FINAL TECHNICAL REPORT FOR NASA EXOBIOLOGY GRANT NAG5-9430
6/1/00 – 5/31/04
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Introduction

Most of the proposed objectives in this grant were achieved during the 3 year duration of the grant and its one year extension. In addition, shortly after initiation of the grant, the discovery of gullies on Mars apparently formed by recent seepage of fluids was announced. Together with partial support from the Astrobiology Institute, I devoted considerable effort during the grant interval into understanding the origin of these gullies because of their astrobiological significance. In addition, longstanding investigations of the environmental conditions of the Early Earth initiated years ago under previous NASA and NSF funding reached fruition and these were presented and published. This report summarizes the significant findings reported during the grant interval. Some of the work initiated during this interval has been completed under the subsequent Exobiology grant and will be reported at the appropriate time.

Mars brines

Having worked on the geochemistry and isotope geochemistry of terrestrial brines for many years, it became apparent to me before the news conference announcing the discovery of gullies on Mars was over that brines have the low freezing points and other properties necessary to account for all aspects of the observed features on Mars. A quick review of the literature on what was known about a possible hydrosphere on Mars led to the conclusion that *IF*: 1) Mars outgassed an early hydrosphere, 2) lost most of its water to space (to account for the high D/H ratio), and 3) subsequently froze down, *THEN*: highly concentrated brines *must* have formed and become lodged in the megaregolith. A brief letter to this effect was published in *Science:*

- Knauth, L.P., Klonowski, S., Burt, D (2000) Ideas about the surface runoff features on Mars (letter). Science, 290, 711-712.

I then aired these new ideas in published abstracts and presentations at 4 national meetings in order to get feedback:

- Knauth, L.P., Burt, D.M. and Klonowski, S. (2000) Dense, eutectic, valley-forming, intermediate latitude (DEVIL) brines on Mars. Geologic Society of America Abstracts with Programs A-303, Annual Mtg Reno.

- Knauth, L.P. and D.M. Burt (2001) "Follow the water, beware the brine": Astrobiological Implications of aqueous seeps on Mars. Second

Atrobiology Science Conference, April 10-12, Carnegie Institution of Washington, Washington, DC. p. 187-188.

- Knauth LP, Burt DM, and Tyburczy, JA, 2001, Highly conductive eutectic brines rather than water expected in the martian subsurface. In Conference on the Geophysical Detection of Subsurface Water on Mars, p. 60-61. LPI Contribution No. 1095, Lunar and Planetary Institute, Houston.

- Knauth, L.P., 2001, Is the hydrology of Mars the hydrology of brines? Arizona Hydrological Society Annual Symposium, Tucson, 11/12/01-11/15/01.

- Knauth, L.P. 2001, Importance of brines and caliche in the search for past life on Mars. EOS Trans. AGU, 82(47), Fall Meet. Suppl. Abstract P21C-05.

Two papers were then published in major refereed journals:

- Knauth, L.P. and Burt, D.M. (2002) Eutectic brines on Mars: Origin and possible relation to young seepage features. (*Icarus*, v. 158, 267-271).

- Burt, D.R. and Knauth, L.P. (2002) Electrically conducting, Ca-rich brines, rather than water, expected in the martian subsurface. *Journal of Geophysical Research*, V. 108, No. E4, 8026, doi:10.1029/2002JE001862.

The basic result is that, by analogy with Earth, any initial hydrosphere outgassed on Mars would have had large amounts of Cl (as evidenced by significant Cl in the soluble component of SNC meteorites and high Cl at the Viking lander sites). Loss of water from the martian atmosphere via several proposed mechanisms would necessarily have caused the remaining hydrosphere to become evapoconcentrated into a brine. This brine, lodged in the megaregolith, would necessarily have reacted with the basaltic materials and evolved into even more concentrated brine. With the onset of global freezing, the brine in the megaregolith would have undergone eutectic freezing to produce water ice, salts, and highly concentrated, residual brine with freezing points below current martian equatorial temperatures. This was discussed in detail in the Icarus paper. The JGR paper provided further details and gave a test of the hypothesis, namely, geophysical remote sensing of megaregolith electrical conductivity.

