6.5.21

Evidence of a high-O_2, high-CO_2 and low-CH_4 Archean atmosphere in the 3.46 Ga Marble Bar Chert, Western Australia

H. OHMOTO[1], M. NEDACHI[2], Y. KATO[3], D. BEVAQUA[1] AND Y. WATANABE[1]

[1] Astrobiology Research Center, Penn State Univ., University Park, PA 16802 USA (hqo@psu.edu)
[2] Kagoshima Univ., Kagoshima 890-005, Japan
[3] Faculty of Technology, Tokyo Univ., Tokyo, Japan

The Marble Bar chert/jasper unit, ~50-100m thick and exposing in a several km^2 area in the Pilbara district of Western Australia, deposited ~3.46 Ga ago, probably at a water depth >500 m on or near a mid-ocean ridge. Surface outcrops of this unit are characterized by alternating layers of red (hematite-rich)-, black (magnetite and/or organic carbon-rich)-, green (siderite-rich)- and white (Fe-poor) cherts. The red jasper has been an enigma for proponents of an anoxic Archean atmosphere; they have interpreted the hematite (Fe_2O_3) crystals as modern oxidation products of siderite ($FeCO_3$). The Astrobiology Dilling Project (ABDP) carried out its first drilling at Marble Bar in order to examine the mineralogical and (bio)geochemical characteristics of "fresh" jaspers and interbedded pillow lavas.

The drill cores from ~100-300m depths (i.e., much below the modern ground water table) are characterized by essentially the same types of jasper as those in the outcrops (i.e., abundant red japer) and by heavily hematitized pillow basalts. Fresh, euhedral crystals (<~2 mm size) of pyrite (FeS_2) are abundant, especially in numerous veinlets (~mm thick and <10 cm long) and networks in the chert/jasper and basalt. The textural and paragenetic relationships of the various iron-bearing minerals suggest the hematite and siderite crystals in the jasper and pillow lavas formed 3.46 Ga ago on the seafloor as a result of mixing of Fe^{2+}-, silica- and H_2S-rich submarine hydrothermal fluids with O_2- and $\sum CO_3^{2-}$ ($\approx CO_2 + HCO_3^-$)-rich deep ocean water, while the pyrite crystals were forming from the simple cooling of hydrothermal fluids beneath the seafloor. From thermodynamic and kinetic evaluations of the formation conditions of iron-bearing minerals, together with an ocean-circulation model, we suggest the 3.46 Ga atmosphere contained $pO_2 > 0.4$ PAL, $pCO_2 > 100$ PAL, and $pCH_4 \approx 1$ PAL.

The drill core samples from this site are also characterized by the abundance of organic carbon-rich layers (<1 to ~5 mm thick) in the chert/jasper unit. They probably represent remnants of microbial mats that developed on the seafloor during the quiescence periods of submarine hydrothermal activity.

6.5.22

Significance of Archean $\Delta^{36}S/\Delta^{33}S$

J. FARQUHAR[1], D.T., JOHNSTON[1], B.A WING[1], C. CALVIN[2] AND K. CONDIE[3]

[1] University of Maryland, College Park MD 20742, USA
[2] Brown University, Providence RI 02912, USA
[3] New Mexico Tech, Socorro NM 87801, USA

Interpretation of anomalous sulfur isotope signatures in the geologic record has relied for the most part on the relationships between $\delta^{34}S$, $\delta^{33}S$, and $\Delta^{33}S$. The lack of $\Delta^{36}S$ data is largely attributable to the difficulty in making $\delta^{36}S$ measurements, but the importance of this measurement should not be overlooked. Observation of a negative correlation between $\Delta^{33}S$ and $\Delta^{36}S$ for samples 2.45 Ga and older has been presented as evidence that atmospheric reactions are responsible for the Archean sulfur isotope anomalies [1,2] (Figure 1), and experimental studies suggest that $\Delta^{36}S/\Delta^{33}S$ varies when sulfur dioxide is irradiated by UV light under different conditions [3]. The measurement of $\Delta^{36}S$ in addition to $\Delta^{33}S$ has the potential therefore, to provide information about the atmospheric chemistry early in Earth history that cannot be provided by $\Delta^{33}S$ alone. We have reproduced and extended the observation of a negative correlation between $\Delta^{33}S$ and $\Delta^{36}S$ with analyses of shales from the Kathu borehole, South Africa (Figure 1) and are presently investigating whether $\Delta^{36}S$ analyses can be used as a tool to study secular variations in atmospheric chemistry in the Archean.
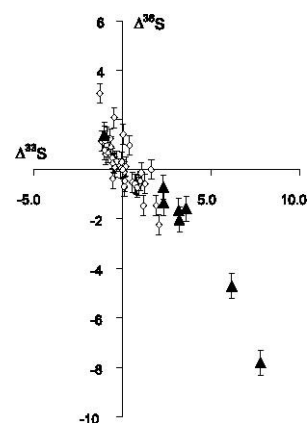

Figure 1. Plot of $\Delta^{36}S$ vs. $\Delta^{33}S$ for data from [1] (diamonds) and present study (triangles).

References
[1] Farquhar J., Bao. H. and Thiemens M.H. (2000) *Science* **289**, 756-758
[2] Farquhar J. and Wing B.A. (2003) *EPSL* **213**, 1-13
[3] Farquhar J., Savarino J., Airieau S. and Thiemens M.H. (2001) *JGR* **106**, 32829-32839.