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Lewis and Clark Fund for Exploration and Field Research in Astrobiology
Project Title: *A Study of Precipitation in Diffusion – Controlled Systems: Implications for the Formation of Terrestrial and Martian Hematite Concretions*

Project Report:

We carried out a 6-day field excursion to sites in Southeast Utah to observe the formation of mineral precipitates in the Navajo Sandstone. This trip is supplemental to my laboratory work in which I simulate precipitation of iron compounds at a moving reaction front, using gels as the diffusion medium. Gel diffusion experiments can be used to simulate processes that may occur in nature at the interface between reducing and oxidizing fluid fronts, as is believed to occur as groundwater moves through porous sedimentary rock. This is the same mechanism thought to be responsible for the formation of hematite concretions and Liesegang bands in the Navajo Sandstone, and has been proposed as an explanation for the hematite "blueberry" spherules found on Mars. Our laboratory work has shed some light on the processes by which minerals precipitate in diffusion-controlled systems, and the effects the diffusion medium has on precipitation, but until now we did not have a natural analog with which to compare our lab results. This field excursion was extremely useful in helping us interpret the precipitation structures we form in the laboratory, and observation of the varied kinds of concretion forms in Utah have greatly clarified the direction our future lab work must take.

Overview of Field site and Project Goals:

The Navajo Sandstone formation, formed ~150 million years ago from aeolian sand dunes, is spread across much of southeastern Utah, as well as northern Arizona, northwest Colorado, and parts of Nevada. Navajo Sandstone in the Grand Staircase Escalante National Monument, where this study was carried out, frequently occurs as rounded domes and bluffs that are white, yellow or red in color. Distinct layers of red, bleached, and recolored sandstone are visible in many locations. The bleaching and recoloration of rock is due to removal and re-precipitation of iron minerals in the sandstone pores. These ironstone precipitates are very resistant to erosion compared to the surrounding sandstone, causing the precipitation structures (such as spherical concretions, hollow spheres, "pipes", and bands) to weather out.

The goals of this field excursion were to locate hematite concretions weathering out of the sandstone and make observations to determine the process of their formation, to observe Liesegang banding in environments where micro concretions also form, and to observe the effects of pore size and grain size on precipitation structure. The many structures we observe in iron precipitation experiments in the laboratory suggest that very small variations in fluid composition, pH, and reactant concentration can greatly affect the morphology of the final precipitated structure. In the laboratory we have produced crystals and Liesegang bands of iron minerals, and "micro-concretions" (1-2mm spheres) of other minerals in diffusion-controlled systems. By observing the forms that precipitation of iron oxide creates in this natural system, we aim to construct hypotheses that can explain the unusual results we see in laboratory diffusion experiments.

Site 1: Spencer Flat, Escalante, UT

The first two days were spent at various sites in Spencer Flat, a short driving distance from Escalante, UT.

Both red and white sandstone was observed in this region, suggesting dissolution of hematite grain coatings (responsible for the red color of the sandstone) by some reducing fluid, that removed the iron and left the sandstone bleached white. There were also many sections that had been colored yellow, which is a secondary recoloring event that occurred after the initial bleaching, depositing goethite in the sandstone pores.

There were several types of features in this region that have importance to diffusion and flow:

- **Joints:** The sandstone in this region contained many joints (fractures where there was little rock movement) through which water appears to have flowed, judging from the yellow mineral residue emanating in a flow pattern from these cracks. Liesegang bands occur parallel to the flow lines (usually perpendicular to the joints).
- **Mini-concretions:** Hematite spheres about 1-2 mm in diameter, distributed throughout the sandstone matrix. It is unclear whether there is any pattern to the spatial distribution of mini-concretions within the sandstone, since it appears random in some places and like a nearest-neighbor distribution in others. These concretions are strong and resistant to weathering, and collect in low-lying areas on the surface once weathered out.
- **"Freckles":** Similar appearance to mini-concretions (hematite spheres 1-2 mm in size) but not as well cemented, and do not weather out of the sandstone. The "freckles" are much weaker than the other concretions and will crumble like the rest of the quartz sand if any force is applied. We also observed less well-defined freckles which we termed "paint spatters" for their irregular appearance. Like the freckles, they were a few millimeters in size, weak, and not resistant to weathering, but had more oval shapes and sometimes even rind-like appearances.
- **Hematite "rind" concretions:** Hollow spheres of hematite, about 3-6 cm in diameter, in which a solid spherical rind (about 3 mm thick) surrounds a region of sandstone. The interior of these concretions is made of sandstone that is easily scratched out, unlike the strong outer shells. Many of the rind-like concretions have what appear to be diffusion patterns in their interiors, consisting of "target" shapes, sometimes a secondary ring of red-colored quartz sand inside the rind, and sometimes a "nucleus" sphere of sand that appears to have undergone secondary coloration. However even when the interior of the concretions contains some color pattern, the composition is still porous sandstone that is not heavily cemented.