The brine hypothesis has not received any criticism and I am currently using it to readily explain all observed features at the Opportunity landing site as an alternative explanation to the highly publicized claims that the light colored units at Meridiani are lake deposits. The idea that brines can easily account for the gullies under present martian conditions was completely eclipsed by highly

publicized announcements that melting snow is the best explanation. Melting snow does not account for the clear indications in MOC imagery that fluid is emerging from local and regional aquifers. Stay tuned.

CALICHE AS A POTENTIAL TARGET FOR ASTROBIOLOGICAL PROSPECTING ON MARS

On Earth, basalt exposed to weathering in arid climates is rapidly encrusted with $CaCO_3$ which also fills interior vugs, amygdules, and cracks. If it ever rained on Mars with CO_2 in the atmosphere, $CaCO_3$ should have formed as a weathering product as it does on Earth. Caliche on Earth entombs remnants of microbes, roots, lichens, and other organisms that either lived at the site or were blown in by winds. Work done under this grant showed that the $CaCO_3$ contains a distinctive isotopic biosignature, possibly the first ever that does not require knowledge of the isotopic composition of C of the global reservoir. White fracture fills and other void-fillings in caliche on Mars would be readily detectable in surface missions and is an excellent target for microfossils of past life, whether such life existed at the site or was blown in by martian winds.

Remarkably, the first-ever basalt boulder "ratted" into by the SPIRIT lander has imaged white fracture-fill material and interior cavities lined with white material exactly as seen on Earth! Regrettably, the instrumentation cannot detect $CaCO_3$ unless it is a major component of the 3 cm footprint of the analytical instruments. Even if it were present as a major component, the APXS would have to integrate for 12 hours (I have been told) in order to detect C. There also is a clear prejudice developing by many of the team members and others that the surface of Mars was "acid washed" and that carbonate cannot be present (this prejudice reinforced by the putative presence of jarosite, which can easily be explained in other ways). Hopefully, surface instruments capable of detecting $CaCO_3$ will eventually be put on Mars. $CaCO_3$ must be present as an alteration product of martian basalt if it ever underwent chemical weathering in an atmosphere containing H_2O and CO_2.

Studies of caliche sponsored by this work were initially presented at meetings for feedback:

- Knauth, L.P. (2001) Isotopic biosignature in calcite formed during weathering of basalt: Implications for past life on Mars, early life on land, and ALH 84001. Second Astrobiology Science Conference, April 10-12, Carnegie Institution of Washington, Washington, DC. p. 185-186.
- Bungartz, F., L.A. Garvie, Nash, T.H., and L.P. Knauth. 2001, Biologicallly-Induced mineralization by the endolithic lichen Verrucaria Rubrocincta Breuss in the Sonoran Desert. Eos Trans. AGU, 82(47), Fall Meet. Suppl., Abstract B32C-07.
- Garvie, L.A.J., Bungartz, F., Nash III, T.H., and Knauth, L.P. (2000) Caliche dissolution and calcite biomineralization by the endolithic lichen

Verrucaria rubrocincta Breuss in the Sonoran Desert. Goldschmidt 2000, Jour. Conf. Abstracts 5(2), 430.

- Bungartz, F., Garvie, L.A.J., Nash III, T.H., and Knauth, L.P. (2000) Simultaneous mineral dissolution and biomineralization fo caliche by the endolithic lichen Verrucaria Rubrocincta Breuss in the Sonoran desert. International Ass. Lichenology, IAL4 Conference, Barcelona.

