

News & Views

Biosignatures in Ancient Rocks: A Summary of Discussions at a Field Workshop on Biosignatures in Ancient Rocks

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Preface

A FIELD WORKSHOP, "Biosignatures in Ancient Rocks (BAR)," was held September 17 to September 27, 2007, in Ontario, Canada, under sponsorship of the NASA Astrobiology Institute, the Agouron Institute, the Canadian Institute for Advanced Research, the Ontario Geological Survey, and Laurentian University. Research and education of astrobiology were the primary goals, especially regarding the origin, evolution, and distribution of life on early Earth. Astrobiologists recognize a variety of morphological, mineralogical, and geochemical characteristics in ancient sedimentary rocks and soils that may be used to decipher the history of life and the environment in which it evolved on Earth and possibly on other planets. These signatures of life and biology-related environments (*e.g.*, CH₄ rich or O₂ rich water bodies) are here called biosignatures. They include, but are not restricted to, microfossils and microbialites (stromatolites); carbon skeletons derived from biomolecules (biomarkers); the isotopic compositions of C, N, H and other elements in organic matter; sulfur isotope ratios of minerals; and the relative abundances and isotopic compositions of redox-sensitive elements (*e.g.*, Fe, Mo). Understanding the relationship between a specific signature in a rock and a specific organism or environment it represents is crucial to the search for past early life on Earth as well as on other planets.

Nevertheless, debate continues as to whether some or all of these characteristics are real and original or false and diagenetic. Even comprehensive signatures of life and specific biological environments are problematic for conclusively determining the presence of life. Biosignatures in existing databases were collected from geologic formations that are restricted in both space and time, which further limits their reliability. Therefore, the first objective of this workshop was to determine what we know now about early Earth biosig-

natures, what the remaining major questions and problems are, and how we can answer and solve them. Fifteen senior scientists in the astrobiology field primarily led these discussions: Ariel Anbar, Marilyn Fogel, Katherine Freeman, Hans Hofmann, Heinrich Holland, Clark Johnson, Balz Kamber, Paul Knauth, Donald Lowe, Hiroshi Ohmoto, Shuhei Ono, Bruce Runnegar, Bill Schopf, Dawn Sumner, and Malcolm Walter.

Another major objective was to encourage the next generation of astrobiologists to join in and conduct collaborative, multidisciplinary investigations of geologic formations in various Archean terrains around the world. For this reason, 40 young and active astrobiologists (*i.e.*, professors, research associates, postdoctoral fellows, PhD and master's students from the USA, Canada, England, Denmark, and Japan) who are currently conducting cutting-edge astrobiological science were invited to participate in this workshop (Fig. 1).

Summary of Activities

Bill Schopf and Bruce Runnegar opened the workshop by presenting public lectures at Science North (Science Museum) in Sudbury on September 17. Additional lectures by senior scientists, oral and poster presentations of new research by participants, and working group discussions were held in the Willet Green Miller Center of Laurentian University and Ontario Geological Survey on September 18 and 20. The papers selected by the lecturers for discussion are listed in the workshop website http://psarc.geosc.psu.edu/RESEARCH/New_Conference/Ontario_new.htm. Abstracts of oral and poster papers presented by the participants are presented in the Appendix.

Field excursions were held to examine (1) the Huronian Group in the Elliot Lake area, which encompasses a key sequence for the Great Oxidation Event (GOE) ~2.3 Ga; (2) the

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FIG. 1. Participants of the BAR Workshop at Laurentian University, Ontario, Canada (September 17-20, 2007).

Left. *Front row:* Kate Freeman. *Second row:* Barbara Sherwood Lollar, Marilyn Fogel, Tais Dahl, Juraj Farkas, Don Lowe, Marilyn Vogel, Verena Starke. *Third row:* Adriana Heimann, Bruce Runnegar, Ernesto Pecoits, Gregory Webb, Boswell Wing, Stefan Lalonde, Noah Planavsky, Cynthia Schultz, Dominic Papineau, Tom Weber. *Fourth row:* Jim Cleaves, Neil Banerjee, Clark Johnson, Kurt Konhauser, Simon Poulson.

Right. *Front row:* Hiroshi Ohmoto, Paul Knauth. *Second row:* Dick Holland, Bill Schopf, Ian Johnson, Ariel Anbar, Dawn Sumner, Jane Shen-Miller, Shuhei Ono, Jake Bailey, Dina Bower, Phil Thurston. *Third row:* Phil Fralick, Tsubasa Otake, Niki Parenteau, Penny Morrill, David Wacey, Alison Wright, Balz Kamber, Geoffrey Baldwin, Jim Morran, Chris House.

Those not in the photo: Hans Hofmann, Malcolm Walter, Elizabeth Turner, Yuichiro Ueno, Carra Harwood, Hiroshi Hamasaki, Yumiko Watanabe.

~1.8 Ga Sudbury intrusive, impact structure, impact ejecta, and biosignatures in the Sudbury area; (3) ~2.7 Ga submarine volcanic sequences, including BIFs (banded iron formations), cherts, and black shales in the Temagami–Kirkland Lake–Kidd Creek–Wawa areas; (4) the ~1.8 Ga Gunflint Formation (*i.e.*, BIFs, black shales, carbonates, stromatolites) and the Sudbury impact ejecta and tsunami deposits in the Thunder Bay area; and (5) ~2.9 Ga stromatolites at Steep Rock. The following geologists guided these field trips: Gerry Bennett, Gary Grabowski, David Guindon, Brian Atkinson, Ann Wilson, and Mark Smyk (Ontario Geological Survey), Doug Tinkham (Laurentian University), Phillip Fralick (Lakehead University), Paul Pufahl (Acadia University), William Addison (local geologist), and Ray Bernatchez (consultant). Participants also had the opportunity to sample drill cores at Ontario Geological Survey core storage facilities at Kirkland and Thunder Bay. Guidebooks for these excursions can be accessed at: http://psarc.geosc.psu.edu/RESEARCH/New_Conference/Ontario_new.htm.

The success of the field workshop could be measured by the lively discussions between senior and junior scientists at meals, on long van rides, and in the field. Discussions were held in a very constructive manner, with no one dominating the discussions or imposing his or her ideas. Even though participants realized that they held strong opinions, they genuinely tried to accomplish the goals of “openness” in this workshop. Attendees learned many new things (*e.g.*, microbiologists learned a lot of Precambrian geology, and geologists learned new developments in microbiology), generated many new ideas (*e.g.*, have some biochemical pathways disappeared over geologic time?), and returned home with enthusiasm to carry out new astrobiological research. One measure of the great impact of this workshop was the submission of approximately 100 abstracts, more than half from participants of the BAR Workshop, to several sessions on “Biosignatures” at the 2008 Astrobiology Science Conference in Santa Clara, California.

Below, we present summaries of discussions held at the BAR Workshop. Section I focuses on the current knowledge and questions related to “Biogenicity of ‘Biosignatures’ in Ancient Rocks,” and Section II centers on those related to “Evolution of Life and Environment on Early Life.” Section III summarizes discussions on how to solve the major questions about biosignatures in ancient rocks.

I. Biogenicity of “Biosignatures” in Ancient Rocks

Possible indicators of specific organisms and their environments in ancient rocks include the following: (1) stromatolites, biominerals (*e.g.*, magnetite, pyrite), and microfossils; (2) carbonaceous matter (*e.g.*, kerogen, bitumen, molecular biomarkers) and its chemical and isotopic compositions; (3) redox-sensitive heavy elements (*e.g.*, Fe, Mo, Cu, U, Ce) and their isotopes; and (4) sulfur and its isotopes. Below is a summary of what we know, what the remaining important questions are, and what we can do to answer those questions with regard to issues related to these “biosignatures.”

1.1. Stromatolites, biominerals, and microfossils

Stromatolites represent the activity of many different, biologically diverse communities. They have never been the product of individual species of organisms. Stromatolite

morphology reflects both the environment in which organisms grew and the biota that constructed them. Even more than the tests, shells, and bones of more advanced organisms, stromatolites reflect the interaction of both biota and environment. This added complexity implies that similar stromatolite morphologies may result from the activity of different microbial communities living under similar environmental conditions. Therefore, it is difficult to utilize stromatolites and stromatolite evolution to subdivide Precambrian time.

The known microfossil and stromatolite record (*e.g.*, Walter *et al.*, 1992; Hofmann, 2000; Schopf *et al.*, 2007) fits our tentative understanding of life’s evolution. Based on evolutionary relationships and phylogenetic studies, the inferred taxa, ecology, and metabolism of the oldest microbial remains are consistent with what we perceive the earliest organisms and their metabolisms should have been. However, an important question is how we can better assign domains (or more-restricted other taxa) to microfossils and stromatolites in the geologic record. Currently, the simple morphologies of most microbial microfossils and stromatolites cannot be used as the basis of a taxonomic classification scheme, nor are the criteria for biogenicity of remains unambiguous in many cases (*e.g.*, Hofmann, 2004; Brasier *et al.*, 2006). How can we better interpret biological processes from morphology? For example, can we recognize if photoheterotrophs, as opposed to photoautotrophs, built stromatolites? Were pre-2.2 Ga stromatolites largely created by anoxygenic or oxygenic photoautotrophs?

Most astrobiologists agree that the morphology of many (if not most) stromatolites, minerals, and microfossils is ambiguous and an unclear indicator of biogenicity, because simple shapes can be produced by a variety of both abiotic and biotic processes (*e.g.*, Grotzinger and Knoll, 1999; Brasier *et al.*, 2002; Lindsay *et al.*, 2005). For example, experts attending the field workshop could not agree whether strange “black wiggles” on a bedding surface of ~1.8 Ga sandstone in Sudbury (Fig. 2) were created by biological or abiological



FIG. 2. Don Lowe examining potential ancient biosignatures on a ~1.8 Ga sandstone bedding surface at a location near Sudbury, Ontario.

processes. Similarly, consensus could not be reached on whether the ~2.9 Ga stromatolites at Steep Rock (Fig. 3) were biogenic or abiogenic. Some at the field workshop were opposed to the notion that any stromatolites are biogenic structures; they instead proposed that stromatolites should be viewed as sedimentary structures whose origin varies from abiogenic precipitates to structures with a strong microbial influence. Clearly, additional information and generally different data sets are required to establish the biogenicity of individual stromatolites, minerals, and microfossils. Given the presence of life, important issues include: (a) what taxonomic groups, both known and unknown, were present, (b) which metabolic pathways the organisms utilized, and (c) which environments they inhabited.

1.2. Carbonaceous matter

Not all information about early life is centered on microfossils or stromatolites. The geologic record is full of organic, carbonaceous matter that is perhaps best represented by the variety of carbonaceous particles and laminations seen in black cherts and black shales. These materials are likely of biological origin, and their distribution and morphology can perhaps provide useful information about the ecology and activity of early microbial communities, even in the absence of fossils and stromatolites (Tice and Lowe, 2006).

Recent genomic work has elucidated the biosynthetic pathways for several key lipid compounds (*e.g.*, hopanes and steranes) that are compelling chemotaxonomic biomarkers

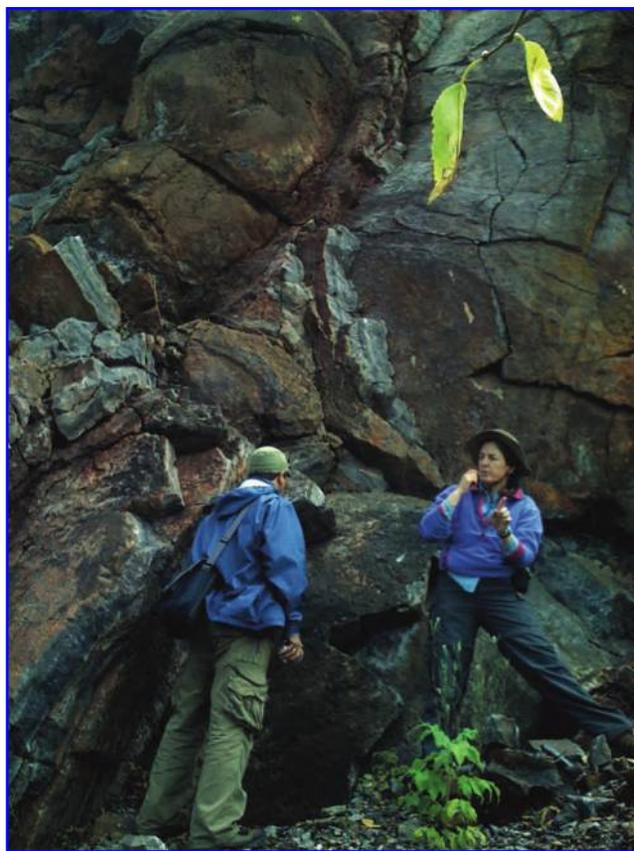


FIG. 3. Dawn Sumner with ~2.9 Ga stromatolites at Steep Rock, Ontario.

(*e.g.*, Dutkiewicz *et al.*, 2006; Eigenbrode and Freeman, 2006; Fischer and Pearson, 2007). Such work has allowed us to determine where in the tree of life and when in the history of Earth the biochemical pathways for their synthesis arose. Both hopanes and steranes have been detected in Proterozoic and Late Archean samples by at least 2 laboratories with MRM-GCMS (*i.e.*, Metastable Reaction Monitoring–Gas Chromatography Mass Spectrometry) instruments, which are required for their positive identification (*e.g.*, Brocks *et al.*, 2003; Eigenbrode, 2007). The recent characterization of these organic materials, including hopanes and steranes, from single fluid inclusions in Proterozoic rocks provides a new approach for investigating such geologic features (Dutkiewicz *et al.*, 2006). Fluid inclusions serve as a potential archive of ancient biosignatures and provide a promising avenue for further research. The key problem in evaluating fluid inclusions and their contents is determining the timing and environment of inclusion formation. Some important issues regarding the use and identification of biomarkers in very ancient rocks are whether some (or most) biomarkers in Archean shales are later contaminants (*e.g.*, Proterozoic petroleum, contamination by drilling fluids) and whether a biomarker is in fact specific to certain organisms (*e.g.*, hopane to cyanobacteria, sterane to eukaryotes) or to a specific environment (*e.g.*, oxic, anoxic, sulfidic).