Fluid reaction boundaries were clearly visible at the boundary between red and white (bleached) sandstone. "Freckles" and mini-concretions still embedded in the rock were only found in the unbleached red sandstone, not in the adjacent white regions. This suggests that red is the original color and bleaching occurred to remove the iron in the rocks, followed by secondary coloring that produced yellow flow lines and bands emanating from the joints where water flowed. The large rind-like concretions were observed embedded in the white sandstone, and many times the hematite rind surrounded an untouched sphere of red sandstone with freckles, similar to the unbleached sandstone adjacent to the bleached area. The yellow flow lines and Liesegang bands coming out of the joints surround the concretions as if they stood in the way of the flow, or were possibly formed in the same event. That the concretions in bleached sandstone contain interiors of unbleached sandstone suggests that the rind may have formed in a fluid flow event that occurred prior to (or concurrent with) the bleaching. It is possible that the hematite rinds, mini-concretions, and flow patterns are formed by advective flow of groundwater, but once the hematite rind is formed it is mostly impermeable and the concretion interior becomes diffusion-

controlled. If this is the case, the patterns in the interior of the concretions are a secondary event that occurred after the formation of the rind.

Site 2: Coyote Buttes, UT

The last part of the trip was spent at Coyote Buttes, UT, which is about an hour's drive from Page, AZ. In particular we looked at the region known as The Wave.

This region contained many different colors of sandstone that were sharply defined in layers of orange, red, white, and yellow. Not many large rind-like concretions were found in this area; however micro-concretions and Liesegang banding were abundant.

There were several features indicative of fluid flow:
- **Liesegang bands:** Bands that form through slow diffusion of one reactant-containing fluid into another. The formation of finely banded precipitates is dependent on many factors such as relative reactant concentration, the properties of the diffusion medium (in this case sandstone), and the presence of competing impurities. In Coyote Buttes bands were observed in many locations: red bands in red sandstone, yellow bands in bleached sandstone, red bands in bleached sandstone, and so on.
- **Micro-concretions:** Micro-concretions appear to have formed near the reaction fronts (where bands also occur, at the interface between bleached and unbleached sandstone). Micro-concretions occurred in both bleached and unbleached rock, although they tended to appear more in the red sandstone. Many areas where micro-concretions were found also had associated Liesegang bands that separated the bleached from the unbleached area.

The fluid boundaries were very well defined in most of this region. A common sight was red sandstone with micro-concretions embedded in the rock, bordered by yellow and red Liesegang bands, next to a region of bleached sandstone. It is possible that in such regions, the concretions, banding, and bleaching are all part of the same fluid flow event. It was also common to see regions of Liesegang banding overlaying already formed bands and bleaching fronts, as if a second fluid flow event occurred after the original one.

In this region concretions appear to be strongly associated with Liesegang bands, rather than being two separate processes, and since bands usually form in diffusion-controlled environments (where convection and advection are absent) this suggests that concretions should be able to be formed in diffusion controlled systems as well.

Conclusions / Future Work:

In laboratory diffusion experiments we have produced precipitation forms such as micro concretions, Liesegang bands, crystals, and colloidal particles. The relationship of these structures to one another and the conditions under which each will form is not clear, and to use the morphology of a precipitation structure to constrain properties of the fluid that formed it requires a more complete understanding of precipitation and diffusion in porous systems. In this natural environment we observe that Liesegang bands and concretions of various size form next to one another, possibly in the same fluid flow event, and why large concretions form in some situations and micros associated with banding form in others is still a mystery. The aquisition of photos and samples from this field excursion, coupled with future lab work, will hopefully shed some light on these processes and enable us to make educated guesses about the processes that formed mineral precipitates on Mars.

Figure 1: (Left) Large hematite concretion embedded in bleached sandstone. The concretion interior is unbleached and contains small iron precipitates ("freckles"), yet the sandstone surrounding it is bleached with yellow Liesegang bands and fluid tracks. (Right) Concretion in bleached sandstone, with fluid tracks going around it.

Figure 2: Unbleached red sandstone next to bleached white sandstone (with secondary coloring in the form of yellow Liesegang bands)

Figure 3: Joint in bleached sandstone with flow tracks. The yellow coloration is from iron minerals (probably goethite) precipitating. Liesegang bands are formed as fluid diffused perpendicular to flow tracks.

Figure 4: Concretions from Spencer Flat. All have the hard outer rind and soft sandstone interior. Many have diffusion patterns, Liesegang banding, and "freckles" in their interiors.

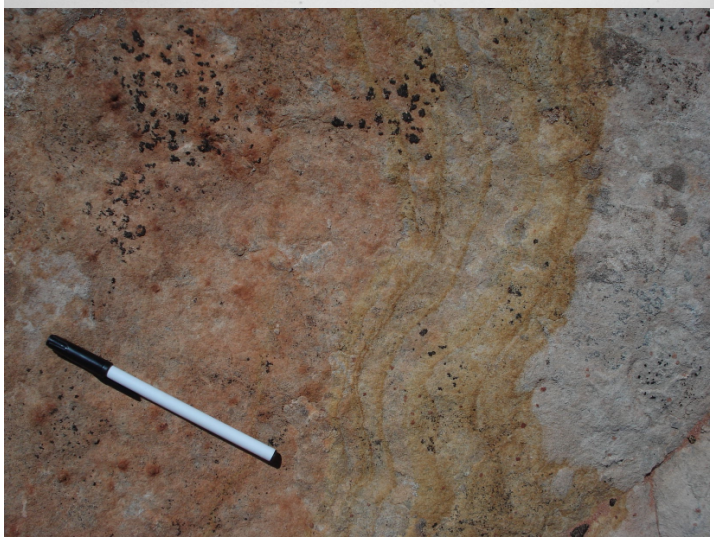

Figure 5: Coyote Buttes - red sandstone containing mini-concretions, followed by yellow Liesegang banding, followed by bleached sandstone.