The first paper dealing with the isotopic biosignature and implications for life on Mars, carbonate in ALH 84001, and life on land in the Precambrian was published in 2003 and was selected by the publisher for inclusion in the new *Virtual Journal of Geobiology.*:

- Knauth, L.P., Brilli, M., and Klonowski, S. (2003) Isotope geochemistry of caliche on basalt. *Geochimica et Cosmochimica Acta*, 67, 185-195. (Selected for inclusion in *Virtual Journal of Geobiology*, http://earth.elsevier.com/geobiology)

SECONDARY SILICA IN VOLCANIC ROCKS

Part of the funded research dealt with an exploration of secondary silica found in fractures and vugs in volcanic rocks. Preliminary work had indicated that certain varieties of this material could result from low temperature weathering rather than being late-stage hydrothermal activity, as commonly assumed. If formed during low-temperature weathering, this type of silica could preserve microfossils of what was on the land at the time and could be a new kind of silica to use for exploring the record of life on land in the Precambrian.

The funded study was carried out by MS student Gerald Pollack, who investigated secondary silica in the Tertiary Superstition Mountains, Arizona. Pollack confirmed our previous isotopic work that most of the secondary chalcedony and opal in these silicic volcanic rocks was, indeed, low temperature silica. He spent a some time searching for microfossils but really did not have the training or time to do the tedious microscopic searches necessary. Numerous candidate examples of microfossils entombed in silica were found, but he had to leave before these could be adequately evaluated. I am currently seeking out experts to collaborate on this. In any case, we now know that this is a new and excellent target material for microfossil prospecting in the Precambrian. Pollack's thesis may or may not get published soon. He is currently busy as a PhD student at the University of Michigan.

- Pollack, Gerald, 2001, The origin of secondary silica in volcanic rocks, Superstition Mountains, Arizona, M. S. thesis, Arizona State University. 55p.

PALEOKARST AND LIFE ON LAND IN THE PRECAMBRIAN

The exploration of Precambrian paleokarst has been a major component of my Exobiology research for many years. In the current grant interval, extensive data for a Neoproterozoic and a 1.2 Ga paleokarst were compiled and used to assess the magnitude of the photosynthesizing biomass that produced ^{13}C depletions and microfossils in secondary carbonate formed during the weathering event. The result was that the phytomass was producing isotopic imprints similar to those documented for modern karsts and Pleistocene paleokarsts on Caribbean islands. There must have been an equivalent phytomass on the Precambrian land surface. The Precambrian karst terranes were green! Prior to this work, it was widely assumed that Precambrian land surfaces were basically free of organisms. The published paper is:

- Kenny, R. and L.P. Knauth (2001) Stable isotope variations in the Neoproterozoic Beck Spring and Mesoproterozoic Mescal paleokarst: Implications for life on land in the Precambrian. Bulletin Geologic Society of America, 113, 650-658.

A major effort was undertaken and completed to thoroughly map and explore the 1.2 Ga Mescal paleokarst in Central Arizona. This unit holds the oldest known microfossils of Precambrian land life. At the start of the project, we did not know if we had found the outcrops most suitable for life on land in the Precambrian studies because the area had only been previously mapped in a superficial way. Graduate student Steve Skotnicki mapped about 400 km^2 of the Sierra Ancha Wildnerness area, some of the most rugged and inaccessible terrain in the lower 48 states. He devoted specific attention to the location of the best exposed and least metamorphically altered paleokarst and also discovered beautiful collapsed cave systems complete with silica speolethems and possible cave deposit microfossils. Our previously published microfossil locality lay at the west end of a 5 Km strip that extends onto the Fort Apache Indian reservation; we had indeed been searching from the beginning at one of the best localities.

Skotnicki's map and fieldwork constitute his dissertation:

- Skotnicki, Steven J., 2001, "Timing of silicification of the Middle Proterozoic Mescal Paleokarst and the transition from the Mescal to Troy Quartzite, Central Arizona, Ph.D dissertation, Arizona State University 293 p.+map

The map was incorporated into a larger map from Skotnicki's previous mapping with the Arizona Geological Survey and was published as an open file report by that organization.

Other technical results from Skotnicki's dissertation work, including a manuscript on the astonishing cave deposits with their possible record of a Precambrian cave biota are still being prepared for publication. Some of the

geological aspects of this work were presented at a regional meeting of the Geological Society of America:

- Skotnicki, S.J. and L.P.Knauth (2001) Timing of silicification of the Middle Proterozoic Mescal paleokarst and the transition from the Apache Group to the Troy Quartzite in Central Arizona. Geologic Society of America Abstracts with Programs v. 33, no.5, A-41, Mtg Albuquerque.

