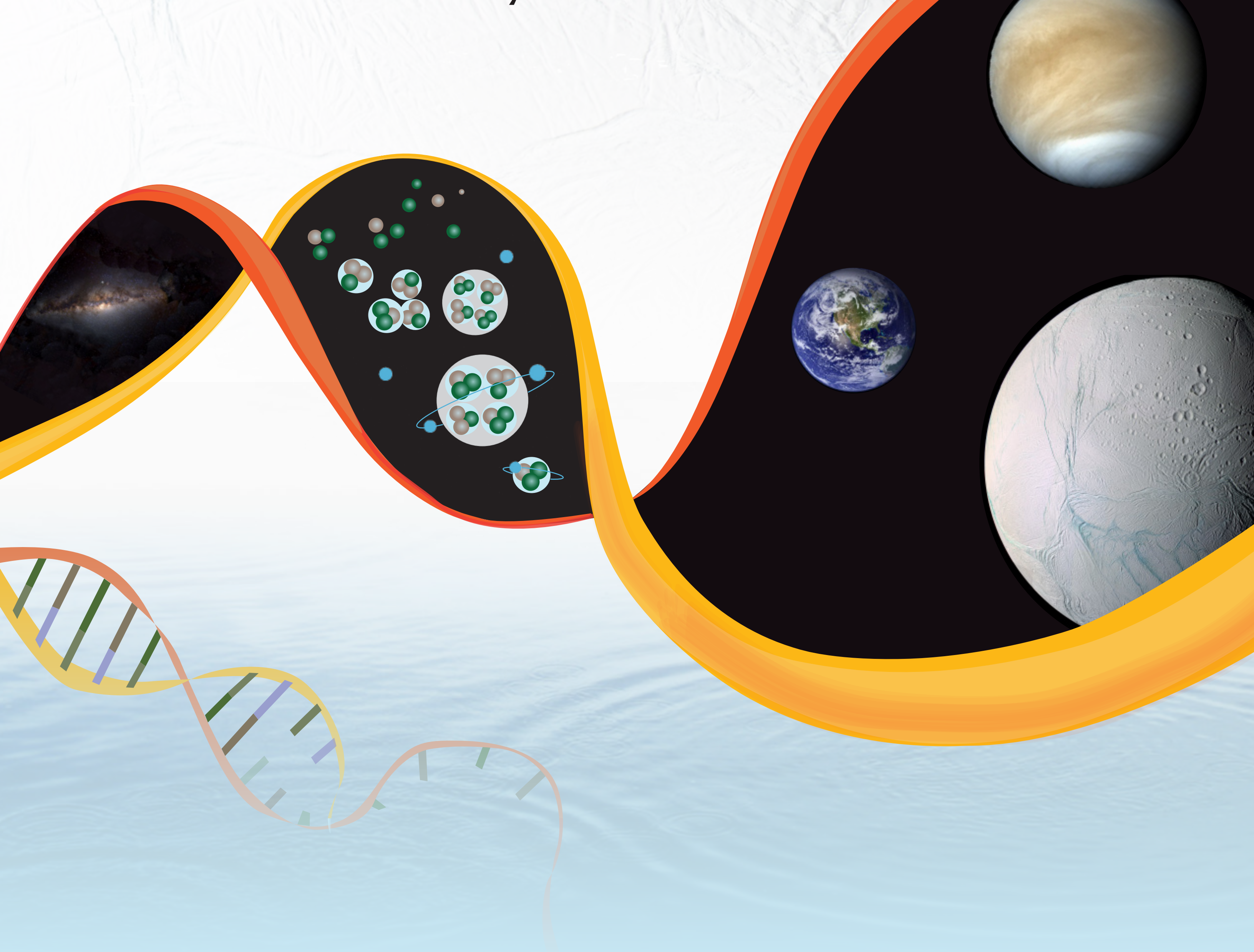
National Aeronautics and Space Administration

NASA Astrobiology Institute 2016 Annual Science Report

Team Report:

Habitability, Life Detection, and the Signatures of Life on the Terrestrial Planets,

University of Wisconsin–Madison



Habitability, Life Detection, And The Signatures Of Life On The Terrestrial Planets

Lead Institution:
University of Wisconsin-Madison

Team Overview

Principal Investigator:
Clark Johnson

The Wisconsin Astrobiology Research Consortium pursues research and education on habitability, life detection, and the signatures of life on the terrestrial planets, with a focus on Earth and Mars. This effort is fundamentally built around a broad interpretation of *Life Detection*, which includes not only detection of the organic signatures of life in modern and ancient environments, on Earth or other planetary bodies, but also the inorganic signatures of life, which may have the greatest fidelity over billion-year timescales and complex geologic histories. Biosignatures developed from laboratory experiments are field-tested in modern and ancient environments on Earth, which in turn inform new experimental studies, producing an iterative process of testing and evaluation. The goal is to ultimately develop the interpretive context needed to evaluate the potential for life on other planetary bodies, as well as to understand the evolution of life on Earth.

