

MARS SEDIMENT ANALOG? DARK BIOMINERALIZED MN-OXIDE/HYDROXIDE CEMENTED SANDSTONE OF LOW-T SPRING ORIGIN. J. L. Berkley, Department of Geosciences, SUNY Fredonia, Fredonia, NY 14063 and Kaitlyn Dykstra, Department of Biological Sciences, Carnegie Mellon University, Pittsburgh, PA 15213.

Introduction: Detailed petrological analysis of a dark black to dark brown conglomeratic sandstone in southwestern New York State shows that its cementing agent is composed mainly of mixed Mn oxide-hydroxide minerals (MOH), some with significant Ba (~10 wt%). Lamellar textures of these mineral precipitates strongly suggest bacterial or other microbiotic deposition. This study includes an attempt to characterize possible microbial species involved in precipitating this cementing agent. Although our sandstone occurs in an inactive, fossil spring setting, active springs and aqueous seeps occur nearby that may portray a model environment for the creation of our samples.

The deposition environment of this sandstone may mimic early Martian environments where subsurface bacteria-laden water deposited Mn minerals as thinly-laminated biofilm structures along clastic grain boundaries. The resulting indurated sedimentary rocks would likely take on a uniformly dark color.

Analytical: Samples of the black sandstone were analyzed using standard light-optic petrographic techniques, scanning electron microscopy with quantitative EDS spectrography (SEM incl. BSE; SUNY Buffalo), x-ray fluorescence (XRF) semi-quantitative analysis (SUNY Fredonia), and by quantitative electron microprobe (SEMQ; RPI, Troy, NY). Genomic DNA was isolated from 4 samples of the active biofilm using a Qiagen DNeasy kit. Sequencing of the PCR amplified 16S rRNA gene was performed on a LiCor 4300 DNA Analyzer at SUNY Fredonia and was classified using the Ribosomal Database Project [<http://rdp.cme.msu.edu>].

Textures: Framework grain size ranges from silt-size through small pebbles (~1-3 cm dia.), but most grains fall in the "sand" range, averaging 1.5 mm dia. Grains are generally angular and consist of mostly quartz, feldspar (K- and plagioclase), mafic silicates, and opaque oxides along with shale fragments from the local Devonian bedrock (Gowanda Fmn.). Manual point counts suggest a porosity of about 15%.

MOH cementing minerals attached to framework grains occur as compositionally homogeneous space-filling patches, and as finely laminated colloform or botryoidal structures (fig. 1). The latter texture is dominant and ubiquitous throughout the rocks, and is consistent with an origin by bacterial agents, e.g., [1,2,3]. Biofilm production progressed by adding new MOH layers upon early layers at the interface with

permeating hydrous fluids. The speckled layers in fig. 1 commonly produce lower-than-normal electron microprobe totals along with chlorine peaks, possibly indicating the presence of trapped organic material some of which may be remnant bacteria remains [2,3].

Mineral Compositions: SEMQ spot analyses of botryoidal precipitates show at least two different dominant compositions, one Ba-rich and the other Ba-poor. Ba-rich areas average about 50 wt.% Mn and 10 wt.% Ba, while Ba-poor areas average 51 wt.% Mn and 0.5 wt.% Ba. Calculated oxygen in both cases is slightly over 16% with minor (<<1%) abundances of Na, Al, Si, Cl, K, Ti, and Ca. Totals for analyses are consistently low, ~ 78% for high-Ba points and 70% for low-Ba points. These low totals suggest the presence of hydroxide or other amorphous or volatile components.

Mn oxides and hydroxides commonly occur as intimate intergrowths in "bog" ores and other terrestrial Mn deposits. Point analyses of Mn-rich cement suggest a fine mixture of pyrolusite (MnO_2) plus hollandite ($\text{Ba}_{0.2}(\text{Mn,Fe,Al})_8(\text{O,OH})_{16}$) or romanechite ($\text{Ba}_2\text{H}_2\text{O}_2$)

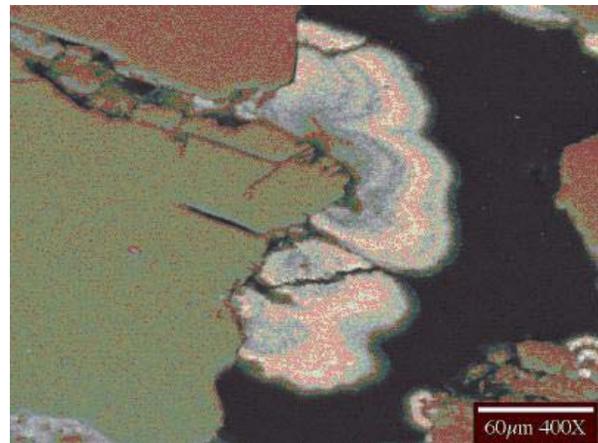


Fig. 1. Backscattered electron (colorized BSE) image of laminated MOH minerals. Framework grains (mostly left) are feldspar (lower) and quartz (upper). Dark area is pore space.