Numerous possible sources of abiological organic compounds exist in ancient rocks (*e.g.*, Steele *et al.*, 2007); therefore, the ability to differentiate them from degraded or non-degraded biological organic matter is essential. For instance, it is increasingly recognized that there is no biologically indicative “magic value” for carbon isotope evidence, as both biogenic and abiogenic processes can result in a similar range of $\delta^{13}\text{C}$ values (*e.g.*, Lindsay *et al.*, 2005; Alexander *et al.*, 2007; Morrill *et al.*, 2008). However, consideration of isotopic fractionation between different carbon pools does provide information on the formation pathway of organic molecules (*e.g.*, Scott *et al.*, 2006). Yet it is generally agreed that chirality in organic biomarkers may be an excellent biosignature (*e.g.*, Bada, 1995). A robust strategy for the development of compelling lines of supporting evidence for life must incorporate a more detailed knowledge of the abiological baseline.

1.3. Redox-sensitive heavy elements and their isotopes

Over the past decade, major progress in research on paleo-redox conditions of the oceans and atmosphere has come from new proxies that utilize (a) abundance ratios of redox-sensitive elements (*e.g.*, $\text{Fe}^{2+}/\text{Fe}^{3+}$; $\text{S}/\text{C}_{\text{org}}$; $\text{Mo}/\text{C}_{\text{org}}$; $\text{U}/\text{C}_{\text{org}}$; U/Th ; Ce/Ce^* ; Y/Ho) in sedimentary rocks (*e.g.*, Holland, 1984; Kamber and Webb, 2001; Lawrence and Kamber, 2006; Ohmoto *et al.*, 2006b) and (b) their isotope ratios (*e.g.*, Fe, Mo) (*e.g.*, Anbar and Knoll, 2002; Anbar, 2004; Yamaguchi *et al.*, 2005; Johnson and Beard, 2006; Crosby *et al.*, 2007; Planavsky *et al.*, 2008). Rapid advances in isotope geochemistry promise more new proxies. Variations in U and Hg isotopes that are probably related to redox transformations have been published recently (Ridley and Stetson, 2006; Jackson *et al.*, 2008; Weyer *et al.*, 2008), and various groups are exploring the isotope systematics of Re, Ce, and other redox-sensitive elements (*e.g.*, Suzuki *et al.*, 2004; Tazoe *et al.*, 2007; Miller *et al.*, 2008). More traditional approaches, such as the

examination of changes in the sedimentary abundances of redox-sensitive elements such as Mo, Ce, and Eu, are being reinvigorated by new technologies (*e.g.*, inductively coupled plasma mass spectrometry) (*e.g.*, Lawrence and Kamber, 2006; Alexander *et al.*, 2008; Frei *et al.*, 2008).

Important questions surrounding the application of redox-sensitive element geochemistry in astrobiology include, but are not restricted, to: (a) How might the elemental and isotopic systematics of these elements differ between biological and abiological processes? (b) Do the elemental and isotopic systematics of these elements reflect the processes and environmental conditions during sediment (or soil) formation or during a diagenetic, hydrothermal, or metamorphic stage? In what way do the abundances and ratios of elements in sediments relate to the contemporaneous abundances in ancient oceans, and how do various geologic processes (*e.g.*, diagenesis, metamorphism, hydrothermal alteration) affect the preservation of these signals?

1.4. Sulfur and its isotopes

Notable differences exist between Archean and younger sedimentary rocks in bulk-rock $\delta^{34}\text{S}$ and $\Delta^{34}\text{S}_{\text{py-SO}_4}$ ($= \delta^{34}\text{S}_{\text{py}} - \delta^{34}\text{S}_{\text{SO}_4}$) values* (Canfield and Teske, 1996; Habicht *et al.*, 2002; Ohmoto, 2004). This suggests that some fundamental changes in sulfur biogeochemical cycles occurred around 2.4 Ga ago. However, we do not know whether these changes are due to changes in atmospheric chemistry (*e.g.*, GOE); the evolution of S-utilizing microbes (*e.g.*, sulfate-reducing, sulfide-oxidizing, and sulfur-disproportionating bacteria); sulfur chemistry of the oceans (*e.g.*, SO_4^{2-} and H_2S concentrations); the availability of easily digestible organic compounds for S-utilizing bacteria; temperature; or other applicable ocean conditions. Sulfur isotope analyses on individual pyrite grains in some sedimentary rocks using SIMS (secondary ion mass spectrometry) and nano-SIMS have revealed $\Delta^{34}\text{S}_{\text{py-SO}_4}$ values that are identical to those in Phanerozoic sediments (Kamber and Whitehouse, 2007; Wacey *et al.*, 2008); these data suggest that these pyrite crystals formed by sulfate-reducing bacteria in seawater under conditions similar to those in typical Phanerozoic oceans (*i.e.*, possibly high SO_4^{2-} concentration). Analyses of multiple sulfur isotope ratios may provide insights into the detailed mechanisms (pathways) and environments for biogenic pyrite formation (Johnston *et al.*, 2005; Ono, 2008).

Also important are investigations of the sulfide-sulfur and organic carbon contents of Archean shales. The "Canfield Ocean" model (Canfield, 1998), which postulates a global sulfidic ocean beneath the oxygenated photic zone during the period ~ 1.8 to ~ 0.8 Ga, was proposed with an assumption that BIFs did not form during this period; the model was supported by the presence of ~ 1.8 Ga pyritic black shales that overlie the ~ 1.9 Ga Gunflint BIF (Poulton *et al.*, 2004). However, an important question is whether the basic assumption concerning BIFs is justifiable (see Section 2.3.5). The participants of the BAR Workshop were also impressed by the abundance of pyritic black shales in the ~ 2.7 Ga greenstone belts in Ontario. Therefore, it is important to determine whether the similarities and differences in chemical and iso-

topic characteristics of sedimentary rocks reflect local or global signatures.

The origin(s) of SO_4^{2-} in the Archean oceans remains unclear, whether SO_4^{2-} was derived mostly by microbially mediated weathering of pyrite and evaporite under O_2 poor or O_2 rich atmosphere (Farquhar and Wing, 2003; Ohmoto *et al.*, 2006b) or by the UV photolysis of volcanic SO_2 in an O_2 poor atmosphere, as suggested by many investigators who have used multiple sulfur isotopes (Farquhar *et al.*, 2000; Farquhar and Wing, 2003; Ono *et al.*, 2003).

Although it has been almost a decade since its initial discovery (Farquhar *et al.*, 2000), MIF-S (mass-independently fractionated sulfur isotopes) analyses continue to provide interesting new data for discussion and interpretation. MIF-S signatures have been identified when $\Delta^{33}\text{S}$ ($= \delta^{33}\text{S} - 0.515 \times \delta^{34}\text{S}$) values fall outside of $0 \pm 0.2\%$ or $\Delta^{36}\text{S}$ ($= \delta^{36}\text{S} - 1.90 \times \delta^{34}\text{S}$) values fall outside of $0 \pm 0.4\%$ ranges. However, a recent trend is to use a combination of $\Delta^{33}\text{S}$, $\Delta^{36}\text{S}$, $\delta^{34}\text{S}$, $\delta^{33}\text{S}/\delta^{34}\text{S}$, and $\delta^{36}\text{S}/\delta^{34}\text{S}$ values (*e.g.*, Farquhar *et al.*, 2007; Lasaga *et al.*, 2008). Observations so far suggest that MIF-S signatures have been found almost exclusively in sedimentary rocks older than ~ 2.4 Ga in age (*e.g.*, Farquhar *et al.*, 2000; Ueno, 2008; Wing, 2008; Ono, 2008). Most investigators believe that the MIF-S signatures were created by UV photolysis of volcanic SO_2 in an essentially O_2 free and ozone-free atmosphere (*e.g.*, Farquhar *et al.*, 2000; Kamber and Whitehouse, 2007; Ueno, 2008; Wing, 2008; Ono, 2008). Based on MIF-S data, some researchers (Ono *et al.*, 2006b; Philippot *et al.*, 2007) suggest that most pyrite crystals in Archean sedimentary rocks were formed by S^0 reducing bacteria (or by abiological processes) utilizing the S^0 formed during atmospheric UV photolysis of volcanic SO_2 .

However, questions have been raised because no single experiment has captured all the covariation between the sulfur isotopes observed in the Archean rock record. This mismatch is more pronounced when experiments are limited to those conducted with broadband light sources that most closely approximate the solar spectrum (*e.g.*, Poulson *et al.*, 2008); the experimental products typically exhibit much larger $\delta^{34}\text{S}$ fractionations for comparable $\Delta^{33}\text{S}$ variations as those observed in the Archean record. There are also periods (or regions) in the Archean when (or where) the MIF-S signatures are possibly absent, or at least different from those observed in ~ 2.7 – 2.5 Ga black shales in the Pilbara and Kaapvaal Cratons (*i.e.*, large variations in $\Delta^{33}\text{S}$, $\delta^{33}\text{S}/\delta^{34}\text{S} \approx 0.7$, and $\Delta^{36}\text{S}/\Delta^{33}\text{S} \approx -1$) (Farquhar *et al.*, 2000; Ohmoto *et al.*, 2006a; Ono *et al.*, 2006a; Farquhar *et al.*, 2007). There also exist some post-2.0 Ga sedimentary rock samples with abnormal $\Delta^{33}\text{S}$ or $\Delta^{36}\text{S}$ values (Farquhar *et al.*, 2000; Ono *et al.*, 2006b) that warrant further investigations. Finally, shales with strong MIF-S signatures appear to possess distinct geochemical characteristics (*e.g.*, high organic C, abundant siderite, hydrothermal alteration) (Watanabe and Ohmoto, 2008). These questions, together with the discovery of distinctive MIF-S signatures (*i.e.*, $\Delta^{33}\text{S}$ up to $+2.1\%$) in products of thermochemical sulfate reduction experiments (Watanabe *et al.*, 2008), have led some researchers to propose that MIF-S signatures in sedimentary rocks may have been created by chemisorption processes that involve organic matter, minerals, and sulfur-bearing solutions at elevated temperatures during the early diagenetic stage of organic-rich sediments (Watanabe *et al.*, 2006; Lasaga *et al.*, 2008).

*Subscripts py and SO4 refer to pyrite and sulfate, respectively.

The interpretation of MIF-S signals in ancient sedimentary rocks and the relationships of the S isotope records to the evolution of the biosphere are major goals for future research. To attain these goals, it is important that the researchers agree on how to identify mass-independently fractionated compounds. It is essential that we conduct (a) controlled laboratory experiments, both biological and non-biological, to investigate the mechanisms of MIF-S creation, and (b) systematic investigations of S isotope characteristics ($\Delta^{36}\text{S}$, as well as $\Delta^{33}\text{S}$ and $\delta^{34}\text{S}$ values) and the geochemical characteristics of sedimentary rocks that were deposited under a variety of geologic environments, from the Archean to Proterozoic eons. Such investigations may determine whether the variations in $\Delta^{33}\text{S}$ and $\Delta^{33}\text{S}$ — $\Delta^{36}\text{S}$ relationships in Archean sedimentary rocks were due to variations in atmospheric $p\text{O}_2$ or the UV radiation or due to some other processes (e.g., Ohmoto *et al.*, 2006a; Farquhar *et al.*, 2007; Lasaga *et al.*, 2008). Because the products from photochemical experiments may have very different sulfur isotopic compositions from the reactants, it is important that research groups collaborate to determine the accuracies of sulfur isotope analyses, especially on samples with $\delta^{33}\text{S}$, $\delta^{34}\text{S}$, and $\delta^{36}\text{S}$ values that differ from reference materials by more than $\sim 30\%$.

II. Evolution of Life and Environment on Early Earth

Investigations of biosignatures in Archean and Proterozoic rocks have played essential roles in our understanding of the evolution of life and environment on early Earth. Below is a summary of our knowledge and the remaining important questions for future research.

2.1. Origins of life: when and where

Multiple lines of evidence strongly suggest that life goes back to at least 3.5 Ga; living organisms possibly arose >3.5 Ga. In spite of proposals to the contrary and questions that have arisen concerning particular assemblages of putative microfossils or stromatolites (e.g., Hofmann, 2000; Lindsay *et al.*, 2005), most participants of the BAR Workshop agreed that the geologic record was most consistent with the interpretation that life was present and abundant during deposition of the oldest, relatively unmetamorphosed sediments at 3.5 Ga. But the question remains: How much earlier did life evolve on Earth?

Life on Earth probably originated under a reducing atmosphere. However, we do not know (a) whether the early atmosphere was strongly reducing (*i.e.*, rich in H_2 , NH_3 , CH_4 and CO) or mildly reducing (*i.e.*, N_2 rich and CO_2 rich); (b) whether key biomolecules were delivered from elsewhere or synthesized on Earth; and (c) whether the formation of complex organic molecules and emergence of life occurred in shallow water, in non-marine environments, or in deep submarine hydrothermal environments (e.g., Cody, 2004).