The three research components of our program are:

- Developing methods for life detection on Mars and in Mars analog environments
- Biosignatures: developing the tools for detection of ancient life and determining paleoenvironments
- Life detection in the ancient terrestrial rock record

Team Website: http://geoscience.wisc.edu/astrobiology

2016 Executive Summary

The research portfolio for 2016 included 17 projects that spanned the Team's three research themes on life detection, biosignature development, and the ancient terrestrial rock record. This research effort involved 14 lead investigators from eight institutions, and major collaborations with seven other current and former NAI Teams, as well as astrobiologists in the U.S., Europe, Israel, Japan, China, Australia, and South Africa. Mission involvement included *EXPOSE-2* and *Mars Science Lab*. The results of these efforts were published in 33 peer-reviewed publications, and comprised the theses of three graduate degrees that were awarded in astrobiology from UW-Madison.

Fig. 1. Graduate student Franklin Hobbs loading a sample of microbial dolomite for XRD analysis. Image credit: Huifang Xu.

Work on Mars and Mars analog environments continued with two projects in Yellowstone. The production and preservation of lipid biomarkers by chemolithoautotrophs, which oxidize Fe(II) to power their metabolism, was studied in detail to test for the likelihood that such materials might be detected on Mars. In addition, microbiological and genomic approaches, and associated isotope studies, documented dissimilatory microbial iron reduction in the same springs, demonstrating microbial iron redox cycling. Two additional projects related to Mars included discovery of new highly magnetic nano-phase iron oxides, which may help explain the remanent magnetization on Mars. In addition, using observations by the Curiosity rover, the first mud rocks found on another planet were studied to determine potential pore water chemistry and its relation to habitability of the subsurface of Mars.

The Team's effort on biosignature development continued with seven projects. Study of ancient enzymes documented relatively high temperatures in the Archean oceans. Such high temperatures would require high atmospheric CO_2 contents, and experimental studies showed that the extent of Ca substitution in Fe carbonates might be used as a CO_2 proxy. In addition, incorporation of Mg in carbonates was found to require binding to biological ligands, suggesting a mineralogical biosignature. Deciphering the weathering conditions on the ancient Earth, and Mars, was the focus of developing a new stable isotope system using potassium isotopes. Additional work on stable Si isotopes discovered an important role for microbial iron reduction in producing silica-magnetite associations in iron formations. Two additional projects were aimed at improving *in situ* chemical and isotopic analysis of samples, either on rovers or in large laboratories.

Fig. 2. Team scientists, with Australian Center for Astrobiology Director Martin Van Kranendonk, filming the NOVA special "Life's Rocky Start" at the Trendall Locality (3.4 Ga stromatolites in Strelly Pool chert, Pilbara Craton, W. Australia). Image credit: John Valley.

Fig. 3. A group of Madison middle schoolers begin a tour of the UW Geology Museum with EPO Lead Brooke Norsted. The museum's 6-foot diameter globe is a great place to launch astrobiology tours with a discussion of our Earth's place in the Solar System.

Studies of Archean and Proterozoic rocks involved six projects aimed at understanding paleoenvironmental conditions and ancient microbial ecosystems. New studies of Hadean zircons developed the criteria for identifying ancient impact events. New work on continental weathering showed much more extensive weathering >3 Ga than previously thought, which has implications for nutrient delivery to the oceans. Application of laboratory-calibrated "clumped isotope" temperatures was tested in Archean carbonates. Carbon isotope studies using *in situ* analysis of the oldest known organic carbon-carbonate sequences showed autotrophic fixation of carbon by 3.5 Ga. Study of rocks across the Archean-Proterozoic transition documented large changes in methane, sulfur, and carbon cycling prior to oxygen rise, and provided evidence that the first rise in oxygen attained very high levels prior to later decline in the Proterozoic.

Education and Public Outreach (EPO) activities included those aimed at the general public, as well as at the university level. Development of an astrobiology-themed tour of the UW Geology Museum was a major focus, which involved a partnership with the Madison Metropolitan School District to bring middle- and high-school classrooms to the museum for hour-long tours to learn about habitability, biosignatures, Earth's oldest rocks and fossils, among other astrobiology-related topics. Team researchers were involved with a NOVA production in collaboration with other NAI Teams and astrobiologists in Australia. University-based Instruction in astrobiology involved approximately 300 students, including freshman non-science majors, undergraduate science majors, and graduate students.

