oceans formed their
mafic floor.
Did anyone hear the roar of that shrew?
Our planet's first mammals made their hairy
debut in the terrific Triassic.

Now when I say Jurassic, you think Jurassic Park.
But let's embark a little deeper and shed some
light into this dark.
Birds first flew in the skies above
and frogs and salamanders also made their
debut shove.
Just like a glove, the coasts of Africa and South
America fit perfectly and in the Jurassic, this
land mass began to break itself free,

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* Author's Note: The word queerly is used in a purely non-derogatory way as in the traditional definition of the word meaning strangely or oddly.


Grand Canyon, Arizona (USA)


Volcanologist sampling lava.

forming a narrow but expanding sea that would
eventually be the Atlantic Ocean.
Blessed be.
The Cretaceous was sensateous
with a chalky aftertaste. We can learn a lot from
the dinosaur bones encased in rock
as Earth's clock ticks on and on,
as life continues to be drawn to spawn until
everything's gone. Hey, don't yawn at the
writing on the wall!
An exciting mass extinction is *so* enthralling!
All in all, destiny may be stalling the final
blow but at the end of the Cretaceous,
as we're beginning to know and act more
philosophic about,
an impact and catastrophic route caused the
Earth to react.
And the fact of the matter is the matter of fact.
Dinosaurs eventually died out and they
never came back.

But have no fear!
That mass extinction occurred 65 million
years ago and so much continues to slowly
change;
it's holy yet strange.
The Cenozoic heroically introduced
the Age of Mammals, which gave a boost to the
existence of us.
Can you believe that I have barely discussed *us*?
Earth history is just so long!
It's so much more than this song's rhyming
refrain can contain. It's not even within the
scope of a professional telescope.
Its worth is beyond the range of the New
York Stock Exchange and things just keep
changing and changing
and all so slowly rearranging over time. It's
more than enough to blow your mind!
It's the stuff that fills the deepest geologic time.
It's the climbing to the top of the mountain
peak
and stopping to catch your breath but before
you can speak, erosion has erased the
mountain to the ocean's deep.


Devil's Tower, Wyoming (USA)


Carboniferous ferns

And it's all about scale and without fail,
CHANGE is the Earth's constant prevailing
force,
which provides for interesting discourse, of
course.
But we still don't know the source of this
cosmic sorcery or just exactly what it means
to be alive
and to be free, to feel and to be.
It's a mystery but we can learn a lot from
history.
Like in the Pleistocene, beginning 1.8 million
years ago,
much of the Northern Hemisphere was covered
by glacial snow. And I mean an *ocean* of ice,
which shaped our landscape up real nice
and filled our valleys with various types of
rocks,
which geologists consider to be the Earth's
natural ticking clock.
It shouldn't stop so don't worry about hurrying
it up and be sure to avoid those Styrofoam
cups.
It makes a difference what we consume
so please don't assume that the Earth was
created just for you. Just coexist with Nature
and that should do. That should do.

We are brewing up our knowledge and filling
colleges with folks who acknowledge the
importance of our granite-bearing planet.
Can you stand it as you stand *on* it? It's micro,
it's macro,
it's quantum and fun.
It's exciting and living
thanks to radioactivity and the Sun.
Has the story only begun?
And are we the only ones?
The universe doesn't really seem that lonely
or secluded, but the human quest for
knowledge is hardly concluded. And now it's
our turn,
this generation-tech,
to build on the foundation of our foreparents'
track. Understanding the difference between
black and gray... and sometimes you've got
to just call it a day.
But the Earth will go on, beyond our tears and
our fun.
It's so much better than any rerun on T.V., it's
the story of our planet's ancestry.

Geology is a great study
for girls and boys
who enjoy the joy
of the Earth's worth
and place in this universe of space.

The pace of the race for knowledge
is all dependent upon the scale.
But if you start to follow your heart,
you'll get smart and never fail.
And if you fail, just try again
with the new insight you have gained
and hold on tight
to life's sweet flight
because so much still waits
to be explained.

The author won the Geological Society of America's Best Student Presentation Award in 2008 for her memorized performance of Tectonic Petrameter in a Geoscience Education session related to alternative ways to teach the geological time scale, which has since been performed extensively throughout the US and Europe. Posner's geology-inspired poetry and music will be featured in a 2024 US-based tour of "PhD, The Musical". Contact eposner.elements@gmail.com for more information.

Calling all geo-poets!

The natural world provides a wealth of inspiration for creative expression. *Elements* wants to hear your voice. Please submit your geoscience-inspired poetry/prose (<2000 words) to eposner.elements@gmail.com

CALENDAR

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

2022

July 19–21 2022 **International Archean Symposium**, Perth, WA Australia. Web page: 6ias.org/

July 24–29 **12th International Symposium on the Geochemistry of the Earth's Surface (GES-12)**, Zürich, Switzerland. Web page: ges12.com.