2.2. Life and environment on Earth before 3.5 Ga

The chemical and isotopic compositions of Earth's oldest zircons, found as detrital grains in Precambrian sandstones and quartzites, suggest that evolved rocks of broadly granitic composition had started to form on Earth by 4.4 Ga (Li and Lee, 2004; Kamber *et al.*, 2005; Cavosie *et al.*, 2006; Grimes *et al.*, 2007; Menneken *et al.*, 2007; Turner *et al.*, 2007). However, there are questions yet to be answered, as follows:

et al., 2007; Menneken *et al.*, 2007; Turner *et al.*, 2007). However, there are questions yet to be answered, as follows:

- Did these granitic masses evolve into stable cratons (e.g., Lowe and Byerly, 2007)?
- What was the redox state of the mantle before ~ 3.5 Ga?
- How did the continents and oceans grow with time?
- When did plate tectonics begin?
- What was the environment like, and what, if anything, lived on land and in the oceans before ~ 3.5 Ga?

Uncertainties abound because igneous and sedimentary rock formations older than ~ 3.5 Ga have not been found, except in the Isua supracrustals (~ 3.9 to ~ 3.8 Ga). The lack of pre-3.9 Ga rocks may be due to destruction by the Late Heavy Bombardment, subduction, or by the overlying of younger rocks. Sedimentary rocks in the Isua supercrust are too highly metamorphosed and deformed for conventional paleontological and biogeochemical studies.

2.3. Life and environment on Earth during the Archean eon and Early Proterozoic (Neoproterozoic) era

2.3.1. Diversification of organisms. The most energy efficient form of photosynthesis produces oxygen; therefore, understanding the history of oxygen on Earth is tightly coupled to understanding the evolution of biological energy capture. Based on biomarkers and C isotope data on carbonaceous materials in ~ 2.7 Ga shales from Western Australia, many astrobiologists agree that methanogens, cyanobacteria, sulfate-reducing bacteria, and eukaryotes evolved by ~ 2.7 Ga, which implies that they separated genetically into the 3 domains (*i.e.*, Bacteria, Archaea, and Eukarya) before ~ 2.7 Ga (Brocks *et al.*, 1999, 2003; Eigenbrode and Freeman, 2006). However, a question remains as to whether the molecular biosignatures extracted from Archean shales may represent later contamination (e.g., Proterozoic petroleum migration, drilling fluids). Molecular biomarkers from fluid inclusions in the Huronian Group are probably unquestionable evidence for the emergence of cyanobacteria and eukaryotes by 2.2 Ga (Dutkiewicz *et al.*, 2006). The oldest remnant of life on land, probably microbial mats, has been found in a ~ 2.6 Ga paleosol section in South Africa (Watanabe *et al.*, 2000). However, we do not know what constituted the microbial mats (oxygenic photoautotrophs and anaerobic heterotrophs?). Currently, there is no molecular evidence that suggests cyanobacteria and eukaryotes evolved or did not evolve before ~ 2.7 Ga, because most pre-2.7 Ga rocks are highly metamorphosed and unsuitable for biomarker investigations.

2.3.2. Diversification of environment: local and global redox structures of the atmosphere and oceans. There is strong evidence that the atmosphere became oxic by ~ 2.3 Ga when the red beds of the Huronian Supergroup were formed. However, we do not know precisely the level of $p\text{O}_2$ at ~ 2.3 Ga. If the model for the GOE is correct, a major question is why it took ~ 400 Ma (or more) for oxygen to accumulate in the atmosphere, especially if cyanobacteria evolved at (or prior to) 2.7 Ga. Several explanations for the "time delay" have been proposed (e.g., Holland, 2002; Catling and Claire, 2005; Goldblatt *et al.*, 2006; Kump and Barley, 2007), but it is

not clear which of the proposed explanations, if any, are correct. The evolution of oxygenic photosynthesis has been projected to have evolved after anoxygenic photosynthesis, and the evolutionary pathway is complex (Blankenship *et al.*, 2007).

A currently popular view is that the atmosphere was primarily anoxic prior to the GOE and the majority of ocean waters were anoxic, Fe rich, and SO_4^{2-} poor, except locally in "oxygen oases" and evaporating SO_4^{2-} rich basins that developed near shore (*e.g.*, Eigenbrode and Freeman, 2006) and during short-lived, mild oxygenation events occurring before 2.3 Ga (Anbar *et al.*, 2007; Kaufman *et al.*, 2007). Important unanswered questions include the nature of biomass in the surface layer outside the inferred oxygen oases, as well as that in deep, open oceans. Wind, current, and waves must have transported cyanobacteria worldwide. Yet, did anoxygenic photoautotrophs dominate the surface layer while anaerobic heterotrophs controlled deep oceans? What determined the geographic distribution of oxygen oases, and how did it change during the Archean?

Some researchers (Dimroth and Kimberley, 1976; Clemmey and Badham, 1982; Ohmoto, 2004; Ohmoto *et al.*, 2004, 2006b) have suggested that various mineralogical and geochemical data for BIFs, carbonates, evaporites, and paleosols of Archean age are compatible with a hypothesis of early (>3.5 Ga) development of an oxygen-rich atmosphere and SO_4^{2-} -rich, H_2S poor, and Fe poor oceans, except in local anoxic basins analogous to the Black and Red Seas. Pushing back the frontiers of chemical and isotopic biomarker research may help decide which scenario took place. In addition, further prospecting for new Archean-age rocks will help to determine whether multiple scenarios could have occurred.

Important questions concerning the emergence of cyanobacteria include

- How could PSII (Photosystem II) organisms emerge in a world dominated by PSI (Photosystem I) organisms?
- How did PSI organisms respond to the emergence of PSII organisms?
- How did PSII organisms conquer the world?

Another important question is whether other major domains of life, in addition to Eukarya, Bacteria, and Archaea, existed in the Archean and are now extinct.

2.3.3. Climate and greenhouse gas. Global glaciations with possible Snowball Earth scenarios have most likely occurred at ~2.3 Ga (Evans *et al.*, 1997; Kirschvink *et al.*, 2000). However, we do not know whether the 2.9 Ga glaciation was a low-latitude or a high-latitude glaciation, or both, and whether it was local or global in extent (*e.g.*, Young *et al.*, 1998). It is also unknown what initiated and terminated the 2.3 Ga (and possibly 2.9 Ga) low-latitude glaciations or what the effects of such events were on the marine and terrestrial biospheres.

Except during the above glacial episodes, Earth's surface remained warm, possibly much warmer than today (Knauth, 1994, 2005; Knauth and Lowe, 2003; Lowe and Tice, 2004). Because CH_4 is not as effective a greenhouse gas as previously thought, CO_2 (and possibly ethane) may have been the major greenhouse gas compensating for the lower solar flux on early Earth (Kasting, personal communication, 2006).

Outstanding questions concerning climate and greenhouse gas include

- Was the atmospheric $p\text{CO}_2$ much higher than 100 PAL (present atmospheric level) *ca.* 2.5 Ga (Lowe and Tice, 2004; Ohmoto *et al.*, 2004)?
- How did the higher $p\text{CO}_2$ and possibly warmer climate influence the geochemical cycles of bioessential elements and the nature of early biosphere on land and in the oceans?
- What were the processes that caused the atmospheric $p\text{CO}_2$ to decrease to the present level over geologic time?
- How has the evolution of atmospheric CO_2 been linked to that of atmospheric O_2 ?

There also remain fundamental questions about the extent of large continental blocks at 3.5–3.0 Ga (*e.g.*, Lowe and Byerly, 2007) and the temperature of the surface environment within which organisms would have lived. Was it hot (Knauth and Lowe, 2003; Lowe and Tice, 2004, 2007) or was it cold (*e.g.*, Bada *et al.*, 1994)?

2.3.4. Effects of giant impacts. Global-scale redox perturbations have been implicated as a cause of the greatest of the Phanerozoic mass extinctions at the Permian-Triassic boundary (*e.g.*, Korte *et al.*, 2003; Payne *et al.*, 2004; Payne and Kump, 2007; Riccardi *et al.*, 2007). Large-scale redox changes have been suggested in association with other biological and environmental transitions, such as the Cretaceous anoxic events and the Paleocene-Eocene boundary (*e.g.*, Schlanger and Jenkyns, 1976; Tremolada *et al.*, 2007). Redox perturbations caused by giant impact events, such as that at the Cretaceous-Tertiary boundary (Alvarez *et al.*, 1980), may also have been important on early Earth if an oxic/anoxic structure had already existed in the Archean oceans. Progress in understanding the connections between redox changes and massive bio-environmental perturbations requires a better understanding of the giant meteorite impact history (*e.g.*, 1.8 Ga Sudbury impact) and paleo-redox record in ancient sediments (Anbar and Knoll, 2002; Addison *et al.*, 2005). In addition, large impacts may have played a fundamental role in perturbing global surface systems during the Archean, including influencing crustal tectonics, transitory global climates, and sedimentary environments and depositional basins (*e.g.*, Glikson, 2001; Lowe *et al.*, 2003). Assessing the role of large impacts on crustal, surface, and biological evolution during the Archean remains an essential task.

2.3.5. Origins of banded iron formations (BIFs). Most of the giant BIFs are typically thought to have formed between ~2.7 Ga and ~1.8 Ga on shallow continental shelves (*e.g.*, Holland, 1984; Klein and Beukes, 1992). However, BIFs have formed episodically throughout geologic time, from ~3.8 Ga (Isua BIFs) to Phanerozoic time, in a variety of environments (Ohmoto *et al.*, 2006b). For example, participants of the BAR field excursion examined the BIFs that appear to have been deposited in a deep (>2 km) ocean, at near shore, and in deltaic environments. Major issues regarding the origin of BIFs include (a) the role of biology (*e.g.*, Fe-oxidizing bacteria) in the formation of BIFs (Konhauser *et al.*, 2005; Konhauser, 2008); (b) the effects of diagenesis and metamorphism on BIF mineralogy and geochemistry (Morris, 1993;

Otake *et al.*, 2008); (c) the sources of Fe (*e.g.*, deep, open oceans, local hydrothermal discharge, groundwater); (d) the differences in formation mechanisms and environments for oxide-, carbonate-, sulfide-, and silicate-type BIFs; and (e) whether any of the above differ between BIFs of ~2.7 to ~1.8 Ga and those of other geologic ages, and, if so, why?

III. Recommendations

A large portion of the BAR field workshop was devoted to discussions on how to answer major questions regarding biosignatures in ancient rocks and the connections between the evolution of life and environments on early Earth. Below is a summary of recommendations for (1) specific approaches and topics of this research and (2) specific types of support from the NASA Astrobiology Institute (NAI) and other funding agencies.

3.1. Recommendations for research

3.1.1. Understand the geologic context of samples. The geologic context is essential, but often lacking, for samples collected for biosignature studies. There is no substitute for knowing the detailed litho-stratigraphic context of a sample suite, its sedimentary environment, paleogeography, igneous and hydrothermal history, and tectonic setting.

3.1.2. Adopt multiple approaches. It is highly unlikely that any “silver bullet” or “smoking gun” line of evidence will unequivocally be recognized as a biosignature or specific paleoenvironmental indicator. For example, the $\delta^{13}\text{C}$ value of organic matter alone cannot determine whether it is biogenic or abiogenic. Similarly, carbon isotopes in carbonates should not be considered in isolation but should be interpreted in terms of possible co-variations with the oxygen isotopes. Multiple approaches that incorporate investigations of the morphology, texture, chemistry, and isotopes are needed to constrain the nature of organisms and their environmental conditions.

3.1.3. Adopt *in situ* high-resolution microanalyses. It is necessary to utilize state-of-the-art analytical techniques in studying biosignatures in ancient rocks (*e.g.*, Orphan *et al.*, 2001; Schopf *et al.*, 2005; House, 2008; Wacey *et al.*, 2008). Such techniques include (but are not restricted to) confocal laser scanning microscopy, laser Raman spectroscopy, (high performance) liquid chromatography–tandem mass spectrometry, liquid chromatography–gas chromatography–isotope ratio mass spectrometry, metastable reaction monitoring–gas chromatography mass spectrometry, Fish-SIMS (Fluorescent *in situ* hybridization–secondary ion mass spectrometry), nano SIMS, and scanning electron microscopy, high-resolution–transmission electron microscopy, and atomic force microscopy. The development of microanalytical techniques to determine the structure and chemistry of biomarkers and their isotopic compositions from a single microfossil or fluid inclusion will also be invaluable.

3.1.4. Focus on drill core samples. Ideally, ancient rock samples selected for biosignature investigations should be free of post-depositional hydrothermal alteration and modern weathering and contamination. The extrapolation of typical, global conditions from local measurements that could

represent unusual locations or episodes requires understanding the broader geologic context of sedimentary basins. To obtain this context, it is necessary to have (a) a high density of sampling, in both time and space, of sediments deposited during critical time intervals; (b) integrated, multiproxy interrogation of these sediments; and (c) improved age control of key sedimentary sequences. Continuous drill core samples, obtained specifically for paleoenvironmental research, are particularly important as seen in several recent studies (Ohmoto *et al.*, 2006a; Anbar *et al.*, 2007; Farquhar *et al.*, 2007; Kaufman *et al.*, 2007). Future research should take advantage of the numerous drill cores that were recovered from various Archean terranes by mining companies for mineral exploration. Astrobiological drilling targeted at specific geologic formations, with a typical core length of 100–300 m, should be carried out when suitable cores are unavailable.