Team Members

Joost Aerts
Brian Beard
Lucas Berg
Nicolas Beukes
Eric Boyd
Geoffrey Bruce
Kathryn Bywaters
Evan Cameron
Aaron Cavosie
Suvankar Chakraborty
Piyali Chanda
Max Coleman
Morgan Cox
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Huan Cui
Andrew Czaja
Pascale Ehrenfreund
John Eiler
Andreas Elsässer
David Emerson
Yihang Fang
Kay Ferrari
Nathan Fortney
Phil Fralick
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Franklin Hobbs
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Kouki Kitajima
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Stephanie Napieralski
Evan Neidholdt
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Brooke Norsted
Richard Quinn
Eric Roden
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Christopher Romanek
Jane Roughen
Aaron Satkoski
J. William Schopf
Mike Spicuzza
Roger Summons
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Project Reports

Developing Methods for Life Detection on Mars and in Mars Analog Environments

The remarkable discoveries of an early habitable Mars, as revealed by *in situ* observations via rovers, as well as studies of Martian meteorites (including work by the Wisconsin Team), has continued to motivate several research projects on Mars and Mars analog environments. Richard Quinn led research on lipid compositions of samples collected from iron seeps at Chocolate Pots Hot Springs in Yellowstone, which were extracted and analyzed using laboratory GCMS methods. These results were compared to analyses of these samples using a European Space Agency ExoMars flight prototype (the RLS Simulator) at UVA-CSIC-CAB. The aim was to compare the types of information revealed by laboratory GCMS to the Raman ExoMars instrument data as a means of calibrating *in situ* measurements with those traditionally used in terrestrial studies.

Eric Boyd and Eric Roden continued research on iron biogeochemical cycling at Chocolate Pots Hot Springs, where they documented microbial iron reduction using geochemical and isotopic methods, as well as molecular genetic tools. This analysis offers the first detailed insight into how microbial iron reduction may impact the geochemistry and isotope composition of an iron-rich, circumneutral pH geothermal environment, such as those that have been proposed to have existed on early Mars.

In a study aimed at understanding the ancient magnetic field on Mars, which bears on its early habitability, Huifang Xu studied nanophase iron oxides that have exceptionally high magnetic coercivity, which led to the discovery of a new nanomineral, luogufengite (ε-Fe_2O_3), which occurs in basaltic rocks and hence may explain unusual magnetic phenomena observed by the Mars Global Surveyor spacecraft.

Max Coleman led a study of the Sheepbed formation in Gale Crater on Mars, using results from the Curiosity rover, which is the first genuine mudrock known on another planet. These studies document, for the first time, rock sequences on Mars that may be analogous to marine shales on Earth, an important component to understanding the sedimentological and diagenetic features of the rocks that provide estimates of pore-water compositions and hence habitability.

Fig. 4. The image reproduced on the cover of the journal Sedimentology is the Curiosity Rover self-portrait at the first rock-drilling site on Mars, made by combining dozens of exposures taken by the rover's Mars Hand Lens Imager (MAHLI). Image credit: NASA/JPL-Caltech/MSSS.

Biosignatures: Developing the Tools for Detection of Ancient Life and Determining Paleoenvironments

The Team continued to pursue developing new biosignatures via an extensive experimental program. William Schopf focused on the thermal stability of ancient reconstructed enzymes, including nucleoside diphosphate kinase, NDK, which is present in virtually all organisms. Schopf's findings indicate that Earth's photic-zone near surface temperature cooled from ~75 °C in early Earth history (~3 billion years ago) to ~35 °C ~400 million years ago (Fig. 5).

Two projects were pursued that investigated carbonates, which have been found on Mars and are extensively used to infer ancient seawater chemistry in the early oceans on Earth. Christopher Romanek explored the influence of solution composition and CO_2 contents on production of mixed-cation carbonates (Ca-Mg-Fe). He found that Ca-substitution into Fe carbonates might be used as a proxy for atmospheric CO_2 contents, a parameter that is critical to understand on early Earth and Mars in terms of temperatures and habitability. Huifang Xu investigated the role of polysaccharides and extra-cellular polymeric substances in catalyzing dolomite formation. Xu discovered that there is a strong correlation between the spatial distribution of dolomite and organics in "ribbon rocks" (laminated carbonates), with sharp boundaries, supporting the hypothesis that biomass promotes dolomite growth.

Brian Beard focused on developing new stable isotope proxies for weathering and biological processes. Stable potassium isotopes (^{39}K, ^{40}K, ^{41}K), impossible to analyze with conventional mass spectrometers, were studied using a collision-cell based instrument, and significant variations were found across different weathering products, authigenic minerals, and seawater, indicating that K isotopes are a promising new proxy for weathering of silicate minerals. In a second project, Beard found that stable Si isotopes (^{28}Si, ^{29}Si, and ^{30}Si) were uniquely fractionated during microbial reduction of Fe(III)-Si gels as compared to abiological processes; this result suggests that the unusual Si isotope compositions of ancient marine iron-chert deposits may require a biological origin.

Finally, two projects led by Max Coleman and John Valley were dedicated to developing new analytical technologies including tunable IR laser spectrometry, for rover-based *in situ* analysis, as well as secondary ion mass spectrometry (SIMS), for *in situ* analysis of samples returned from Mars.

