Jena JOHNSON
Lewis and Clark Fund for Exploration and Field Research in Astrobiology
awarded June 4, 2012

Project Report:

Manganese and the evolution of oxygenic photosynthesis

The evolution of oxygenic photosynthesis and accompanying rise of molecular oxygen in our atmosphere fundamentally changed our planet and its biota. I have been investigating this critical transition in Earth history using two complementary proxies: the ancient manganese cycle and sulfur isotopic measurements. South African Paleoproterozoic cores of the Koegas Subgroup, dated to 2.415 Ga, have manganese enrichments resulting from original manganese oxides, indicating the manganese oxidative cycle was turned on. This discovery is significant: manganese can only be oxidized by O_2 and oxygenated nitrogen (nitrate), although a postulated Mn-oxidizing photosystem has been suggested as a transitional form before oxygenic photosynthesis. Yet the cores' manganese oxides were reduced during post-depositional reactions: isotopic and textural observations indicate the manganese oxides were respired by ancient Mn-reducing bacteria. Without oxygen or nitrate present, it is possible that no manganese would be able to be stable as oxides after deposition, as manganese oxides would be reduced by all other substrates and/or be the most favorable electron acceptor during respiration. Therefore, the redox state and mineral host of the manganese in these ancient deposits may shed light on the oxidation process. Another method to probe the presence of oxygen in the atmosphere is through the use of sulfur isotopes. Interestingly, sulfur isotopic measurements made in bulk and *in situ* from pyrite in these cores suggest atmospheric oxygen had not yet risen. Two intriguing possibilities exist: either manganese is a more sensitive redox proxy and is recording the initial rise of atmospheric oxygen, or the original manganese oxides were formed by transitional manganese-oxidizing phototrophs before water-oxidizing photosynthesis had evolved.

Funded by the Lewis and Clark Grant, I traveled to the cores' origin, South Africa, to distinguish between these two theories by sampling additional cores and field outcrops and contextualizing the cores through field studies. One of my major goals was to sample strata underlying and overlying the cores to characterize the manganese abundance and host mineral, and understand when the manganese enrichments began and when manganese starts to be preserved in oxide form (ie, not reduced biologically in the sediments). Another objective was to sample for pyrite nodules from strata overlying our current samples, to measure when the sulfur isotopic signal changed to indicate atmospheric oxygen had risen. I additionally planned field work in the Koegas Subgroup outcrops to better understand the cores' stratigraphic relationship and to supplement the cores with outcrop observations and samples.

The field portion of the trip was highly successful. The major field sites I targeted were the Naragas section and the Rooinekke Mine section, both of which overlapped the stratigraphy of the cores and allowed complementary observations and sampling, and the United Manganese of Kalahari mine for exposures of strata overlying the cores (Fig. 1). Additionally, I observed and sampled the underlying Kogelbeen, Gamohaan and Kuruman Formations at Kuruman Kop (Fig. 1).

Figure 1: Simplified map of field sections and the University of Johannesburg.

1: Naragas Section (Koegas Subgroup)
2: Rooinekke Mine Section (Koegas Subgroup)
3: United Manganese of Kalahari Mine (overlying Hotazel Formation)
4: Kuruman Kop Section (underlying Kogelbeen, Gamohaan, Kuruman Formations)
5: University of Johannesburg

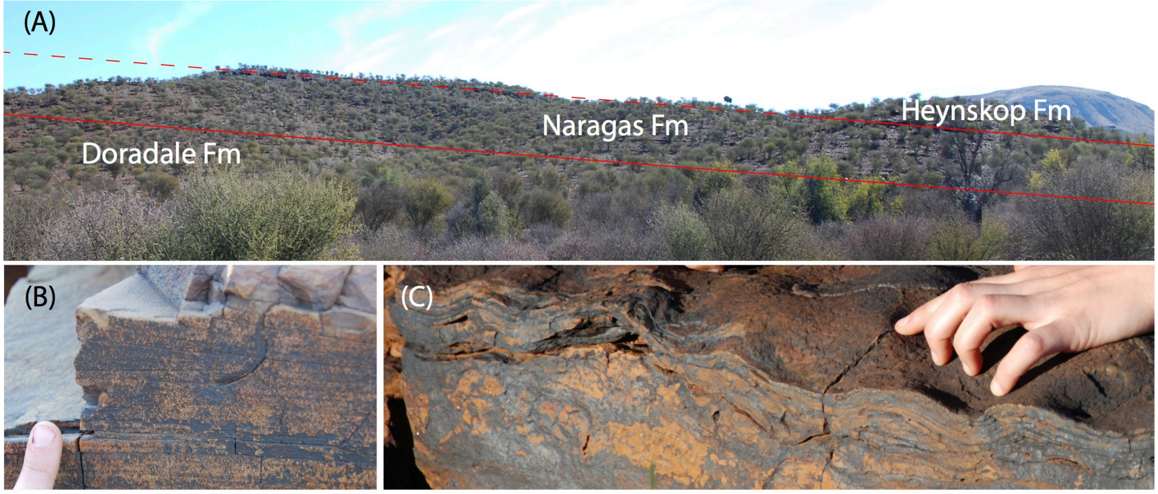

Figure 2: (A) Overview of the Naragas Section. (B) Example of hummocky cross stratification in Naragas Fm. (C) Example of microbialite unit in Heynskop Fm.