This work has led to a broader consideration of life on land in the Precambrian with regard to the bigger picture of the marine vs non-marine setting of early evolution. This was aired at an Astrobiology conference and has just been written up for publication:

- Knauth, L.P. (2000) Life on land in the Precambrian and the marine vs non-marine setting of early evolution. First Astrobiology Science conference, April 3-5, 2000, NASA Ames Research Center, 403.
- Knauth, L.P. (2002) Early Oceans: Cradles of Life or Death Traps? Astrobiology Science Conference 2002, April 7-11, NASA Ames Research Center. p. 9.

Environmental conditions of early earth, use of cherts to extract information about Precambrian

The exploration of the marine vs non-marine evolution of life in the younger Precambrian rock record was pushed back during the grant interval to the earliest rock record. Oxygen isotope analysis of cherts has been an on-going effort of mine for the past 30 years and collaborative work with Don Lowe (Stanford) reached critical mass for publication during the grant interval. Together, we compiled 26 years worth of data on the world's oldest preserved cherts and published a lengthy and detailed discussion of the meaning of O isotope ratios in these and the implications for early climate. We argued that a hot early Earth (50°C -80°C) was the only plausible explanation for the remarkable and now thoroughly documented observation that Archean cherts are dramatically lower in O than are younger cherts. We had reached this conclusion after our initial publication in 1975, but the result was so extraordinary that few took it seriously. With this publication, we hope that will change. There is some evidence that a hot early Earth is gaining traction. We shall see. The new results were first presented for comment at an NAI conference:

- Knauth, L.P. and D.R. Lowe (2001) Environmental conditions of the early Earth at the time of the earliest microfossil record. Second Astrobiology Science Conference, April 10-12, Carnegie Institution of Washington, Washington, DC. p. 242-243.

The final paper is:

- Knauth, L.P. and D.R. Lowe (2003) Archean climatic temperature inferred from oxygen isotope geochemistry of cherts in the 3.5 Ga Swaziland Supergroup, South Africa. *Geological Society of America Bulletin* , V. 115, p. 566-580.

OTHER

Two other efforts were partially funded by this grant. One was a MS thesis by Blair Lindford on the Neoproterozoic Beck Spring Dolomite, in the Alexander Hills, California. This was prompted by the enormous interest in the Neoproterozoic snowball Earth hypothesis that arose during the grant interval. Key to this hypothesis was the widespread notion that $\delta^{13}C$ measurements of Proterozoic carbonates accurately recorded $\delta^{13}C$ of the global marine bicarbonate reservoir. Knowing that many ^{13}C "excursions" simply reflect local conditions (exposure surfaces, restricted basins, etc), we started a low-key project to deconstruct some of the isotope arguments by measuring $\delta^{13}C$ *and* $\delta^{18}O$ variations in 3 stratigraphic sections only 100 m apart. Lindford showed clearly that major "excursions" occurring at some individual horizons peter out laterally and are clearly related to early diagenetic lenses which silicified local areas and also introduced ^{13}C-depleted, non-marine photosynthetic carbon (life on land!) into the system during initial diagenetic stabilization. Lindford's thesis is:

- Lindford, Blair, 2001, Isotope chemostratigraphy of the Beck Spring Dolomite, Southeastern California, M.S. Thesis, Arizona State University.

Further, expanded work is underway on this stratigraphic section under my current Exobiology grant. Stay tuned.

Finally, although the publisher would not allow the grant to be acknowledged, I used some of my grant time to write a review paper on cherts. This included some of the results from the project, but was mainly a broad overview of the sedimentary authigenic silica system. The article was published as one of the major entries (as opposed to the dominantly short entries) in the massive new Encyclopedia of Sedimentology:

- Knauth, L.P. (2003) Siliceous Sediments, *in*: Middleton, G.V., *Encyclopedia of sediments and sedimentary rocks.* Kluwer Academic Publishers, Boston. 660-665.