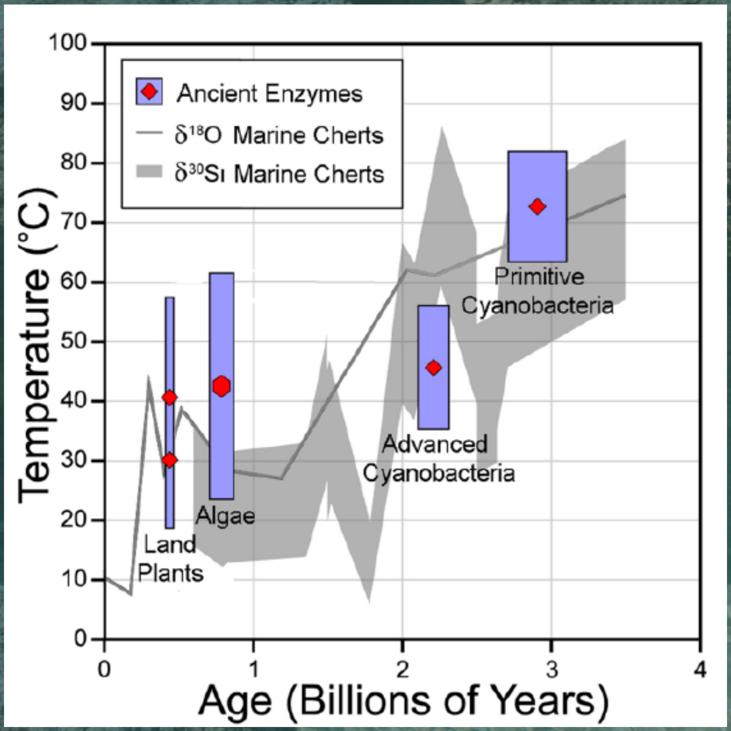

Fig. 5. Changes in Earth's photic zone temperature over geological time inferred from the thermal stability of enzymes reconstructed from the last common ancestors of primitive cyanobacteria, advanced cyanobacteria (nostocaleans), green algae, and land plants. For comparison, the temperature ranges of the shallow oceans suggested by the isotopic composition of marine cherts is shown. Image credit: William Schopf.

Life Detection in the Ancient Terrestrial Rock Record

We focus on early Earth because it remains the only known example of life's origin and evolution, and it provides an interpretive context for the search for life on other planets. Two projects were pursued that explored the habitability of the earliest Earth (Hadean and early Archean). Aaron Cavosie's work is aimed at determining the frequency of shocked zircons in the Hadean, which would indicate large planetary impacts. To calibrate this approach, he studied zircon suites from the U.S., South Africa, and Australia, and this work showed that distinguishing possible shock features from other features in zircons, such as those produced by radiation damage from *in situ* decay, requires detailed microscopic study (Fig. 6).

Clark Johnson led an effort to re-evaluate the Sr isotope evolution of seawater in the Archean, and found that much higher $^{87}Sr/^{86}Sr$ ratios characterize early Archean seawater, indicating more extensive continental weathering than previously thought, which indicates that Earth's early biosphere may have had much higher levels of nutrient delivery than initially assumed. The temperature of the ancient oceans is a topic of great debate, and an approach that is complementary to that based on enzymes (above) is the temperature dependence of stable isotope fractionations. Clark Johnson led an effort to apply the "clumped" isotope thermometer, based on preferential clumping of ^{13}C-^{18}O in carbonates, to Archean carbonate sequences. He found that the thermal history of the carbonates can reset primary isotope clumping, which, although this adds complexity to inferring ancient temperatures, may be of great value in studies of organic matter and its thermal history.

Direct measurement of the early biosphere comes from studies of microfossils and organic carbon, and John Valley led a study of the oldest known stromatolites (3.5 Ga) in the Dresser Formation (Australia), where *in situ* analysis by SIMS documented large carbon isotope ($^{13}C/^{12}C$) fractionations between organic carbon and inorganic carbonate. This indicates enzymatic C fixation by photoautotrophs or chemolithoautotrophs, and is not consistent with alternative proposals of a hydrothermal origin for ancient organic matter.

Two projects were aimed at understanding the details of the first oxygenation event on Earth across the Archean-Proterozoic boundary. John Valley's team combined scanning electron microscopy (SEM) and SIMS to analyze C and S isotopes in a textural context, including mass-independent S isotope variations that constrain atmospheric oxygen contents. Their targets were the Tumbiana, Mount McRae, and Jeerinah Formations of Western Australia, where they found that methane and sulfur metabolisms were closely connected, in part explaining mass-independent S isotope fractionations that became dampened in the late Archean. Clark Johnson led an effort at determining U-Th-Pb geochronology of deep weathering associated with the "Great Oxidation Event" (GOE), and showed complete removal of U on the continents at the same time atmospheric oxygen contents are thought to have temporarily approached modern levels based on C isotopes in marine carbonates, supporting the idea of unusually high levels of oxidative weathering during the GOE.