3.1.5. Capitalize on the extraordinarily well-preserved Archean sedimentary rocks in Ontario. BAR field trip participants were stunned at outcrops that displayed glistening, fresh pyrite characteristic of this recently glacially cleaned erosion surface. They even stood on pyrite beach sands on the north shore of Lake Michigan. The equivalent Archean terranes in Australia are deeply weathered and require drilling to obtain fresh samples. The glaciated outcrops in Ontario have yet to be fully investigated and offer superb opportunities for astrobiologists to study “drill-core fresh,” accessible, and extensive outcrops. Unlike the limitations of drill core samples, these can be taken from outcrops where the complete field context can be ascertained.

3.1.6. Conduct comparative investigations on various Archean terranes. Previous investigations on biosignatures in ancient rocks have been confined to the Kaapvaal Craton of South Africa and the Pilbara Craton in Western Australia. Before ~1.4 Ga, these 2 regions may have been joined (Fig. 4). Therefore, to answer the local vs. global biosignature question (*i.e.*, whether a specific biosignature represents a local or global characteristic), well-coordinated multidisciplinary research in other Archean terranes, such as those in Canada, Russia, India, China, and Brazil, needs to be conducted.

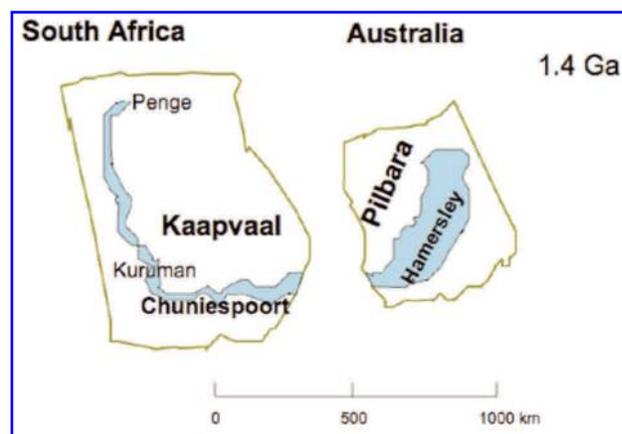


FIG. 4. Paleogeographic reconstruction of the Pilbara and Kaapvaal Cratons at ~1.4 Ga (modified after Cheney, 1996).

3.1.7. Emphasize laboratory experiments. It is extremely important to obtain the fundamental sets of (bio)geochemical data necessary to understand the processes of formation, preservation, and alteration of biosignatures and to assess the validity of many new "biosignatures." Specific issues to be resolved by laboratory investigations will include (but should not be restricted to):

- A. *Abiogenic signatures*: Determine chemical and isotopic characteristics (e.g., C, H, N, O) of organic compounds synthesized abiologically from a variety of starting compounds under a variety of physico-chemical conditions (e.g., T, P, pH, $p\text{CO}_2$). Data from these investigations could become the basis for distinguishing biological and abiogenic signatures in organic materials in rocks.
- B. *Primary biogenic signatures*: Conduct a variety of experiments to assess the elemental requirements for the metabolic pathways of important organisms (e.g., cyanobacteria, Fe-oxidizing bacteria, methanogens, sulfate reducers) under a variety of physico-chemical conditions.
- C. *Alteration of biogenic and abiogenic signatures*: Better characterize the mineralogical, geochemical, and isotopic changes of organic compounds and redox-sensitive elements during diagenesis, hydrothermal, and metamorphic processes.
- D. *Partitioning of redox-sensitive heavy elements and their isotopes*: Determine the biological and abiogenic partition coefficients of redox-sensitive elements (e.g., Fe, Mo, U) and their isotopes between solutions and organic compounds (and minerals) under a wide range of physico-chemical conditions.
- E. *Mechanisms of MIF-S in nature*: Ultraviolet photolysis of SO_2 should be carried out in simulated Archean atmospheres (e.g., H_2 and CH_4 rich atmosphere) with use of broadband UV lamps (Masterson, 2006; Poulson *et al.*, 2008), rather than narrowly focused UV lamps, to investigate self-shielding effects (Lyons, 2007). Such experiments in space stations or on the Moon should be considered. Ultraviolet photolysis of H_2S should also be investigated, because the dominant S-bearing species in volcanic gases on early Earth might have been H_2S , rather than SO_2 . The search for alternative mechanisms to generate MIF-S in sedimentary rocks, such as heterogeneous (surface) reactions involving solid organic matter (e.g., kerogen), minerals (e.g., siderite, goethite) and S-bearing aqueous (and gaseous) species at elevated temperatures (Watanabe and Ohmoto, 2008), should be encouraged. Also important are investigations of multiple S isotope fractionations by a variety of organisms (e.g., sulfate-reducing bacteria, sulfide oxidizers, sulfur oxidizers) under a wide range of conditions (e.g., T, SO_4^{2-} and H_2S concentrations, open vs. closed systems) (Johnston *et al.*, 2005).

3.1.8. Conduct field investigations to complement laboratory experiments.

- A. *Stromatolite diagenesis*: Many, if not most, stromatolites were originally composed of biological materials and carbonate. Phosphate, sulfide, and siliceous varieties are diagenetic in origin. Stromatolites, like other sedimentary materials, are subject to metasomatic processes and

wholesale changes in composition after deposition. Thus, investigations of the effects of diagenesis/metamorphism on texture, mineralogy, and chemistry of stromatolites are important.

- B. *Metamorphic effects on biosignatures*: We should increase our understanding of how chemical and isotopic biosignatures change during metamorphism through field investigations of Proterozoic and Phanerozoic terranes and high T-P laboratory experiments. The knowledge should then be applied in the study of biosignatures in metamorphosed, ancient rocks.
- C. *Stable isotopes in dolomite concretions*: Excellent undeformed dolomite concretions were discovered on the extended BAR field trip in late Archean argillites. Younger examples of such concretions display remarkably large C isotope variations related to O isotope variations and can be interpreted in terms of pore fluid evolution as sediment is buried through the sulfate reduction zone, into the zone of methanogenesis, and then into decarboxylation only (Hennessy and Knauth, 1985). Winter and Knauth (1992) used such variations in a limited sample of Archean examples to argue for the presence of methanogens. Their samples were more metamorphosed than those discovered on the BAR field trip, so this potential isotopic biosignature could be further evaluated at the superb BAR outcrop.

3.1.9. Incorporate geomicrobiology. There is a need for new and improved ways to detect the effects of microbiological processes on sediments and redox proxies, and the effects of redox variations on biota. Progress in this area requires studying key microbiological transformations in the laboratory and in the field, with an emphasis on quantifying biologically mediated reaction rates, as well as research into how geomicrobiological processes are affected by changes in redox conditions. The development and application of proxies for key metabolisms, such as anoxygenic photosynthesis (using Fe^{2+} or H_2S), nitrogen fixation, and denitrification, are also desirable.

3.1.10. Investigate organic matter in meteorites. The assumption that organic matter in meteorites, from simple amino acids and dicarboxylic acids to complex kerogen-like material, was synthesized abiologically in other parts of the Solar System (e.g., tentative reports of evidence of life in SNC meteorites from Mars, *i.e.*, ALH84001) should be actively and vigorously investigated.

3.1.11. Search for pre-3.5 Ga metasediments. Remnants of sedimentary rocks and minerals older than ~ 3.5 Ga in age may be found in (a) xenoliths of younger igneous rocks, (b) younger conglomerates and sandstones, (c) impact breccias in younger sedimentary sequences, and (d) impact breccia on the Moon. Research should aim at conducting geologic surveys worldwide to identify the areas where >3.5 Ga sedimentary formations may be encountered at relatively shallow depths (<10 km) and to recover such rock samples by drilling. These remnants of pre-3.5 Ga metasediments (and minerals in them) are the only materials, besides those in the Isua supracrustal sequence, that may provide useful information about the life and environment before ~ 3.5 Ga.

3.2. Recommendations for support by the NAI and other funding agencies

3.2.1. Continue support for the drilling, curation, distribution, and analyses of the cores. The NASA Astrobiology Institute (NAI), the National Science Foundation (NSF), and Agouron Institute have recently funded continental drilling projects into two of Earth's earliest rock formations in Australia and South Africa. Such efforts should be expanded to other Archean terranes elsewhere in the world.

3.2.2. Develop a database and repository for samples and analyses. Included are programs detailing and comparing isotopic signatures for C, Fe, S, and N in simple molecules (e.g., FeS₂, CH₄, CO₂) to simple organic compounds (e.g., amino acids and hydrocarbons) and to complex molecular structures (e.g., kerogen or macromolecular material containing heteroatoms).

3.2.3. Provide facilities support to broaden access to advanced analyses. This will include both hardware and technical support.

3.2.4. Expand the programs for training young astrobiologists.

- A. *Expand postdoctoral fellowship programs* by selecting additional postdoctorates who are not tied to specific projects.
- B. *Provide more field opportunities* for young scientists to gain good experience and training. The BAR Workshop model is very useful for integrating scientists of different perspectives and experience levels. A comparable workshop should be held annually.
- C. *Expand small grant programs for student field research.* NAI has a field support program—the Lewis and Clark Field Fellowship Program (maximum \$3,000)—for field work in any part of the world, and it funds a limited number of astrobiologists per year, though funding is not sufficient to support all good work that is proposed.
- D. *Create a freestanding annual field camp in astrobiology* (6–8 weeks) that is analogous to the USC/Agouron/NSF International Geobiology Training Course (i.e., the Wrigley Geobiology School).
- E. *Support open-focused, interdisciplinary meetings* to ensure rapid exchange of information and promote synergistic and collaborative interactions among scientists (e.g., PPRG: the Precambrian Paleobiology Research Group).
- F. *Support international collaboration:* Support the efforts of researchers in Canada and other countries to create astrobiology research groups in their own countries, and promote international collaborations in research, education, and public outreach activities.

Looking Forward

The creation of the NAI in 1998 and its continuing commitment to promote astrobiology have been major reasons for the increase in research over the past decade aimed at understanding the origins, evolution, and distribution of life on early Earth, Mars, and other planets. New discoveries in this field have led to the development of many new, though at times controversial, ideas concerning the connection between the evolution of life and environment on Earth and

on other planets. These developments have stirred the interest of many of our brightest students and motivated them to bring fresh ideas to ongoing endeavors in astrobiological research. Those of us who were fortunate to spend many days with these active young scientists (including professors, research associates, postdoctorates, and graduate students) at the BAR Workshop were genuinely impressed and encouraged by their enthusiasm, motivation, and talent. There is no doubt that they will soon find answers to many of the remaining, important questions.

The future of astrobiology is bright.

Acknowledgments

This field workshop could not have been realized without the support of the NASA Astrobiology Institute, the Agouron Institute, and the Canadian Institute for Advanced Research, which have provided the necessary funds; the Ontario Geological Survey, especially Andy Fyon (Director), Gerry Bennett, Gary Grabowski, David Guindon, Brian Atkinson, Ann Wilson, and Mark Smyk, for providing the conference facility, leading field trips, and preparing drill core samples; the Department of Geology of Laurentian University and its staff for providing the facility and various logistic support during the meetings in Sunbury; Doug Tinkham (Laurentian University), Phillip Fralick (Lakehead University), Paul Pufahl (Acadia University), William Addison (local geologist), and Ray Bernatchez (consultant) for leading field trips; and Linda Altamura (Penn State) for handling all the business matter. We also appreciate the comments and suggestions on drafts of this document from Jake Bailey, James Farquhar, Hans Hofmann, Dick Holland, Ian Johnson, Shuhei Ono, Tsubasa Otake, Dominic Papineau, Noah Planavsky, Kate Spangler, and two anonymous reviewers.

Abbreviations

BAR, the "Biosignatures in Ancient Rocks" field workshop; BIFs, banded iron formations; GOE, Great Oxidation Event; MIF-S, mass-independently fractionated sulfur isotopes; NAI, the NASA Astrobiology Institute; NSF, the National Science Foundation; SIMS, secondary ion mass spectrometry.

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Appendix: Abstracts of Papers Presented at BAR Field Workshop

BAR-1. Prospecting for Evidence of Life in Archean Basalts

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Over the past decade, studies of volcanic glass preserved in submarine basalts have demonstrated the importance of endolithic microbes in the alteration process. Newly discovered biosignatures, micrometer-scale mineralized tubes, in the formerly glassy rims of pillow lavas from three Archean greenstone belts, including the Abitibi Greenstone Belt in Canada, suggest they too were colonized by microbes early in Earth's history. These subaqueous volcanic rocks are a new geological setting in the search for early life on Earth. Recent Mars missions have provided new evidence that liquid water once existed on the surface of Mars and renewed interest in the possible presence of palagonite formed by aqueous alteration of basalts as a major component in the martian regolith. Basalts are commonplace on Mars, and the cratered surface likely hosts countless glassy impact breccias and loose fragments that may have interacted with water in the past. This makes terrestrial subaqueous basalts excellent Earth analogues for studies of possible extraterrestrial microbial habitats.

BAR-2. Raman Analysis of Microtextures in Archean Siliciclastic Sedimentary Rocks of the Pongola Supergroup, South Africa

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With the difficulty in proving the biogenicity of microtextures in Archean-aged rocks, it is necessary to use as many lines of evidence as possible. The 2.9 Ga siliciclastic sedimentary Pongola Supergroup in South Africa contains morphological evidence of microbial mats in the form of "Microbially Induced Sedimentary Structures" (MISS). These well-preserved MISS are analogous to those found in modern intertidal siliciclastic environments. In thin sections through those structures, the filamentous textures are displayed, and the fabrics of ancient microbial mats become visible. Raman spectroscopy of these thin sections shows that the filaments are composed of mixed iron oxides, graphitic carbon, feldspars, micas, and quartz. While the host rock contains mainly quartz, feldspars, and micas, the iron oxides and graphitic carbon are only associated with the filaments. The filamentous remains of microbial mats provided a template for mineral growth. Most studies on Archean microfossils are intent on proving biogenicity based on the presence of carbon. Rather than focus only on that aspect, this study characterizes microtextures in terms of morphology and the associated mineralogical content.