The Naragas section (-29° 22' 14.90", +22° 34' 58.73") of the Koegas Subgroup was a nice exposure of most of the formations sampled by the cores (Fig. 2A). The strata were more deformed than the cores, but the formations were recognizable and allowed complementary sampling and more paleoenvironmental contextualizing. Observations of abundant hummocky cross-stratification (Fig. 2B) placed the ancient environmental setting to be approximately at the storm wave base. A unit tentatively assigned as stromatolitic in the cores could be definitively identified as a microbialite (a deposit characterized by an interaction between a former microbial community and sediments) by its trapped-and-bound texture and irregular laminae (Fig. 2C). Manganese-bearing iron formation was sampled for manganese characterization, and the thin microbialite unit appeared to also have abundant manganese and iron. I sampled this microbial unit extensively.

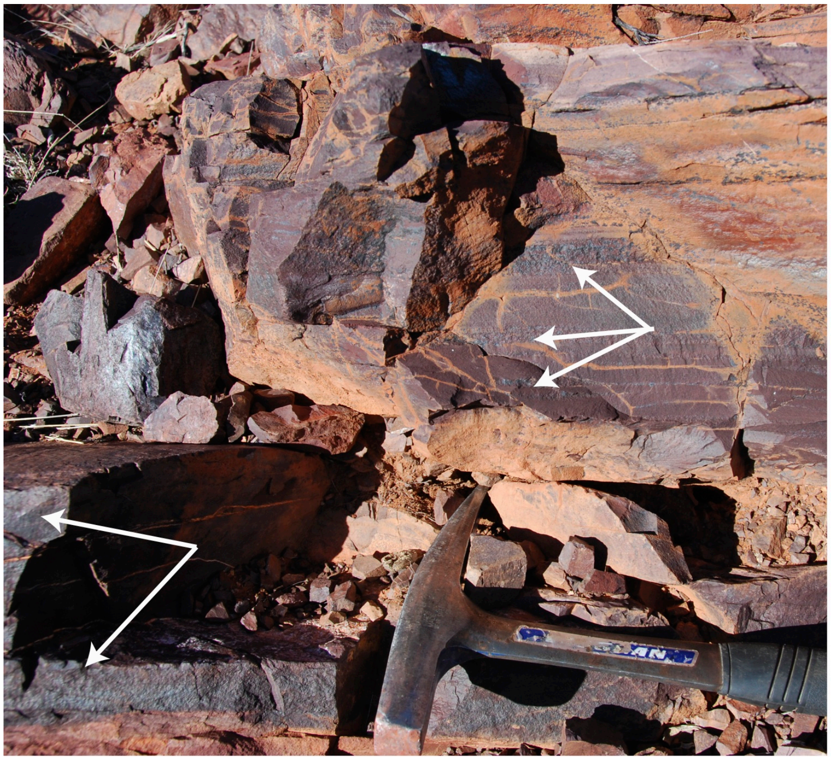

Figure 3: White arrows indicate manganese-enriched intervals in Koegas iron formation as exposed in the Rooinekke Mine section.

The Rooinekke Mine section (-28° 52' 21.36", +22° 42' 55.40") was a less comprehensive portion of the Koegas Subgroup, but nevertheless was informative. This section also had the microbialite unit, but it was less established and looked more like a transitional unit between a purely sedimentary and a microbial-sedimentary deposit. It was also significantly more iron and manganese-enriched, and therefore was sampled extensively. Similar to the Naragas section, the Rooinekke Mine section additionally had manganese deposits in its iron formation (Fig. 3), which I also sampled.

The United Manganese of Kalahari mine (-27° 22' 52.38", +22° 59' 9.41") exposed completely different strata: manganese and iron deposits in the Hotazel Formation overlying the strata of the Koegas Subgroup (Fig. 4). This was an extremely illuminating field stop as it was immediately clear how different the manganese enrichments were in the overlying strata as opposed to the manganese preserved in the cores. These manganese deposits were massive and concentrated, and dominated by manganese oxides although a fair amount of manganese was still hosted in carbonates from early biological reduction in the sediments. I sampled both core and field samples at this mine, and obtained samples both relatively pristine in preservation and also highly altered by later fluids, heat, and pressure, which will be an interesting study in itself and a good database to compare other manganese deposits to, such as the manganese enrichments in the cores.