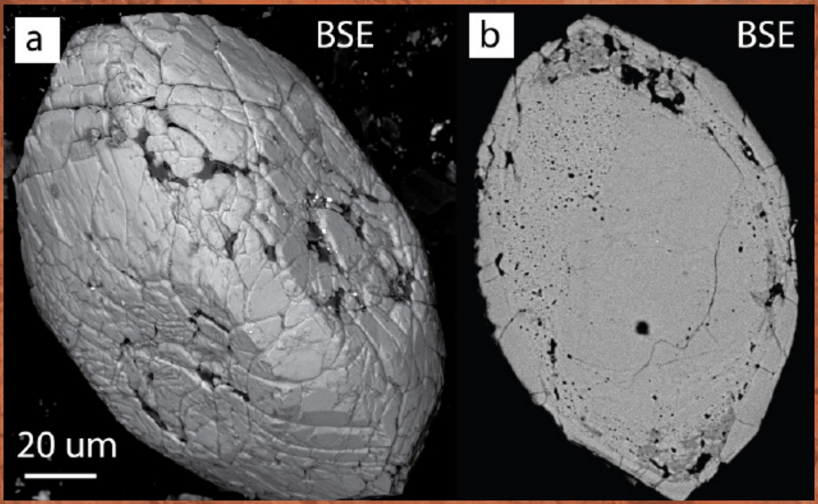

Fig. 6. A) SEM image of a Jack Hills detrital zircon with microstructures indicative of shock deformation. B) Polished SEM image of the same grain shown in (A), demonstrating that the features visible on the surface are not penetrative, and therefore do not record shock deformation. The features visible in this grain are likely a result of natural radiation damage accumulated over time, a process also referred to as metamictization. Image credit: Aaron Cavosie

Fig. 7. The steamy volcanic vent at Chocolate Pots Hot Spring in Yellowstone National Park, an iron-rich, but relatively cool "hot spring" that supports an active dissimilatory iron-reducing microbial community.

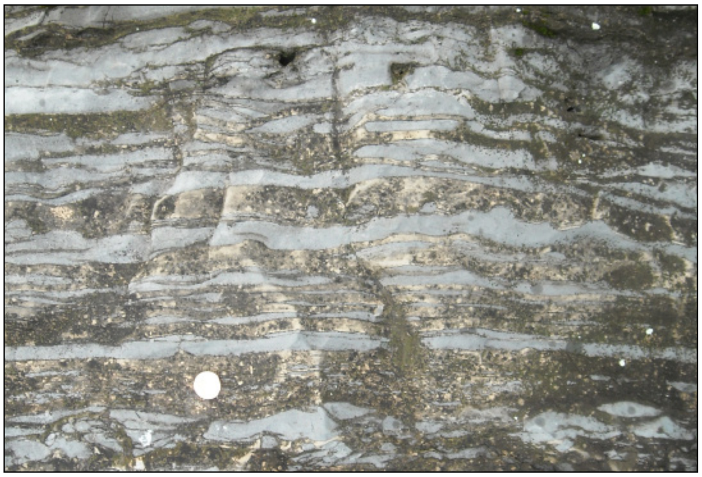

Fig. 8. A "ribbon rock" from Conococheague Formation (upper Cambrian) in Maryland showing oscillatory dolomite (tan) and calcite (light grey) layers, which formed by preferential dolomitization in the microbial biomass-rich layers.

Fig. 9. Ph.D. student Nick Levitt prepares to collect dolomite sample of the 2.6 Ga Campbellrand carbonate, South Africa, for clumped-isotope analysis to determine paleo-ocean temperatures and thermal history of the carbonate.

Field Work

Searching for Biosignatures and Paleoenvironmental Indicators in Modern and Ancient Environments.

Field-based geologic studies provide an opportunity to test ideas on habitability and life signatures developed in the laboratory, and geological studies by our Team encompass both modern and ancient environments.

In 2016, field work included studies in Mars analog sites in Yellowstone and the Atacama Desert. Work on Chocolate Pots springs (Fig. 7) was aimed at understanding the potential for dissimilatory microbial iron reduction and associated iron isotope fractionation, and was accompanied by extensive molecular biology analysis. Field work in the Yungay region, centered in the arid core of the Atacama Desert, took advantage of the fact that this is one of the driest natural environments known on Earth. The region is being used a terrestrial environmental end member to test methods for characterizing biomarker preservation and life detection that may be applied to Mars.