BAR-3. Detection of Biomarkers in Terrestrial Sedimentary Sulfate Minerals: Implications for the Search for Evidence of Life on Mars

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The search for evidence of organic compounds, especially those of biological origin, is a major goal of Mars exploration. Strong evidence for evaporitic sulfate minerals such as jarosite on Mars has been found recently. Organic molecules are often co-deposited with salts in terrestrial evaporites. Amino acids can be detected at very low levels using modern analytical techniques, including ones that potentially can be used to carry out spacecraft-based *in situ* analyses. Their distribution and chirality provide a unique biological signature, making amino acids excellent targets in the search for evidence of life on Mars. We report here the detection of amino acids and their degradation products in ancient terrestrial sulfate minerals and their remarkable degree of preservation in such environments. These results demonstrate that biological organic material is well preserved in sulfate minerals on Earth and suggest that they would also be on Mars.

BAR-4. Mo Isotope Variations in Meromictic Lake Cadagno

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Mo isotope systematics can be used to infer the extent of ocean oxygenation in the past. Large isotope fractionation is believed to occur only in oxygenated waters where Mo is soluble.

It has been proposed that adsorption onto Mn oxides exerts an important influence on the isotopic composition of the oceanic Mo reservoir today. Measurements indicate that isotope fractionation was less important between 1.7–1.4 Ga compared to today (Arnold *et al.*, 2004) which is consistent with other lines of evidence for low oxygen levels (Canfield, 1998). However, quantitative interpretation of Mo isotope variations in ancient sediments requires an understanding of how Mo isotopes fractionate in sulfidic environments in which Mo removal from the water column is not quantitative.

The alpine Lake Cadagno in Switzerland offers an opportunity to examine Mo isotope fractionation in a sulfidic water column. Mo exists as the soluble molybdate anion in the oxic surface zone. Mo concentration decreases by 30–50% below the chemocline, where Mo speciation presumably is dominated by particle-reactive oxythiomolybdates. Mo is adsorbed onto organic particles in the sulfidic zone and can be rapidly removed from solution. Isotopically, in the oxic part of the lake we find $\delta^{97/95}\text{Mo} = 0.5\text{--}0.6\text{‰}$, matching the riverine inflow. In contrast, the sulfidic deeper waters are heavier: $\delta^{97/95}\text{Mo} = 1.1\text{--}1.2\text{‰}$.

Two possible mechanisms can explain the isotopically heavy bottom waters. Dolomitic subaquatic springs which carry a heavy Mo component could be dominating $\delta^{97/95}\text{Mo}$ in the deep waters. Alternatively, thiomolybdate scavenged to the sediment could be isotopically light. Improved understanding of Mo isotope fractionation in sulfidic environments such as Lake Cadagno is necessary to interpret the Mo isotope record of the past S.

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BAR-5. Calcium Isotope Record of the Phanerozoic Oceans: Implications for the Chemical Evolution of Seawater and its Causative Mechanisms

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Calcium isotope data from brachiopods of Ordovician to Cretaceous age, complemented by published data from belemnites and planktonic foraminifera, are used to reconstruct the evolution of the seawater calcium isotope composition ($\delta^{44/40}\text{Ca}_{\text{SW}}$) over the Phanerozoic. The compiled $\delta^{44/40}\text{Ca}_{\text{SW}}$ record shows a general increase from about 1.3‰ (SRM 915a) at the beginning of the Ordovician to about 2‰ at present. Superimposed on this trend is a major long-term positive excursion from the Early Carboniferous to Early Permian as well as several short-term, mostly negative, oscillations.

A numerical model of the global cycles of calcium, carbon, magnesium, and strontium was used to estimate whether the recorded $\delta^{44/40}\text{Ca}_{\text{SW}}$ variations can be explained by varying magnitudes of calcium input and output fluxes to the oceans. The model uses the record of marine $^{87}\text{Sr}/^{86}\text{Sr}$ ratios as proxy for seafloor spreading rates, a record of oceanic Mg/Ca ratios to estimate rates of dolomite formation, and reconstructed atmospheric CO_2 , discharge, and erosion rates to estimate continental weathering fluxes.

The model results indicate that varying magnitudes of the calcium input and output fluxes cannot explain the reconstructed $\delta^{44/40}\text{Ca}_{\text{SW}}$ trends. The isotope signatures of these fluxes must also have changed. As a possible mechanism we suggest variable isotope fractionation in the sedimentary output flux controlled by the dominating mineralogy in marine carbonate deposits, *i.e.*, the oscillating “calcite-aragonite seas.” The ultimate control of the calcium isotope budget of the Phanerozoic oceans appears to have been tectonic processes, specifically variable rates of oceanic crust production that modulated the hydrothermal calcium flux and the oceanic Mg/Ca ratio, which in turn controlled the dominant mineralogy of marine carbonates, hence the $\delta^{44/40}\text{Ca}_{\text{SW}}$. As to the causes of the short-term oscillations recorded in the secular $\delta^{44/40}\text{Ca}_{\text{SW}}$ trend, we tentatively propose that these are related to variable rates of dolomite formation and/or to variations in the chemical composition of the riverine flux, in particular $\text{Ca}^{2+}/\text{HCO}_3^-$ and $\text{Ca}^{2+}/\text{SO}_4^{2-}$ ratios, induced by variable proportions of silicate vs. carbonate and CO_2 vs. SO_2 weathering rates on the continents.

BAR-6. Helium and Carbon Geochemistry of Hydrothermal Fluid from SEPR7-32 Degree S

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The Southern East Pacific Rise (SEPR) is one of the fastest-spreading mid-ocean ridges on Earth, with spreading rate of ~14 cm/yr. The SEPR is known for a lot of hydrothermal fields related to active ascent of magma. Volatiles within hydrothermal fluids are delivered from magma degassing. Therefore chemical and isotopic composition of volatiles is strongly controlled by geochemical characteristics of magma, the source. The sampling of hydrothermal vent fluids at SEPR over 25 degrees of latitude reveals broad existence of mantle heterogeneity within ambient mantle flow beneath the SEPR. The factors are CO_2 and He. These gases are thought to be primordial in origin; thus its anomaly was reflected by heterogeneity of mantle. Along the SEPR from 7.4S to 31.8S, we found two significant anomalies in the $\text{CO}_2/{}^4\text{He}$ and ${}^3\text{He}/{}^4\text{He}$ (R/Ra) ratio of the hydrothermal fluids. One is detected around 31.2S and 31.8S, which would be related with influence by Juan Fernandez hot-spot activity, as discussed in Resing *et al.* (2004). The other anomaly in the $\text{CO}_2/{}^4\text{He}$ ratio was not so much drastic but was found in rather a wide region from 17.4S to 21.6S. As Konhäuser *et al.* (2005) demonstrated based on noble gas isotope systematics, mantle heterogeneity caused by contribution from the lower mantle in this region well explains the observed anomalies, because the lower mantle is enriched in CO_2 and ${}^3\text{He}$ compared with the upper mantle. Since this heterogeneity is considered as related with superfast spreading activity of SEPR, our data indicates that enrichments in CO_2 and ${}^3\text{He}$ in the hydrothermal fluids are typical characteristics of hydrothermal systems in such a tectonic setting, which in turn implies that CO_2 flux from the Earth's interior to the ocean could be proportional to the spreading activity.

On the other hand, $\text{CH}_4/{}^4\text{He}$ and $\text{H}_2/{}^4\text{He}$ ratios are likely to be related to the venting temperature. These ratios of the SEPR are typically low corresponding to those of mid-oceanic-ridge environments, as these species are minor species and sensitive to geochemical environment. As Seewald *et al.* (2003) discussed, concentration of these species would be controlled by hydrothermal water-rock interaction or by geochemical conditions just beneath the seafloor. The concentration of CH_4 increased with increasing isotopic temperature calculated by the formula of Bottinga (1969) between $\text{CO}_2(\text{aq})$ and $\text{CH}_4(\text{g})$.

BAR-7. Redox States During the Hadean

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The accretion of the Earth and the formation of its core probably took place in less than *ca.* 50 Myr. During this period metallic iron and Fe^{2+} containing silicates were present in the mantle. The oxidation state of volcanic gases must have been close to that of the iron-wüstite (IW) buffer. At this fO_2

the H_2/H_2O ratio at 1100°C is between 1 and 10 (see for instance Holland, 1984), *i.e.*, these gases were considerably more reducing than volcanic gases today.

After core formation the mantle may have been free of metallic iron. Melting would then have generated magmas with values of f_{O_2} close to that of the fayalite-magnetite-quartz (FMQ) buffer. This is close to the oxidation state of many volcanic gases today, seems to have been close to the average oxidation state of volcanic gases during the past 3.5 Ga (Li and Lee, 2004), and could have been the average oxidation state of volcanic gases during all but the first 50 Myr of Earth history. However, a small amount of metallic iron could have been retained in the mantle during core formation due to incomplete separation of the metallic and silicate phases. If so, volcanic gases would have been buffered close to the f_{O_2} of the IW buffer, at least during the first episode of melting after core formation. The atmosphere would then have been very reducing, perhaps with a composition close to those of the Miller-Urey experiments during the period when life may have originated.

Currently we have no rocks older than 4.03 Ga. However, the 4.0–4.4 Ga zircons from the Jack Hills of Western Australia carry information regarding the oxidation state of the magmas in which they crystallized. With few exceptions they have strong positive Ce anomalies (Cavosie *et al.*, 2006). These are due to the presence of Ce^{4+} in the parent magmas. Ce^{4+} is smaller than Ce^{3+} and is therefore preferentially incorporated in the zircon structure. The magnitude of the Ce excess in most of the pre-4.0 Ga zircons analyzed to date is similar to that in modern zircons from MORs (Grimes *et al.*, 2007). On the other hand, lunar zircons do not have a Ce anomaly (Ireland and Wlotzka, 1992). It is likely, therefore, that the f_{O_2} of the magmas from which the Jack Hill zircons crystallized was much higher than that of the lunar basalts. It is not clear that their f_{O_2} was equal to that at the FMQ buffer, because the magnitude of the Ce anomaly has not been calibrated sufficiently well.

A number of the Jack Hills zircons contain inclusions. Menneken *et al.* (2007) have found 45 zircons which contain diamond and/or graphite inclusions. These suggest that the zircons originated in ultrahigh pressure (UHP) terrains. Neither the YREE pattern of these zircons nor the isotopic composition of the diamond/graphite inclusions has been reported. The presence of the inclusions suggests a relatively low f_{O_2} during zircon growth. However, the suite of inclusions spans the entire age range from 3.06 to 4.25 Ga. This observation does not support the notion of a significant change in the oxidation of the mantle during this period.

Thus, the currently available evidence does not favor a mantle f_{O_2} close to IW during the past 4.4 Ga of Earth history. If life started more recently than 4.4 Ga, it probably did so in an atmosphere-ocean system in which the redox state of volcanic inputs was close to FMQ.

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- BAR-8. Secondary Ion Mass Spectrometry, a Method for Investigating Microorganisms, Past and Present**
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- Secondary Ion Mass Spectrometry, or SIMS, is a powerful method for investigating microorganisms, past and present. In particular, a cell's carbon isotopic composition can be determined. The importance of these techniques is that the cells targeted for study can be environmental species that cannot currently be grown in the laboratory, or they can be ancient microfossils. These techniques promise to become critical for working out the interactions, metabolic activities, and food webs of microorganisms in their natural setting, whether it is sediment, soil, a water column, or an ancient sediment.
- Previous SIMS research has targeted preserved biomass from the Proterozoic (*e.g.*, House *et al.*, 2000; Kaufman *et al.*, 2003) and Archean (*e.g.*, Mojzsis *et al.*, 1996; Ueno *et al.*, 2002; McKeegan *et al.*, 2007) sediments and metasediments. For modern environments, the linking of molecular taxonomy (including 16s rRNA) to environmental geochemistry is a powerful way to work out the interactions, metabolic activities, and food webs of microorganisms in their natural setting, whether it is sediment, soil, or a water column. To this end, we developed a method for coupling an extant microorganism's genetic information with geochemical data derived from the direct analysis of its cell. FISH-SIMS combines fluorescent *in situ* hybridization (FISH) with SIMS (Orphan *et al.*, 2001, 2002). FISH is a culture-independent technique used to visually identify naturally occurring microorganisms by staining their ribosomal RNA. Secondary ion mass spectrometry (SIMS) is a method by which geochemical information can be obtained from microsamples. Using FISH-SIMS, a researcher can measure a target cell's isotopic or elemental composition in a mixed environment.
- Recent advances in instrumentation have aimed at reducing the spatial resolution of the analysis. These advances include the NanoSIMS, as well as the addition of a Ga ion source to the 1270 at UCLA. Also, there has been limited work on using halogenated probes to phylogenetically label cells with a detectable element before SIMS.
- BAR-9. Possible Lateritic Paleosol beneath the Earth's Oldest (~3.42 Ga) Recognized Land Surface in the Pilbara Craton, Western Australia**
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Previously unrecognized Fe pods have been discovered beneath the Earth's oldest (~3.42 Ga) recognized land surface in the North Pole Dome region of the Pilbara Craton, northwestern Australia. In the study area the unconformity separates the predominately felsic-to-mafic volcanics of the Warawoona Group (~3.5 Ga) and the overlying Strelley Pool Chert sediments (~3.43 Ga) and Euro Basalt (3.35 Ga). The Fe rich (~20 to 90 wt%) pods occur below and parallel to the unconformity surface in a clay-rich alteration zone within the currently vertically tilted Warawoona Group. The Fe pods are 1–6 m thick by 1–50 m long, well crystalline ferric-enriched bodies that form horizons up to 150 m in length along strike. These horizons have been located at 7 separate sites that span a ~30 km linear distance across the craton. At two of these locations the Fe rich horizons visibly dip steeply into the plane of the present groundwater table. Within the alteration zone, the pods are bounded sharply at the top by a pyrophyllite/sericite-rich horizon and gradationally at the bottom by a chlorite-rich horizon. Below the unconformity the felsic-to-mafic volcanic rocks show mineralogical, petrographic, and chemical changes that are consistent with a top-down weathering profile. With decreasing depth from the unconformity contact, these changes are accentuated by (1) a disappearance of rock texture, (2) depletion of major cations (except K), and (3) as much as 80% rock mass loss. Past researchers have attributed the alteration zone to the downward circulation of hydrothermal fluid associated with the emplacement of the Euro Basalt (Van Kranendonk and Pirajno, 2004). We developed a set of 24 criteria from field observations to determine the relationship between the alteration processes and associated Fe pods. These criteria are compared against the expected characteristics of 11 processes, including *in situ* weathering, hydrothermal alteration, and sedimentary accumulation under both oxic and anoxic conditions. The chemical and physical characteristics of the alteration and Fe pods are also compared to the ~2.2 Ga Hekpoort lateritic paleosols in South Africa–Botswana, well-developed and characterized Precambrian analogues for *in situ* weathering. The results indicate that the alteration and Fe mineralization in the North Pole Dome region beneath the Earth's oldest recognized land surface may be the by-product of ~3.42 Ga pedogenic and groundwater-type lateritic paleosol formation.