July 25–29 **AIPEA-XVII International Clay Conference**, Istanbul, Turkey. Web page: icc.aipea.org/

July 31–August 4 **Microscopy & Microanalysis 2022**, Portland, OR USA. Web page: www.microscopy.org/events/future.cfm.

August 14–19 **Meteoritical Society Annual Meeting**, Glasgow, UK. Web page: www.metsoc2022.com/.

August 2–8 **2nd IAGC International Conference (AIG-14 and WRI-17)**, Sendai, Japan. Web page forthcoming.

August 6–12 **Geoanalysis Conference 2022**, Frieberg, Germany. Web page: geoanalysis2021.de/en/.

August 15–19 **12th International Kimberlite Conference**, Yellowknife, NT Canada. Web page: www.12ikc.ca.

August 21–25 **Fall ACS National Meeting & Exposition**, Chicago IL, USA. Web page: www.acs.org/.

August 23–26 **ISEG 2022 (International Symposium on Environmental Geochemistry)**, Moscow, Russia. Web page: iseg2022.org.

August 28–September 2 **SEG/AAPG International Meeting for Applied Geoscience and Energy**, Houston, TX USA. Web page: www.aapg.org/events/conferences/ace.

September 2–4 **Pan-American Current Research on Fluid Inclusions (PACROFI)**, Edmonton, Canada. Web page: cms.eas.ualberta.ca/pacrofi/.

September 5–9 **International School: "Understanding Oxygen Fugacity in Geoscience"**, Trieste, Italy. Web page: fo2school.units.it/index.php.

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, FR. Web page: emaw2021.sciencesconf.org/.

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

September 19–21 **SIMP-SGI-SOGEI Congress: Geosciences for a Sostenible Future**, Torino, Italy. Web page: www.geoscienze.org/torino2022/index.php/en/

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.

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: https://www.hou.usra.edu/meetings/ices2023/

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

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: forthcoming.

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 24–2? **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

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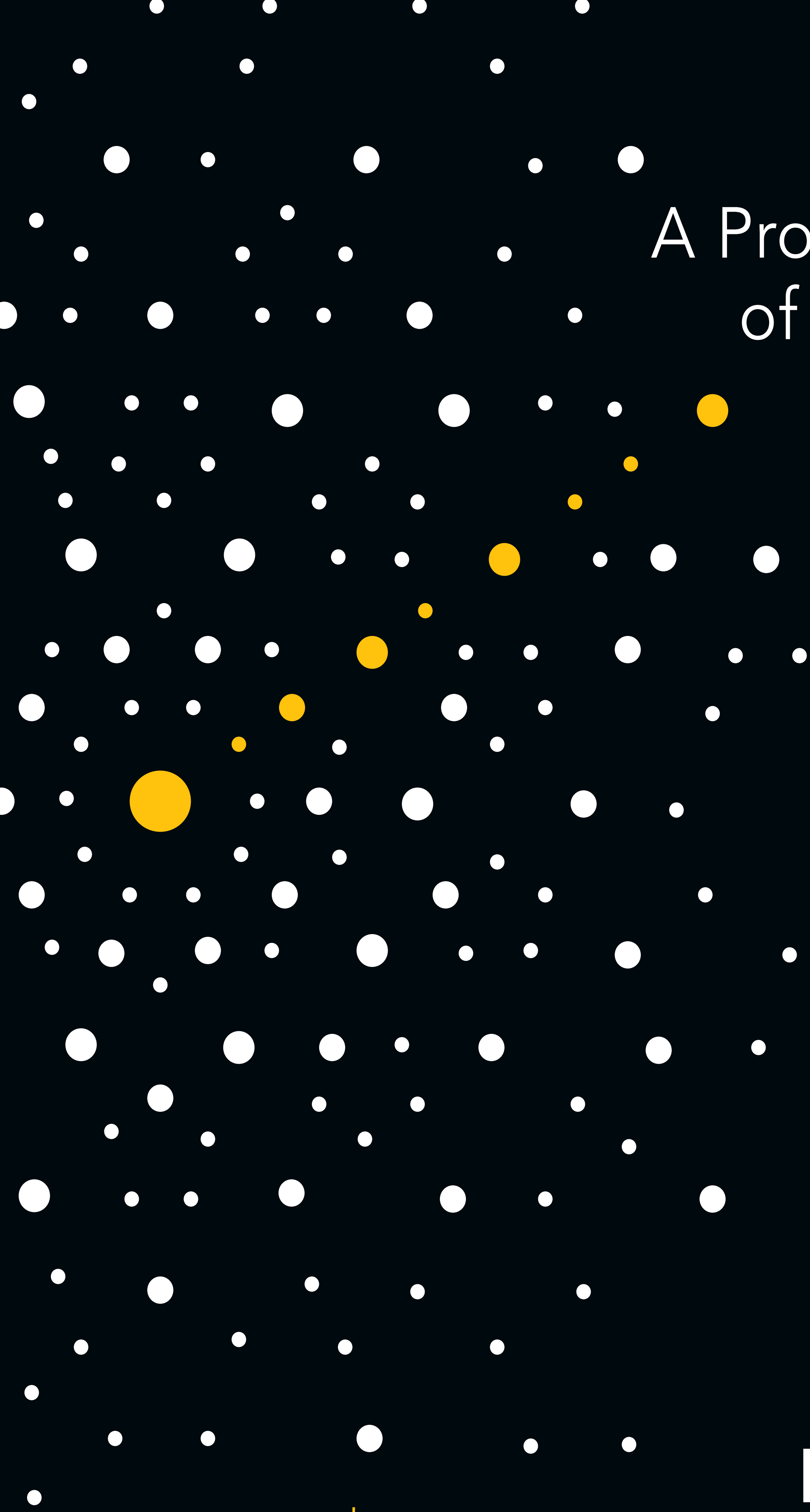