Mn_5O_{10} and may explain our non-stoichiometric analyses. Extremely low values of Fe (0%) and Al (avg. 0.33wt%) suggest that romanechite (psilomelane) is the more abundant Ba-rich oxide in the mix. Neither of those species, however, have been previously reported as biologically deposited species. On the other hand, both Ba-rich and Ba-poor MOH minerals occur in laminated deposits (fig. 2), so if these laminae are,

in fact, biological products the Ba-rich phases may be the first reported occurrences of biological Ba-Mn minerals. Commonly reported Mn bacterial products are Todorokite $Mn_4O_7 \cdot H_2O$ and Birnessite $Na_4Mn_4O_{27} \cdot 9H_2O$ [5], the latter eliminated in the current study by its high Na. Notably, common oxides like pyrolusite MnO_2 have not been analyzed as individual grains in the black sandstone. Figure 2 shows typical distribution of MOH in sandstone cement distinguished by Ba-Mn content.

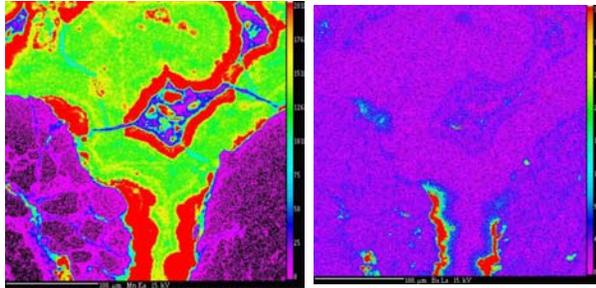


Figure 2. Left: Mn distribution in oxide/hydroxide cement (x-ray map: red=high; blue=low). Framework grains at left and right (violet). Right: Ba distribution in same area. Note that Ba enrichment is not universal, and highest Ba concentrations were deposited early.

Depositional Environment: The black manganese-rich sandstone of this study originated as loose, mostly glacially-derived fluvial sediments now overlain by roughly 2.5 meters of post-glacial flood plain silt and clay mud. It is exposed by erosion of the current modern stream (Canadaway Creek; Chautauqua Co., NYS) as an outcrop measuring ~20 cm thick and 3 meters wide. Numerous modern springs enter the creek nearby (fig. 3), waterflow in most cases being controlled by buried stream channel deposits. The black sandstone seems to have had a similar origin, but is no longer an active spring. The source of Mn for the black cementing agent is easily explained as hydraulic leaching of this ubiquitous element (12th most abundant) from the varied Canadian Shield glacial materials along the path of the spring water. Ba occurs as a component of alkaline feldspars and in barite.

The virtual complete lack of Fe-bearing cement is problematic, but could have been controlled by water pH, neutral or slightly basic conditions favoring Mn transport over Fe. Another possibility is that the bacterial agents in these spring sands were adapted to oxidizing Mn, not Fe. It is well known that metal oxidizing bacteria specialize in the kinds of metal species they utilize to provide energy [4,5]. Rust-colored biofilms (fig. 3) with brittle iridescent surface films occurring along Canadaway Creek have been shown to pos-

sibly have the effect of converting loose sediments into poorly indurated black sandstone, similar to the more indurated sandstone in this study. Preliminary sequence analysis of these modern biofilms using the highly conserved 16S rRNA gene [6] shows that the sequence obtained is most likely from the genus *Gallionella*, however our sequence similarity was only approximately 90%. More sequences will have to be obtained before any conclusions are developed as to the biological origin of the sandstone or the presence of bacteria involved in the biogeochemical cycle of barium. Even so, *Gallionella* has been documented to produce biofilms and while the more common *Gallionella ferruginea* is an iron oxidizing bacteria, there are also manganese oxidizing bacteria within the genus.



Mars Connection:

Climatic conditions on Mars suitable to facilitate the production of biogenically deposited Mn^{4+} (and Fe^{3+}) oxides would have prevailed in the period 4.2 to 3.5 billion years ago during a period of Earth-like conditions [7].

Figure 3. Microbial ooze in an active spring, sampled for DNA analysis.

Groundwater at that time should have been sufficiently basic to encourage inorganic aqueous mobilization of Mn, to be later precipitated with the help of indigenous bacteria, assuming such organisms existed in subsurface spring flows. The Mn-rich black sandstone of this study shows how such rocks can form in a restricted environment given proper geochemical and geological conditions.

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References: [1] Schieber J. (2005) *LPS XXXVI*, Abst 1972. [2] Chafetz H.S. et al. (1998) *J. Sed. Res.* **68**, 404-412. [3] Chafetz, H.S. (2005) *LPS XXXVI*, Abst 1084. [4] Frankel, R.B. and Bazylinski, D.A. (2003) *Min. Soc. Am. Reviews in Mineral. and Geochem.* **54**, 95-114. [5] Brown, D.A. et al. (1998) *Am. Min.*, **83**, 1419-1425. [6] Giovannoni, S.J. et al. (1990) *Nature* **345**, 60. [7] Bell, J. (2006) *Sci. Am.* **29**, 62.