BAR-10. Anaerobic Microbiological Processes in BIF Deposition

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Precambrian banded iron formations (BIFs) have been studied for decades, particularly regarding their potential as archives of the early Earth environment. In spite of this effort, the mechanism(s) of their deposition, and in particular whether microorganisms drove the precipitation of BIF minerals, is still uncertain. Increasing evidence of an anoxic Earth until ~2.5–2.4 Ga forces the investigation of O₂ independent mechanisms for much of BIF deposition. For this reason, re-

cent studies have explored the long-standing proposition that BIFs may have been formed and transformed by anaerobic microbial activities, specifically Fe(II)-based photosynthesis, known as photoferrotrophy.

Although there is no actual physical or chemical evidence for the existence of Fe(II)-oxidizing phototrophs in the Archean oceans, 6 independent lines suggest their potential role in BIF deposition.

- (1) While the plausibility of an anoxygenic Fe(II)-oxidizing metabolism had long been speculated based on thermodynamic considerations (Hartman, 1984), such organisms have only recently been discovered (*e.g.*, Widdel *et al.*, 1993). We now know that a number of purple and green phototrophic bacteria, both freshwater and marine, can use Fe(II) as a reductant for CO₂ fixation.
- (2) Of the seven known strains of photoferrotrophs, six of them have been classified as *Proteobacteria*. Parsimony and distance analysis of photosynthesis genes places bacteriochlorophyll biosynthesis before the rise of chlorophyll biosynthesis and specifically sets purple bacteria at the root of photosynthetic evolution (Xiong *et al.*, 2000). Given the evidence for cyanobacteria at 2.7 Ga (Buick, 1992), it is then likely that photoferrotrophs existed at the onset of major BIF deposition.
- (3) In Archean oceans, phototrophic bacteria would not have had widespread access to H₂S/HS⁻ or H₂ as electron donors. This leaves dissolved Fe(II) as the most available reductant for anoxygenic photosynthesis.
- (4) Recent analysis of the 1.6 billion-year-old Barney Creek Formation in northern Australia, a subtidal marine deposit, yielded okenane, the fossil hydrocarbon biomarker of the precursor, okenone. This carotenoid pigment is exclusively found in purple sulfur bacteria and in recent sediments under euxinic conditions (Brocks, 2005).
- (5) Laboratory experiments aimed at defining ⁵⁶Fe/⁵⁴Fe isotopic fractionations by anoxygenic Fe(II)-oxidizing phototrophs in pure culture show that the ferric hydroxide products are enriched in the heavy isotope by 1.5 +/– 0.2‰ relative to dissolved Fe(II) (Croal *et al.*, 2004). These modern experiments correlate well with values recovered from Archean to early Proterozoic BIF of the Transvaal Supergroup, South Africa (Johnson *et al.*, 2003).
- (6) Ecophysiological studies of modern strains of photoferrotrophs have been utilized to test their plausibility as a BIF depositional mechanism, with specific regards to the carbon and Fe(III) oxide productivity. Models and experiments have shown that photosynthetic Fe(II) bacteria could have accounted for all of the Fe(III) initially deposited in BIF sediment (Konhauser *et al.*, 2002; Kappler *et al.*, 2005).

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BAR-11. Decoupling Photochemical Fe(II) Oxidation from Shallow-Water BIF Deposition

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Oxidized Fe minerals in Archean-Paleoproterozoic banded iron formations (BIFs) are commonly taken to indicate the presence of biogenic O₂ or photosynthetic Fe(II)-oxidizing bacteria in the oceans' photic zone. However, at least one viable abiogenic oxidation mechanism has been proposed. Prior to the rise of atmospheric oxygen and the development of a protective ozone layer, the Earth's surface was subjected to high levels of ultraviolet radiation. Bulk ocean waters that were anoxic at this time could have supported high concentrations of dissolved Fe(II). Under such conditions, dissolved ferrous iron species, such as Fe(OH)⁺, would have absorbed radiation in the 200–400 nm range, leading to the formation of dissolved ferric iron [Fe(III)], which, in turn, would have hydrolyzed to form ferric hydroxide [Fe(OH)₃] at circumneutral pH (Cairns-Smith, 1978; Braterman *et al.*, 1983). This process has been invoked to account for BIF deposition without need for biology (François, 1986). We evaluated the potential importance of photochemical oxidation using a combination of experiments and thermodynamic models. The experiments simulated the chemistry of ambient Precambrian seawater mixing with Fe(II)-rich hydrothermal fluids with, and without, UV irradiation. We found that if Fe(II) was effused from relatively shallow seamount-type vent systems directly into an anoxic photic zone, the photochemical contribution to solid-phase precipitation would have been negligible. Instead, most of the Fe(II) would have precipitated rapidly as an amorphous precursor phase to the ferrous silicate mineral greenalite

[Fe₃Si₂O₅(OH)₄], and/or the ferrous carbonate, siderite (FeCO₃), depending on different simulated atmospheric pCO₂ levels. Conversely, in experiments where Fe(II) was exposed either to phototrophic Fe(II)-oxidizing bacteria or to O₂, ferric hydroxide formed rapidly, and the precipitation of ferrous iron phases was not observed. If, as suggested on mass balance grounds, BIF deposition requires that Fe be sourced from shallow seamount-type systems, we are driven to conclude that oxide-facies BIFs are the product of a rapid, non-photochemical oxidative process, the most likely candidates being direct or indirect biogenic oxidation, and that a significant fraction of BIFs could have initially been deposited as ferrous minerals, only later to be oxidized.

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BAR-12. Partitioning of P, V, Mo, and Ni during Precipitation of Ferric Oxyhydroxides and Implications for Archean Ocean Nutrient Availability during BIF Deposition

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During the Archean and Paleoproterozoic, large amounts of iron precipitated from seawater to yield Banded Iron Formations (BIF). It has been argued that during this time, the presence of abundant and highly reactive iron oxyhydroxides may have limited critical nutrients as a consequence of various adsorption and co-precipitation processes. These arguments have previously centered on the role of phosphorus, which is currently a major nutrient controlling the degree of ocean productivity. In this study, we add to the debate regarding nutrient availability in the ancient oceans at the time of BIF deposition by evaluating the degree to which ferric oxyhydroxides may sequester aqueous Mo, Ni, and V; these transition metals act as enzymatic co-factors that are critical, and at times limiting, for specific biological functions in modern microbes. Furthermore, it is generally assumed that dissolved silica was more abundant at the time of BIF deposition. As dissolved silica may influence elemental partitioning through a combination of competitive surface adsorption and co-precipitation processes, we also consider its role in the sequestration of these nutrients into iron oxyhydroxides. Finally, we evaluate our experimental data in light of the concentrations in which these elements are found in BIF, and estimate their degree of availability in ocean water at the time of BIF deposition.

BAR-13. Distinguishing Biogenic from Abiogenic Reduced Carbon—Reconsidering a Biosignature Paradigm

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Reduced carbon has been detected in the atmospheres of astrobodies such as planets and moons, and in meteorites. Reduced carbon can be a product of biological activity and can thus signal the presence of current or past life. However, abiogenic processes including hydrothermal reactions can also produce reduced carbon. Of these reactions, serpentinization is of particular interest. Through hydration of ultramafic rock this process produces hydrogen gas and the reducing conditions necessary for abiogenic hydrocarbon synthesis but also produces conditions amenable for chemolithotrophic life. Serpentinization is a suspected source of hydrocarbons detected on Mars, Titan, and Europa, and may have played an important role in the prebiotic chemistry of early Earth.

The Cedars, located in Northern California, is a terrestrial site of active serpentinization. Hydrocarbon gases are bubbling from ultra-basic reducing springs. The origins of these gases were identified by comparing geochemical indicators of abiogenic hydrocarbons produced from hydrothermal experiments and traditional indicators of biogenic hydrocarbons.

This research challenges the pre-existing assumption that hydrocarbons which are depleted in ¹³C are solely biogenic in origin. I have both synthesized abiogenic hydrocarbons, and demonstrated that these abiogenic reactions produce ¹³C depleted hydrocarbons similar to those produced by biogenic reactions; this depletion mimics the classic “biosignature.” This research demonstrates how a multiple-lines-of-evidence approach should be applied to determine the source of hydrocarbon gases on early Earth and other astrobodies.

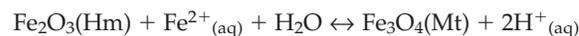
BAR-14. Non-Redox Transformation of Hematite to Magnetite in BIFs under Hydrothermal Conditions

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Magnetite (Fe₃O₄) and hematite (Fe₂O₃) are the two most abundant iron-bearing minerals in Banded Iron Formations (BIFs), particularly for oxide-type BIFs (e.g., ~2.7 Ga Temagami BIF, Canada). Most previous researchers have

thought that the magnetite was transformed from hematite by redox reactions with organic carbon. However, the availability of reductants in BIFs appears to have been too low to account for the transformations of iron oxides through redox reactions.

Here, we report the results of hydrothermal experiments in mildly acidic and H₂ rich aqueous solutions at 150°C, which demonstrate that transformations of hematite to magnetite (and vice versa) occur rapidly without involving reductants (or oxidants):



The transformation products are chemically and structurally homogeneous and typically occur as euhedral single crystals much larger than the precursor minerals.

Petrographic observation of hematite and magnetite in Temagami BIF reveals that the two minerals always coexist in either hematite-rich layers or magnetite-rich layers. Grain size of magnetite is much bigger than hematite, suggesting that hematite [or ferric (hydr)oxides] was a primary mineral and magnetite was formed after hematite. Iron isotope analysis of magnetite and hematite in both BIFs and our experimental products will give us more direct information on whether redox or non-redox reaction was responsible for transformation of hematite to magnetite in BIFs.

BAR-15. Apatite-Graphite Associations in Precambrian BIFs

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Banded iron formations (BIFs) are a common rock type in Archean sedimentary sequences and can be described as Fe rich chemical precipitates characterized by alternating layers of Fe rich and Si rich minerals. Although their existence has been known for more than a hundred years, their origin is still not well understood. Occurrences of microscopic apatite grains associated with graphite in Precambrian BIFs of various ages are common but have not been systematically studied and analyzed by micro-analytical techniques. In this contribution, we report preliminary geochemical analyses of graphite associated with apatite in 3.83 Ga granulite facies BIFs from the Akilia Association, in 2.72 Ga prehnite facies BIFs from the Abitibi Supracrustal Belt, and in 1.85 Ga lower greenschist facies BIFs from the Marquette Supergroup. Observations by optical microscopy of apatite-graphite associations in Akilia BIFs reveal that the microscopic graphite masses have a platy appearance and silvery reflections. Chemical analyses by WDS and X-ray maps generated by SEM and EPMA show that graphite occurs as micron-size inclusions, coat-

ings, and invaginations in apatite crystals ranging in size between 25 and 80 microns. Laser confocal Raman microspectroscopy enables *in situ* analysis of graphite in apatite crystals situated below the surface of the analyte, thereby avoiding issues related to contamination. Raman analyses of dozens of graphite inclusions and coatings in apatites from Akilia BIFs reveal sharp and prominent “G bands” accompanied by small “D bands,” which attests to the high metamorphic grade of the rock. To avoid sample contamination, we have performed FIB (focused ion beam) extractions of thin slices of the apatite-graphite associations in Akilia BIFs. TEM analyses help to characterize the chemical composition of the graphite, while SIMS allows for stable isotopic analyses and mapping to further characterize the graphite. In light of our geochemical data, we will discuss the possibilities that this graphite may be nonbiological or biological in origin.