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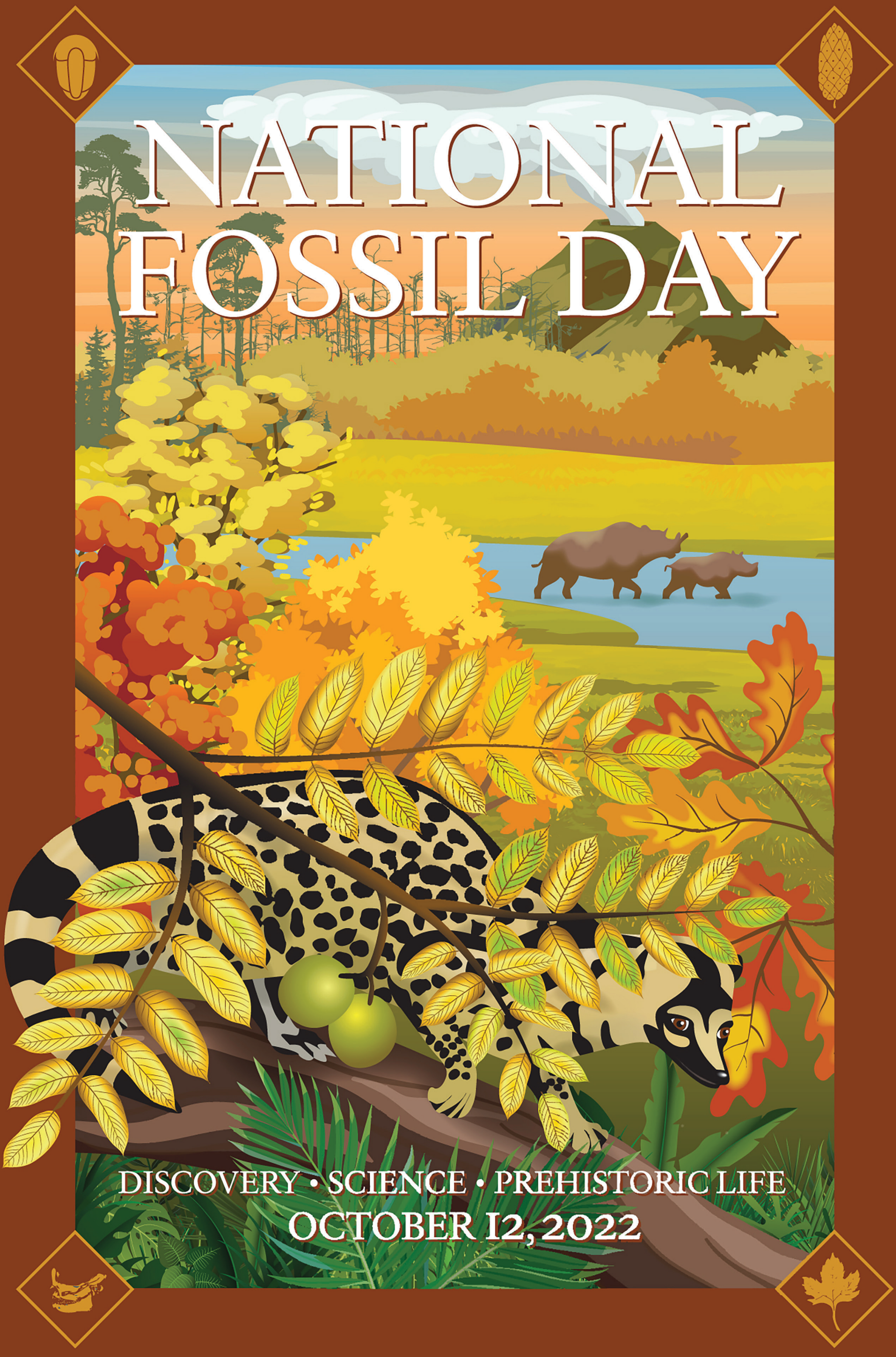

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