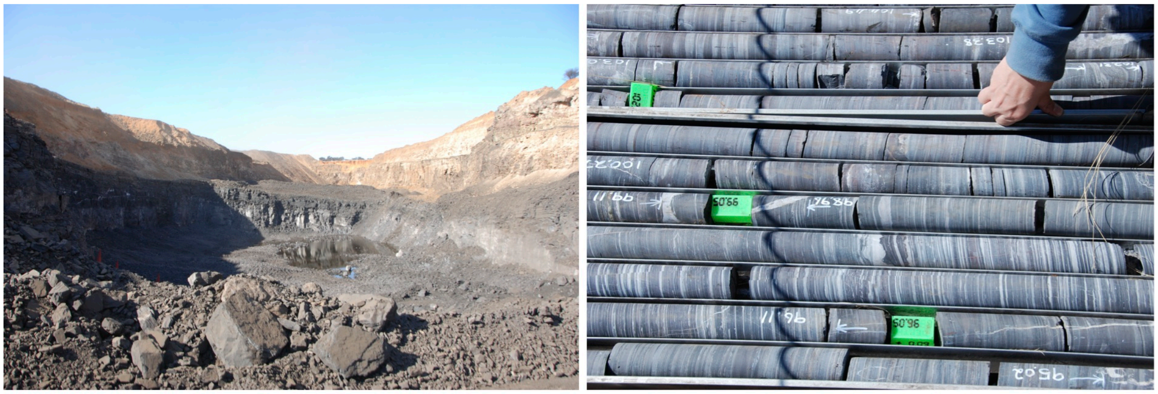

Figure 4: Manganese oxide deposits in the overlying Hotazel Formation, from United Manganese of Kalahari Mine.

A final destination was the Kuruman Kop section (-27° 22' 9.58", +23° 20' 38.52") which exposed strata from the earlier ~2.6 Ga carbonate platform (the Kogelbeen and Gamohaan Formation) and going through to the ~2.5 Ga Kuruman Iron formation. There were no obvious signs of manganese enrichments in these sections, but well-preserved carbonate textures and the overlying iron formation were sampled for manganese abundance.

The suite of field samples was complemented by core samples from the collection of our collaborator, Professor Nic Beukes at the University of Johannesburg (Fig. 1). He provided additional samples of the Kuruman Iron Formation, as well as samples from the Griquatown Iron Formation which lies between the Kuruman and the beginning of the cores' strata. Professor Beukes additionally provided samples of iron and manganese samples from the Hotazel Formation, supplementing the field samples from the United Manganese of Kalahari mine.

This large suite of samples will be thoroughly analyzed using a variety of instrumentation. Unfortunately, no pyrite nodules were found from overlying strata to perform texture-specific sulfur isotopic analyses on. However, I now have a vast collection of samples from which to unravel the ancient manganese cycle.

The abundant microbialite field samples will be examined for possible indications of manganese-oxidizing or manganese-reducing bacteria. Thin sections will be made of the microbialite samples and manganese abundance maps will be generated using the Electron Probe Micro-analyzer at Caltech. Additionally, the samples will be analyzed on the X-ray microprobe at the Stanford Synchrotron Radiation

Lightsource, which generates manganese redox maps and would reveal any signs of manganese oxides.

The returned samples from strata above and beneath the cores' extent will be thoroughly explored. Their manganese content will be determined using atomic absorption spectroscopy housed in the environmental microbiology lab at the University of Southern California. I will then investigate manganese-enriched intervals using two micrometer-scale techniques, which is necessary due to the fine-grained nature of iron formations. The Field Emission Scanning Electron Microprobe (Fe-SEM) with an energy dispersive spectrometer (EDS) and the Electron Probe at Caltech will map both variations in manganese concentration and indicate co-occurring elements. These techniques will yield likely mineral hosts for the manganese and are well complemented by X-ray mapping at a 2 μm scale at the Stanford Synchrotron Radiation Lightsource. Collectively, these analyses will determine when in the South African sedimentary record the manganese enrichments begin and in what form, and additionally, when the manganese begins to be stabilized in the record as an oxide instead of reduced by post-depositional processes.

This Lewis and Clark-funded expedition to South Africa has enabled me to collect a range of samples vital to understanding the evolution of the ancient manganese cycle, shedding light on the evolution of atmospheric oxygen and the development of oxygenic photosynthesis.