Several field-based projects on carbonates were done in 2016, including the Cambrian Conococheague Formation (Fig. 8), to study mixed calcite-dolomite rocks ("ribbon rock") that provides a better understanding of the role that organic molecules may play in producing dolomite. In addition, field work in western South Africa on the 2.6 Ga Campbellrand carbonate platform (Fig. 9) was aimed at sampling this well preserved carbonate sequence for "clumped isotope" analysis to infer the ancient ocean temperatures, as well as thermal history of the sequence. This work helped guide a new drilling program in the Campbellrand rocks in 2016 that is dedicated to organic biomarker studies, and the thermal history revealed by "clumped-isotope" thermometry will be important in the interpretation of biomarker results.

Work was also undertaken in the United States, South Africa, and Australia in the continued search for shocked minerals from known impact craters. This included work at the famous Jack Hills Hadean zircon site in Western Australia, as well as the Vredefort Dome (South Africa), and Meteor Crater (Arizona).

Major field efforts were undertaken in the Pilbara craton of Australia (3.5 to 3.4 Ga rocks) and the Barberton Greenstone Belt of South Africa (3.2 Ga rocks).

Application of stable iron isotopes and uranium-lead geochronology as a tracer of redox conditions and oxygen levels in the ancient oceans continued with new sampling of jaspers in the 3.2 GaMoodies Group (Fig. 10). Results of strontium isotope studies of 3.2 Ga barite deposits in the Barberton Greenstone Belt (Fig. 11) were published in 2016, and this work showed much greater continental weathering at this time than previously thought.

Additional sampling of 3.2 Ga jaspers included continued work on the Manzimnyama Banded Iron Formation, specifically the core that has been made available from the Barberton Scientific Drilling Program, which has provided exceptionally fresh samples (Fig. 12).

Fig. 10. Post-doc Aaron Satkoski prepares to collect jasper sample from the 3.2 GaMoodies Group, South Africa, for analysis of iron isotopes and uranium-lead geochronology, to determine oxygen levels in the early Archean oceans.

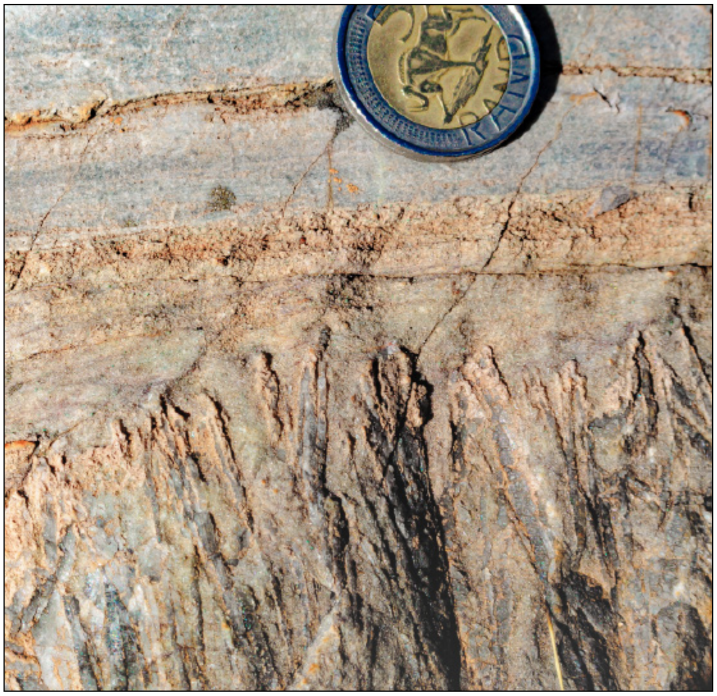

Fig. 11. (Above) Closeup of 3.2 Ga barite (barium sulfate) from "Barite Valley", South Africa. Bladed barite in lower part of image is of hydrothermal origin but layered fine-grained barite in upper part of image is of seawater origin. Study of strontium isotopes in these samples showed extensive continental weathering at 3.2 Ga.

Fig. 12. (Left) Drill core of the 3.2 Ga Manzimnyama Banded Iron Formation, Fig Tree Group, South Africa. In case where deep weathering affects surface outcrops, drill core are essential for studies of elements that are sensitive to oxidation such as iron.

Habitability, Life Detection, and the Signatures of Life on the Terrestrial Planets: 2016 Publications

Aerts, J., P. Ehrenfreund, A. Elsässer, W.F.M. Röling (2016). A contamination assessment of the CI carbonaceous meteorite Orgueil using a DNA-directed approach. *Meteoritics and Planetary Science*, i51: 920–931. DOI: 10.1111/maps.12629

Bentley, M.S., Schmied, R., Mannel, T., Torkar, K., Jeszensky, H., Romstedt, J., Levasseur-Regourd, A.C., Weber, I., Jessberger, E.K., Ehrenfreund, P., Koerberi, C., and Havnes, O. (2016). Aggregate dust particles at comet 67P/Churyumov–Gerasimenko. *Nature* 537:73-75. DOI: 10.1038/nature19091