BAR-16. Linking Metabolism to Biosignatures: the Role of Phototrophs in Fe²⁺ Oxidation and the Formation and Preservation of Their Biosignatures in a Modern Iron-Depositing Thermal Spring

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Debate exists regarding whether abiotic or biotic mechanisms were responsible for the oxidation of Fe²⁺ and the subsequent accumulation of Fe³⁺ assemblages in Precambrian Banded Iron Formations (BIFs). Direct paleontological evidence for a microbial role in the deposition of BIFs has been sought in the occurrence of biosignatures in these structures. The interpretation of this suite of fossil information relies on comparison to extant taxa. This helps to infer the physiology of ancestral organisms and how their metabolism may have altered the paleo- and macroenvironment.

This comprehensive study attempted to establish a direct link between phototrophs, metabolism, and biosignatures in a modern iron-depositing thermal spring. The source waters of Chocolate Pots hot springs in Yellowstone National Park are devoid of O₂ and H₂S, rich in Fe²⁺ (4.7–5.9 mg/L) and Mn (1.4–1.6 mg/L) and are populated by cyanobacteria and anoxygenic phototrophs. Chocolate Pots is not a structural model for the deposition of most Precambrian BIFs. However, it can be considered one of the very few modern analogues of a high-iron anoxic environment populated by phototrophs and exposed to light on early Earth. Thus, it can be treated as a geochemical model of Precambrian Fe²⁺ oxidation.

The role of cyanobacteria and anoxygenic phototrophs in Fe²⁺ oxidation was quantified *in situ* with the use of microelectrodes; and their microfossils, stromatolitic biofabrics, and lipid biomarkers were characterized with optical, scanning electron, and transmission electron microscopy, as well as electron diffraction, X-ray diffraction, and lipid and compound-specific stable carbon isotope analyses.

The *in situ* Fe²⁺ oxidation rate per cell was determined. TEM examination of the cyanobacterial cells revealed iron-mineralized carbonaceous microfossils that retained taxonomic features that allowed their identification to the genus and sometimes species level. A robust suite of geologically significant lipid biomarkers (most notably 2-methyl-bacteriohopanepolyol) were identified and linked to the phototrophic source organisms. These biomarkers were found to survive microbial degradation and the earliest stages of diagenesis in the iron oxide deposits underneath the mats.

This suite of biosignatures can be used to link modern microbial ecosystems to their fossilized equivalents preserved in the geologic record. This type of fossil evidence can be used to infer the paleobiological role of microbes and paleoenvironmental conditions and will establish a means to assess the microbial contribution to ancient iron deposits on Earth (*e.g.*, BIFs) and, potentially, to those found on Mars.

BAR-17. Ni in Banded Iron Formations: Its Origin and Potential Evolutionary Implications

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It has been suggested that the elemental composition of Precambrian banded iron formations (BIFs) provides important clues to ancient seawater composition and the primary productivity of the oceans. Although most previous studies have focused on major nutritional elements, there is relatively little information on enzymatically important trace metals. Accordingly, in this work, we have analyzed various trace elements in the 2.5 Gyr Dales Gorge BIF of the Hamersley Group in Western Australia and compared their concentrations in different mineral assemblages.

Of the many metals analyzed, one of the most interesting findings was the strong inverse correlation between Ni and Fe; that is, the higher concentrations of Ni are accompanied by lower values of Fe. When our data was then compared to other BIFs, we observed distinct temporal variations, with Algonoma-type BIFs of early Archean age from Isua having the highest Ni values, whereas younger Paleoproterozoic Lake Superior-type BIFs (Kuruman–Griquatown sequence and Dales Gorge Member) and Neoproterozoic Rapitan-type iron formations (Rapitan, Braemar, and Urucum) display medium and low Ni concentrations respectively. There are three possible explanations for this pattern based on Ni sources. They include (1) cosmic, (2) continental, and (3) hydrothermal.

Ni is ubiquitous in extraterrestrial materials, and ferromagnetic cosmic microspherule layers have been found in modern and ancient deep-sea sediments. Based on iridium anomalies and shocked quartz in spherule layers associated with the Dales Gorge and Marra Mamba BIFs, it has been previously suggested that impact events would have played a major role during the Early Archean. High Ni values have also been reported in Archean to Early Proterozoic marine shales, indicating an ultramafic dominated source. Whether the source is continental or submarine is unclear given that Ge/Si ratios in BIFs suggest a strong continental source for some components such as silica, yet the low amounts of lith-

ogenous elements such as Al_2O_3 , TiO_2 , and K_2O in these bands suggest the absence of a major continental source. This, however, does not rule out the possibility of a continental source for a fraction of total Ni. In fact, whereas Fe, Al, Ni, Ti, and P are trapped together in modern laterites, in an oxygen-free atmosphere, Fe, Ni and P would likely have been more mobile, leaving behind Al rich clays as the residuum.

Hydrothermal activity along spreading ridges and vents induces serpentinization of oceanic crust composed of basic and ultrabasic rocks. Due to the reducing conditions during hydrothermal hydration of Mg-olivine and orthopyroxene, transition metals (including Ni) will be emitted in variable proportion depending on the $f\text{O}_2$ and $f\text{S}_2$. In modern hydrothermal sediments Ni occurs along with sulfide and sulfate minerals. The lack of sulfur-bearing minerals in Dales Gorge BIF and the widespread distribution of Ni in nearly all different mineral phases indicate a lack of reactive sulfur in both hydrothermal fluids and seawater. Therefore, during BIF deposition Fe and Ni are exclusively associated with oxides, carbonates, and silicates.

The high availability of Ni in Precambrian ocean waters might have had profound environmental implications because Ni is an important component of the coenzymes F430 in methanogens and in the hydrogenases of other species. Furthermore, urease, which is a vital part of the N cycle (in converting urea to carbon dioxide and ammonia), also requires Ni. Therefore, as long as Ni concentrations were sufficient for methanogenic activity, high concentrations of methane might have been generated, but then as Ni concentrations decreased, methane levels may have dropped.

BAR-18. Rare Earth Element Evidence for Redox Structure Evolution

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Rare Earth Elements (REE) systematics have long been used as tool to understand the genesis of banded iron formations (BIFs) and ocean redox-structure evolution. The conclusions of many previous REE studies on BIFs, however, are complicated by analytical inaccuracies, incomplete measurements, and measurement of extremely altered formations. We conducted REE analysis of samples from 26 separate formations and provide a re-evaluation of the conclusions that can be drawn from trace element analysis of detrital free BIFs.

There are several temporal trends in our data that appear to reflect redox structure evolution. No BIFs contain statistically significant negative shale normalized Ce anomalies and positive Ce anomalies are not present in our data set until ~1.9 Ga. Lower Y/Ho and higher light-to-heavy REE ratios than shale composites are only present in ~1.9 Ga and younger BIFs. The lack of significant ocean redox stratification prior to ~2.4 Ga to 2.3 Ga is the most parsimonious explanation of these trends. In a stratified ocean, metal oxides, Ce oxides, and organic matter from oxic waters will be transported below the

redox cline. Oxide dissolution and organic matter remineralization in an anoxic water column will lower the Y/Ho ratio, raise the light-to-heavy REE ratio, and increase the concentration of Ce relative to neighboring REE (La and Pr). Without a distinct redox cline, metal-oxide (assuming an oxidative mechanism) and organic-bound REE sorting would be expected to function essentially the same as today; differences in complexation properties among the REE+Y would drive estuary and basin-scale sorting leading to light REE depletion and positive Y/Ho ratios. Ce in an anoxic, unstratified basin, however, would be unlikely to be oxidized and would not display any significant shale normalized anomaly.

The lack of redox stratification and the apparently low oxidizing potential of shallow environments in Archean oceans question the plausibility of classical—redox stratification breakdown—models of BIF genesis. Anoxygenic photosynthesis is a more likely oxidative source for BIFs, implying that the iron distribution of Archean oceans could have been controlled by metabolic iron uptake and ecosystem stratification rather than the oxidative potential of shallow environments.

BAR-19. Ultraviolet Spectra of SO_2 and Implications for Mass-Independent Fractionation During Photolysis

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The discovery of large mass-independent fractionation of sulfur (MIF-S) signatures ($\Delta^{33}\text{S} \sim -2$ to $+8\%$) in sedimentary rocks older than 2.4 billion years (Gyr) and the absence of MIF-S for younger rocks (Farquhar *et al.*, 2000, and subsequent studies), the discovery of the large MIF-S effects ($\Delta^{33}\text{S} \sim -100$ to $+100\%$) produced by UV photolysis of SO_2 (Farquhar *et al.*, 2001), and the realization that oxygen and ozone strongly absorb UV at the relevant UV wavelengths (180–220 nm), provided powerful experimental evidence for a direct mechanistic link between MIF-S signatures and atmospheric oxygen levels. Ultraviolet photolysis of SO_2 is currently the only experimentally demonstrated process that can produce large MIF-S effects, which is critical due to the possible dilution of any initial MIF-S signature that can result by mixing with sulfur with a MDF signature. These observations and results have promoted almost universal acceptance of the idea that the presence or absence of an MIF-S signature in the rock record reflects the absence or presence of significant atmospheric oxygen, respectively; that is, UV photolysis of SO_2 in the absence of oxygen (atmosphere before 2.4 Gyr) produces significant MIF-S, whereas the presence of oxygen (atmosphere since 2.4 Gyr) inhibits MIF-S.

In order to investigate the interaction between UV light and SO_2 , and, more specifically, the interaction between UV light and the four sulfur isotopologues of SO_2 ($^{32}\text{SO}_2$, $^{33}\text{SO}_2$, $^{34}\text{SO}_2$, and $^{36}\text{SO}_2$), artificially isotope-enriched samples of each sulfur isotope were obtained and converted to pure SO_2 gas, and UV absorption spectra for the four sulfur isotopologues were obtained for the range of 183–230 nm. At the shorter wavelengths, there is a small but distinct isotope-dependent shift of the absorption spectra, with the absorption peaks for the heavier isotopologues being shifted to longer wavelengths. The magnitude of this isotope-dependent spectral

shift decreases with increasing wavelength and virtually disappears at 220 nm.

The isotope-dependent spectral shift provides a possible explanation for many of the results obtained for the SO₂ photolysis experiments. Photolytic degradation of SO₂ requires a significant input of energy, which is available by the absorption of light to attain excited energetic states. However, the relative rates of SO₂ photolysis for the four sulfur isotopologues will be very dependent upon the nature of the UV radiation employed, namely, broadband UV radiation (*i.e.*, a continuum of UV wavelengths, such as UV produced by solar radiation) vs. the very narrowly defined wavelengths produced by lasers or resonance lamps. For the case of narrowly defined wavelengths, the relative rates of photolysis will be very dependent upon the exact wavelength (and also bandwidth) of the UV light with respect to the specific wavelengths of the absorption peaks for the four sulfur isotopologues. Hence, it is possible that the very large MIF effects produced during the photolysis of SO₂ using UV light produced by lasers or resonance lamps may be a product of the narrowly defined UV wavelengths emitted by these light sources and their relationship to the isotope-shifted absorption spectra of the four sulfur isotopologues, resulting in significantly different extents of excitation for each isotopologue, and ultimately, mass independent fractionation of sulfur isotopes.

Our results suggest the possibility that photolysis of SO₂ by the continuum of UV wavelengths generated by solar radiation may not be responsible for the large MIF-S signatures measured for many samples of Archean age. If this is the case, this would remove the direct mechanistic link between MIF-S signatures and atmospheric oxygen levels and imply that some other, as yet unidentified, mechanism is responsible for formation of Archean MIF-S signatures.

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BAR-20. Molecular Techniques for the Detection of Microbial Activity and Diversity in the Arctic

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Cold environments, such as the Arctic, are excellent for studying life and its biosignatures in extreme habitats. As part of the Arctic Mars Svalbard Expedition (AMASE), we study extremophiles and test life-detection instruments in extreme conditions on Svalbard, an island covered by Arctic tundra located at 77° to 80°N. Features such as permafrost, volcanoes, and hot springs on Svalbard provide an analogue to cold, dry Mars. The AMASE team members are international scientists whose work, in geochemistry, geophysics, microbiology, and ecology, synergize in the field to facilitate new discoveries. A goal of AMASE is to explore

and prospect the microbial diversity and their biosignatures of Arctic soils, sediments, and ice while simultaneously developing biotechnology to detect and characterize those life-forms.

To assess the diversity of microbial community structure and its biogeochemical processes in the arctic ecosystem, our group deploys an instrument suite, which includes (i) standard genetic techniques to identify and characterize microbial populations (Polymerase Chain Reaction, or PCR), (ii) protein microarrays for common microbial biomarkers as well as handheld life-detection instruments, such as (iii) an ATP luminometer as an assay for overall metabolic activity, and (iv) a Limulus Amebocyte Lysate (LAL) assay that detects gram-negative bacterial cell-wall materials (living or dead). *In situ* DNA sampling, PCR, and analysis performed in the field using gene-specific primers indicate differences in overall community composition and activity among different rock types.

By characterizing organisms and their habitats, we will learn about molecular structures that define their functionality, which in turn provides potential targets for biomarker investigations. When successful, biosignature correlations strengthen interpretations and may be particularly valuable in the search for life on Mars.

