BIOGENIC BA-RICH MN OXIDE-HYDROXIDE CEMENTED SANDSTONE AS POSSIBLE MARS ANALOG. J. L. Berkley, Department of Geosciences, SUNY Fredonia, Fredonia, NY 14063.

Introduction: A dark black conglomeratic sandstone in a post-glacial spring deposit in southwestern New York State has been found to contain a cementing agent composed mainly of mixed Mn oxide-hydroxide minerals (MOH), some with significant Ba (~10 wt%). Textures of these mineral precipitates suggest biological, probably bacterial deposition. Although oxidation of soluble Mn^{2+} is favored in natural terrestrial waters, bacteria and fungi have been shown to accelerate oxidation to Mn^{4+} oxides, a common occurrence in Earth systems [1].

The deposition environment of this sandstone could mimic early Martian environments where subsurface bacteria-laden water deposited Mn minerals in interstices between loosely indurated clastic grains. Thus, not all black rocks on Mars need be interpreted as basalts. The geochemical and geological conditions necessary to promote Mn-oxide-hydroxide precipitation over other oxides (e.g., iron) is discussed below. Samples of the black sandstone were analyzed using standard light-optic petrographic techniques, scanning electron microscopy (SEM incl. BSE), x-ray fluorescence (XRF) semi-quantitative analysis, and by quantitative electron microprobe (SEMQ).

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., [2,3,4]. Biofilm production progressed by adding new MOH layers upon older layers at the interface with permeating hydrous fluids. The gray, speckled layers in Fig. 1 commonly produced 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 [3,4].

Mineral Compositions: SEMQ spot analyses of botryoidal precipitates shows 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, around 78% for high-Ba points and 70% for low-Ba points. These low totals suggest the presence of hydroxide or other amorphous or volatile component. In addition, analyses do not compute to recognizable stoichiometric formulas of known Mn oxides or hydroxides suggesting mixtures of minerals and possibly amorphous compounds (including organics).

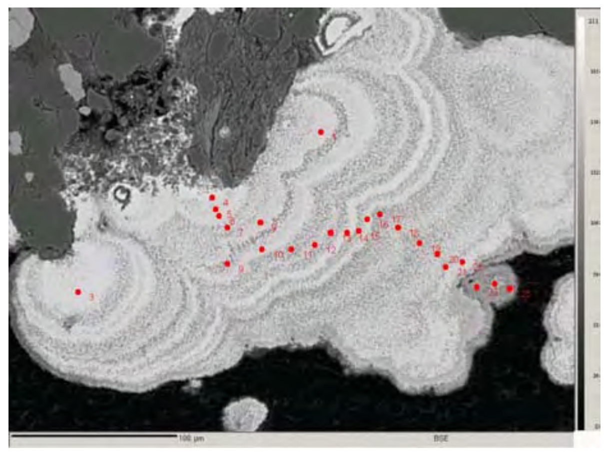

Fig. 1. Backscattered electron (BSE) image of laminated MOH minerals with microprobe analysis spots. Dark framework grains are shale (upper middle) and qtz-feldspar (upper left).

The only realistic candidates for the high-Ba materials are hollandite $(Ba,Pb,Na,K)(Mn,Fe,Al)_8(O,OH)_{16}$ and romanechite $(Ba,H_2O)_2Mn_5O_{10}$, but neither of those species have ever been reported as biologically deposited. On the other hand, both Ba-rich and Ba-poor MOH minerals occur in laminated deposits (Fig. 1), 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 $Na_4Mn_{14}O_{27} \cdot 9H_2O$ [5], the latter eliminated in the current study by its high Na. Notably, common oxides like pyrolusite MnO_2 have not been analyzed in the black sandstone. Figure 2 shows typical distribution of MOH in sandstone cement distinguished by Ba-Mn content.

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, waterflow in most cases being

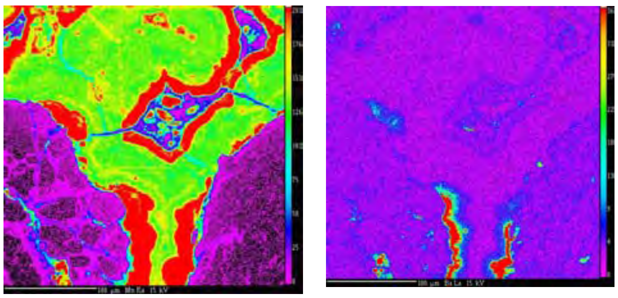

Figure 2. Left: Mn distribution in oxide/hydroxide cement (x-ray map: red=high; blue=low). Framework grains at left and right (violet). Right: Ba distribution in same area. Note that Ba enrichment is not universal.

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 element) from the varied glacial materials (Canadian Shield Grenville basement) along the path of the spring water. Ba occurs as a component of alkaline feldspars and in barite, both sources certainly present in the leached glacial deposits.

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 [5,6]. Rust-colored biofilms with brittle iridescent surface films occurring along Canadaway Creek have been shown to possibly have the effect of converting loose sediments into poorly indurated black sandstone, similar to the more indurated sandstone in this study. DNA sequencing is being performed on these biofilms to identify the host bacteria.

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]. 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. Such deposits are also effective retainers of heavy metals (like Ba) [1], so could be utilized by future Mars explorers as useful metallic ore materials.

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