Cavosie, A.J., Montalvo, P.E., Timms, N.E., and Reddy, S.M. (2016). Nanoscale deformation twinning in xenotime, a new shocked mineral, from the Santa Fe impact structure (New Mexico, USA). *Geology*, v. 44, no. 10, p. 803-806. DOI: 10.1130/G38179.1

Cavosie, A.J., Timms, N.E., Erickson, T.M., Hagerty, J.J., and Hörz, F.P. (2016). Transformations to granular zircon revealed: Twinning, reidite, and ZrO_2 in shocked zircon from Meteor Crater (Arizona, USA). *Geology*, v. 44, no. 9, p. 703-706. DOI: 10.1130/G38043.1

Colman, D.R., J. Feyhl-Buska, K.J. Robinson, K.M. Fecteau, H. Xu, E.L. Shock, and E.S. Boyd. (2016). Ecological differentiation in planktonic and sediment-associated chemotrophic microbial communities in Yellowstone hot springs. *FEMS Microbiology Ecology*. DOI: 10.1093/femsec/fiw137

Di Martino, E., Taylor, P.D., Kudryavtsev, A.B., and Schopf, J.W. (2016). Calcitization of aragonitic bryozoans in Cenozoic tropical carbonates from East Kalimantan, Indonesia. *Facies* 62 (11). DOI: 10.1007/s10347-016-0462-z*

Doglioni, C., Pignatti, J. and Coleman, M. (2016). Why did life develop on the surface of the Earth in the Cambrian? *Geoscience Frontiers* 7 865-873. DOI: 10.1016/j.gsf.2016.02.001

Erickson, T.M., Cavosie, A.J., Pearce, M.A., Timms, N.E., and Reddy, S.M. (2016). Empirical constraints of shock features in monazite using shocked zircon inclusions. *Geology*, v. 44, p. 635-638. DOI: 10.1130/G37979.1*

Ferry, J. M., Stubbs, J. E., Xu, H., Guan, Y., and Eiler, J. M. (2016). Ankerite grains with dolomite cores: a diffusion chronometer for low- to medium-grade regionally metamorphosed clastic sediments. *American Mineralogist*, 100, 2443-2457. DOI: 10.2138/am-2015-5209

Fortney, N. W., He, S., Converse, B. J., Beard, B. L., Johnson, C. M., Boyd, E. S. and Roden, E. E. (2016). Microbial Fe(III) oxide reduction potential in Chocolate Pots hot spring, Yellowstone National Park. *Geobiology*, 14: 255–275. DOI: 10.1111/GBI.12173

Harrold, Z.R., Skidmore, M.L., Hamilton, T.L., Desch, L., Amada, K., VanGelder, W., Glover, K., Roden, E.E., Boyd, E.S. (2016) Aerobic and anaerobic thiosulfate oxidation by a cold-adapted, subglacial chemoautotroph. *Applied Environmental Microbiology*. 82:1486–1495. DOI: 10.1128/AEM.03398-15*

He, S., Tominski, C., Kappler, A., Behrens, S., Roden, E.E. (2016). Metagenomic analyses of the autotrophic Fe(II)-oxidizing, nitrate-reducing enrichment Culture KS. *Applied Environmental Microbiology*. 82:2656-2668. DOI: 10.1128/AEM.03493-15

Lee, S., Shen, Z., and Xu, H. (2016). Study on nanophase iron oxyhydroxides in freshwater ferromanganese nodules from Green Bay, Lake Michigan. *American Mineralogist*. DOI: 10.2138/am-2016-5893

Lee, S. and Xu, H. (2016). Size-Dependent Phase Map and Phase Transformation Kinetics for Nanometeric Iron(III) Oxides ($\gamma \rightarrow \varepsilon \rightarrow \alpha$ pathway). *Journal of Physical Chemistry*. DOI: 10.1021/acs.jpcc.6b05287

Lee, S., and Xu, H. (2016). XRD and TEM studies on nanophase manganese oxides in freshwater ferromanganese nodules from Green Bay, Lake Michigan. *Clays and Clay Minerals*, 64, 488-501. DOI: 10.1346/CCMN.2016.064032

Levitt, N.P. and Romanek, C.S. (2016). An "on-line" method for oxygen isotope exchange between gas-phase CO_2 and water. *Aquatic Geochemistry*, 22, 253 – 269. DOI: 10.1007/s10498-016-9291-5

Li, C., Wang, R., Xu, H., Lu, X., Konishi, H., and He, K. (2016). Interstratification of graphene-like carbon layers within black talc from Southeastern China: Implications to sedimentary talc formation. *American Mineralogist*. DOI: 10.2138/am-2016-5600

Li, W., Beard, B.L., and Li, S. (2016). Precise Measurement of Stable Potassium Isotope Ratios Using A Single Focusing Collision Cell Multi-Collector ICP-MS. *Journal Analytical Atomic Spectroscopy*. DOI: 10.1039/C5JA00487J