BAR-21. Mass-Dependent and Non-Mass-Dependent Sulfate Influx into ca. 3.5 Ga Ocean

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Non-mass-dependent sulfur isotope anomaly of pre-2.3 Ga mineral has demonstrated that atmospheric sulfate aerosol would have been an important sulfur influx into the anoxic Archean ocean (Farquhar *et al.*, 2000). This may be partly due to low flux from oxidative weathering, in contrast with high *p*O₂ modern atmosphere, though sulfate sources into the Archean ocean and their relative proportions are still poorly known. We report multiple-sulfur isotope ratios (³²S/³³S/³⁴S/³⁶S) of the Archean barites in the ca. 3.5 Ga Dresser Formation, Western Australia. The barites show negative Δ³³S and positive Δ³⁶S anomalies, suggesting seawater origin of the sulfate. The Δ³³S negatively correlated with Δ³⁶S (Δ³³S = −9 Δ³⁶S). This Δ³³S/Δ³⁶S trend crosscuts near CDT composition, suggesting the mixing between MD and non-MD sulfate sources. The non-MD component probably represents sulfate aerosol produced by photolysis of SO₂, because the observed Δ³³S/Δ³⁶S slope of −0.9 is similar to those of 193 nm photodissociation of SO₂ (Farquhar *et al.*, 2001). On the other hand, the MD sulfate end-member is characterized by its δ³⁴S values of +12‰, based on the extrapolation of linear δ³⁴S-Δ³³S correlation (Δ³³S = 0.17 × δ³⁴S − 2.02; R² = 0.70). The ³⁴S rich MD sulfate would have been possibly derived from abiogenic hydration or microbial disproportionation of magmatic SO₂ or elemental sulfur but could not have been produced by weathering or microbial oxidation of sulfide. Hence, the result is consistent with the low *p*O₂ condition. In contrast with the modern sulfur cycle, microbial sulfate reduction would not have played a major role in the seawater sulfur chemistry at 3.5 Ga.

BAR-22. Biosignatures in Modern Sulfates: Texture, Composition, and Depositional Environments of Gypsum Deposits at Guerrero Negro, Baja, Mexico

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Gypsum ($\text{CaSO}_4 \cdot \text{H}_2\text{O}$) is an important phase in biogeochemistry and sedimentology as a mineral sink for sulfur, a paleoclimatic indicator, and an endolithic niche for phototrophic and chemotrophic bacteria. Sulfate deposits are also important targets of exploration for evidence of habitable environments and life on Mars. Gypsum deposits from a range of sedimentary environments at the Guerrero Negro crystallizer ponds and sabkha were investigated for microscale structure and composition to differentiate fabrics formed under microbial influence from those formed under abiogenic conditions. Subsedimentary gypsum forms in sabkha environments as mm to cm scale selenite discs [termed bird beak gypsum; Warren (2006)] and selenite disc aggregates. Selenite discs and other subsedimentary gypsum are characterized by a sinuous axial microtexture and poikilolithically enclosed detrital particles. Subaqueous gypsum forms as cements, granules (termed gypsooids), and massive botryoidal crusts that line the sediment water interface and margins of managed crystallizer ponds and natural anchialine pools and channels. Subaqueous gypsum exhibits a wide range of textures and mineral/biofilm associations that include amorphous to euhedral, tabular, needle, and lensoidal morphologies. Elemental sulfur forms rinds on prismatic, growth-aligned gypsum twins, and reticulate magnesite carbonate is interspersed with both twinned crystals and rosette aggregates in stratified subaqueous environments. Intracrystalline biofilms and cell material were observed in association with nearly all subaqueous morphologies, but virtually no samples showed intercrystalline microbial communities. Fine-scale gypsum textures are unlikely to persist through diagenetic alteration, but understanding their primary associations with sulfur and carbonates is necessary for interpreting sulfates or their replacement phases in the ancient record.

BAR-23. Nano-scale Sulfur Isotope Evidence for a Biological Sulfur Cycle in the Early Archean

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Sulfur isotope signals preserved within ancient sedimentary sulfides can be used to trace the activity of sulfate-reducing microbes (SRM) and help to enhance our understanding of the sulfur cycle on early Earth. Sulfides formed as a consequence of microbial sulfate reduction (MSR) have a characteristic light, and often highly variable, $\delta^{34}\text{S}$ isotope signature, compared to their source sulfate. Unambiguous early Archean sedimentary sulfides are, however, rare and

show narrower ranges of $\delta^{34}\text{S}$ compared to younger examples, meaning that the timing of emergence of SRM, and the nature of the Archean sulfur cycle remain controversial. Conventional isotopic analysis techniques lack the necessary spatial resolution required to accurately characterize individual micron-sized features. Hence, it is clear that a technique combining imaging with chemical and isotopic information at submicron-scale resolution would help to resolve this puzzle.

Here we present *in situ* NanoSIMS S isotope data from micron-sized synsedimentary pyrites housed within one of Earth's oldest sandstone units, the ~3430 Ma Strelley Pool Formation of Western Australia. These pyrites show a maximum fractionation relative to assumed seawater sulfate of ~50‰ and a spread of ~75‰. This spread is approximately 3 times greater than fractionations previously reported for the early Archean but directly comparable with modern settings having a biologically coupled redox sulfur cycle. Associated carbonaceous matter, redox-sensitive detrital minerals, and models for fractionation are taken by us to point toward a biologically coupled, anaerobically driven sulfur cycle in beach-type sediments as early as ~3430 Ma.

BAR-24. Linking the MIF-S Record of Sedimentary Rocks to Biological Evolution

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The presence of mass-independently fractionated sulfur isotopes (MIF-S) in pre-2.45 Ga sedimentary rocks, but the general absence in post-2.45 Ga rocks, has been linked to atmospheric oxygen evolution (Farquhar and Wing, 2003; Bekker *et al.*, 2004). However, recent studies have revealed that: (1) Archean sedimentary rocks with no MIF-S signatures are common, particularly during the mid-Archean era (Ohmoto *et al.*, 2006a, 2006b); (2) the magnitude of MIF-S may vary greatly within short (<10 m) stratigraphic intervals (*e.g.*, 2.5 Ga Mt. McRae Formation) (Kaufman *et al.*, 2006); (3) Antarctic snow that accumulated during violent (stratospheric) volcanic eruptions trapped sulfates with small but distinct MIF-S (Baroni *et al.*, 2007); (4) Archean sedimentary rocks with MIF-S are more common in organic carbon-rich black shales with hydrothermal alteration effects than in organic carbon-poor sandstones/carbonates (Ohmoto *et al.*, 2006); (5) Pyrites in a Jurassic ammonite show small but distinct MIF-S (Ono *et al.*, 2006b); and (6) H_2S that generated from the thermochemical reduction of sulfate by organic compounds (amino acids) at 150–200°C exhibits distinct MIF-S ($\Delta^{33}\text{S}$ as high as 0.6‰ and $\Delta^{36}\text{S}$ as low as -1.8‰) (our study). These new discoveries question a simple linkage between the MIF-S record and an atmospheric O_2 evolution model. Here we suggest that thermochemical sulfate reduction (*i.e.*, TSR) by organic matter during sediment diagenesis may have been the primary cause of MIF-S in sedimentary rocks.

The extrapolation of the observed relationships between $\Delta^{33}\text{S}$ values and sulfate reduction rates suggests that, at 100°C, TSR occurs within ~10,000 years and the single-step $\Delta^{33}\text{S}$ values are ~1‰. If recycling and Rayleigh fractionation processes are also considered, the entire ranges (*i.e.*, -4

to +10‰) of $\Delta^{33}\text{S}$ that were observed in pre-2.4 Ga sedimentary rocks are easily accounted for. Furthermore, the $\Delta^{33}\text{S}$ and $\Delta^{36}\text{S}$ relationships of the experimental products are essentially identical to those in pre-2.45 Ga rocks with MIF-S. Therefore, the MIF-S record of sedimentary rocks may be linked to the thermal and biological evolution of the Earth rather than to its atmospheric evolution.

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BAR-25. Biosignatures in Holocene Reefal Microbialites, Great Barrier Reef, Australia: Old Microstructural Approaches versus New Geochemical Techniques

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Microbialites form due to the induction and/or localization of mineral precipitation by microbial biofilms with or without trapping and binding of detritus. Hence, most microbialites owe their preservation to their mineral precipitates (generally CaCO_3). However, precipitation in microbialites is not biologically controlled as in skeletal organisms, so there is a theoretical continuum between biologically induced precipitation associated with biofilms and purely physico-chemical (*i.e.*, abiotic) precipitation. Understanding the origin of such precipitates through time is critical for evaluating issues relating to the origin and early history of life on Earth and for understanding how mineral precipitates may serve as biosignatures in general.

However, differentiation of genuine microbialites from abiotic precipitates may be difficult and, increasingly, is the subject of heated debate. One way ahead is to com-

prehensively characterize the full trace element chemistry of unequivocal microbialites. Modern and ancient microbialites are known to take up metals, such as the rare earth elements (REE), at concentrations greater than those of contemporary abiotic cement. Although elevated REE concentration may not be indicative exclusively of biofilms, it suggests that metals bound to organic ligands in biofilms may be preserved in microbial carbonates. As microbes concentrate a variety of metals in biofilms, we hypothesize that microbialites may preserve vital transition elements that are utilized in microbial metabolism. If so, those metal enrichments may serve as a fingerprint for the biological origin of precipitates and possibly for the presence of particular microbial communities or metabolic pathways. We have analyzed middle Holocene microbialites from reef framework cavities at Heron Reef, Great Barrier Reef, Australia using laser ablation–inductively coupled mass spectrometry (LA-ICP-MS). The microbialites consist of high-Mg calcite that initially formed as poorly structured layers of calcified extra-cellular polymeric substance at the base of the biofilms. Through the life of the overlying biofilm, the crusts gave rise to euhedral scalenohedral crystals that obscure initial organic morphology and preclude preservation of fossil microbes. Robust seawater REE patterns previously documented in the microbialites by solution ICP-MS were reconfirmed using LA-ICP-MS. Reconnaissance LA-ICP-MS analysis of transition metals suggests that the microbialites are enriched in vital elements such as V, Cu, Co, and Sn as compared to accompanying scleractinian coral skeleton. The inclusion of trapped and bound skeletal detritus in the microbialites causes scatter in the data, but analysis of time-series data recorded during ablation allows discrete contaminants to be identified. A case in point regards the element V. Ascidians (tunicates) are abundant in reef cavities at Heron Reef, and their spicules occur within the microbialites. They concentrate V in tunichrome blood pigments, raising the question as to whether V was concentrated in incorporated spicules or was distributed through the microbial carbonate. Time series data suggest that it is disseminated through the carbonate. Hence, V liberated from decaying ascidians in the cavities was concentrated in the biofilms and preserved in the microbialite. Vanadium enrichment may thus serve as a biosignature indicative of ascidians even where spicules not preserved. Although microbial biofilms are highly diverse by their nature, our preliminary results suggest that biosignatures may be identifiable in ancient microbialites.

BAR-26. Fits and Starts: Atmospheric Evolution across the Archean-Proterozoic Boundary from a Sulfur Multiple Isotope Perspective

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A first-order similarity exists between S isotopic anomalies preserved in some Archean rocks and those associated with short-wavelength UV photochemistry of SO_2 (Farquhar *et al.*, 2001). The Archean surface environment, therefore, likely

permitted production and preservation of the isotopic signatures of UV-driven SO₂ photochemistry. Photochemical models indicate that the preservation of S isotopic anomalies is a strong function of atmospheric O₂ and CH₄ levels (Pavlov and Kasting, 2002; Zahnle *et al.*, 2006).

The anomalous S isotopic fractionation that characterizes the Archean record is maintained into the earliest Paleoproterozoic, and the gross isotopic transition to an anomaly-free state has been identified in Paleoproterozoic rocks. It occurred sometime prior to ~2.32 Ga (Bekker *et al.*, 2004). Combined ³³S, ³⁴S, and ³⁶S systematics from rocks of the Transvaal Supergroup, South Africa, indicate that this transition was abrupt. The likely driver was an orders-of-magnitude increase in atmospheric O₂ levels.

In the measured sample set, there appears to be no intimate relationship between the appearance of sedimentary indicators of global climate and the major S isotopic transition. A similar feature is seen in the S isotopic record from the Huronian Supergroup. A global climatic response to changing atmospheric conditions may only occur outside the dynamic range offered by the S isotope proxy for atmospheric evolution.

This work relies heavily on conversations and scientific collaborations with James Farquhar (University of Maryland), Jay Kaufman (University of Maryland), David Johnston (Harvard University), Shuhei Ono (MIT), and Andrey Bekker (University of Manitoba). I appreciate their guidance, criticisms, and friendship.

BAR-27. Characterization of Carbonaceous Material from the Sudbury Impact Structure Using Raman Microspectroscopy

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Samples from the 1.85 Ga Sudbury impact structure have been analyzed using Raman microspectroscopy in order to characterize the carbonaceous material within the rocks. Samples analyzed were from (i) the Ni-Cu-PGE massive sulfide deposits associated with the Sudbury Igneous Complex, (ii) the Onaping Formation (Dowling and Vermilion Members), and (iii) cross-cutting veins of anthraxolite (a carbon-rich anthracite-like asphalt) in the Onwatin Formation. A sample from the 2.4 Ga Elliot Lake Formation was also analyzed. Graphitic and more disordered carbon inclusions were found in chalcopyrite crystals from the Ni-Cu-PGE massive sulfide deposit, similar to those described from the Vermilion sulfide deposit (Ames *et al.*, 2006), suggesting a generic link between the 2 deposits. Raman data also indicates a shared source of carbon for the Errington carbonate-hosted mineralization and the cross-cutting anthraxolite veins. This is considered to be carbon re-mobilized by hydrothermal fluids circulating within the suevites of the Onaping Formation. The disordered nature of this shared carbon suggests that graphite inclusions within the melt fragments did not contribute to the hydrothermal fluids and that carbon was preferentially scavenged from the suevite matrix.