Morag, N., Williford, K.H., Kitajima, K., Philippot, P., Van Kranendonk, M.J., Lepot, K., Thomazo, C., Valley, J.W. (2016). Microstructure-specific carbon isotopic signatures of organic matter from ~3.5 Ga cherts of the Pilbara Craton support a biologic origin. *Precambrian Research*. DOI: 10.1016/j.precamres.2016.01.014

Reddy, T.R., Zheng, X-Y, Roden, E.E., Beard, B.L., Johnson, C.M. (2016). Silicon isotope fractionation during microbial reduction of Fe(III)-Si gels under Archean seawater conditions and implications for iron formation genesis. *Geochimica et Cosmochimica Acta*, 190:85-99. DOI: 10.1016/j.gca.2016.06.035

Satkoski, A., Lowe, D.R., Beard, B.L., Coleman, M.L., and Johnson, C.M. (2016). A high continental weathering flux into Paleoarchean seawater revealed by strontium isotope analysis of 3.2 Ga barite. *Earth and Planetary Science Letters*, 454:28-35. DOI: 10.1016/j.epsl.2016.08.032

Schieber, J., Bish, D., Coleman, M., Reed, M., Hausrath, E.M., Cosgrove, J., Gupta, S., Minitti, M.E., Edgett, K., and Malin, M. (2016). Encounters with an unearthly mudstone: Understanding the first mudstone on Mars. *Sedimentology*. DOI: 10.1111/sed.12318

Schopf, J.W., Calca, C.P., Garcia, A.K., Kudryavtsev, A.B., Souza, P.A., Felix, C.M., and Fairchild, T.R. (2016). *In situ* confocal laser scanning microscopy and Raman spectroscopy of bisaccate pollen from the Irati Subgroup (Permian, Paraná Basin, Brazil): comparison with acid macerated specimens. *Review of Palaeobotany and Palynology*, 233: 169-175. DOI: 10.1016/j.revpalbo.2016.03.004

Schopf, J.W., Sergeev, V.N., and Kudryavtsev, A.B. (2016). A new approach to ancient microorganisms: taxonomy, paleoecology, and biostratigraphy of the Lower Cambrian Berkuta and Chulaktau microbiotas of South Kazakhstan. *Journal of Paleontology*. DOI: 10.1017/jpa.2015.56

Shi, B., Liu, K., Wu, L., Li, W., Smeaton, C. M., Beard, B. L., Johnson, C. M., Roden, E. E., Van Cappellen, P. (2016). Iron isotope fractionations reveal a finite bioavailable Fe pool for structural Fe(III) reduction in nontronite. *Environ. Sci. Technol.* DOI: 10.1021/acs.est.6b02019

Śliwinski MG, Kitajima K, Kozdon R, Spicuzza MJ, Fournelle JH, Denny A, Valley JW (2016). SIMS bias on isotope ratios in dolomite-ankerite, Part II: δ13C matrix effects. *Geostandards and Geoanalytical Research*. DOI: 10.1111/j.1751-908X.2015.00380.x*

Śliwinski MG, Kitajima, K, Kozdon, R, Spicuzza, MJ, Fournelle, JH, Valley, JW (2016). On constraining SIMS matrix effects on δ18O measured in the dolomite-ankerite solid-solution, Part 1. *Geostandards and Geoanalytical Research*. DOI: 10.1111/j.1751-908X.2015.00364.x

Taylor, P.D., Tan, S.H.A., Kudryavtsev, A.B., and Schopf, J.W. (2016). Carbonate mineralogy of a tropical bryozoan biota and its vulnerability to ocean acidification. *Marine Biology Research*. DOI: 10.1080/17451000.2016.1203951*

Urschel, M.R., T.L. Hamilton, E.E. Roden., and E.S. Boyd. (2016). Substrate preference, uptake kinetics, and energetics in a facultatively autotrophic, thermoacidiphilic crenarchaeote. *FEMS Microb. Ecol.* DOI: 10.1093/femsec/fiw069

Williford KH, Ushikubo T, Lepot K, Kitajima K, Hallmann C, Spicuzza MJ, Kozdon R, Eigenbrode JL, Summons RE, Valley JW (2016). Isotopic signatures of ancient life and environment at the microbial scale: Neoarchean shales and carbonates. *Geobiology*. DOI: 10.1111/gbi.12163

Zheng, X. - Y., Beard, B. L., Reddy, T. R., Roden, E. E., & Johnson, C. M. (2016). Abiologic silicon isotope fractionation between aqueous Si and Fe(III) – Si gel in simulated Archean seawater: Implications for Si isotope records in Precambrian sedimentary rocks. *Geochimica et Cosmochimica Acta*, 187, 102–122. DOI: 10.1016/j.gca.2016.05.012

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