Bacterially induced Mn-oxides: Mn^{+4} a biosignature. H. S. Chafetz, Geosciences, University of Houston, Houston, Texas 77204-5007; HChafetz@uh.edu

Mn-rich precipitates accumulate as a constituent in a wide variety of sedimentary deposits, including hot springs, cold springs, spelian, deep marine nodules, desert varnish. In many terrestrial accumulations, precipitation of the Mn-rich minerals have been attributed to microbially influenced processes. The most readily apparent accumulations have an arborescent or shrub-like morphology (Fig. 1). Briefly, the

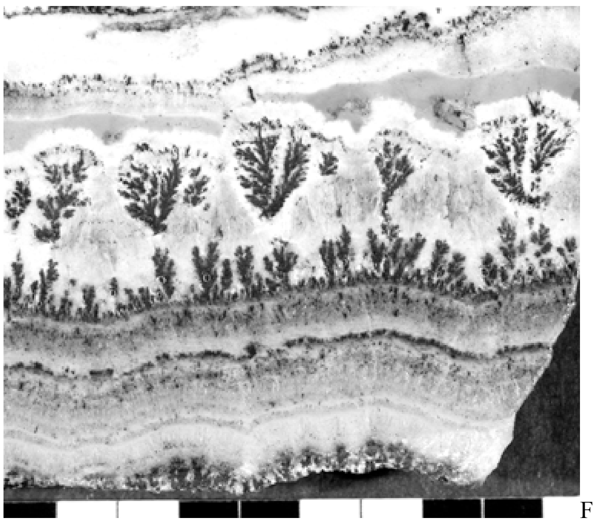

Fig 1. Layers of black Mn-rich bacterial shrubs with typical arborescent form surrounded by white to light tan carbonate. Smaller dark blebs are similar to the bacterial oncoids shown in fig. 2. Quaternary of Morocco, scale bars = 1cm.

shrubs are interpreted as bacterially induced precipitates because: they display a highly irregular, non-crystallographic morphology typical of the garden variety shrub or bush (1), laboratory cultures have shown that bacterial colonies can form aggregates essentially identical to the shrubs (2), the structures commonly display a plethora of bacterial fossils whereas the immediately adjacent enveloping precipitates are essentially fossil free (1), and laboratory experiments have demonstrated that bacteria, acting as catalysts, can speed up the oxidation of Mn-oxides by 4 to 5 orders of magnitude over the rates of abiotic precipitation (3, 4). However, shrubs, while a readily apparent biotically induced deposit, are not the only form of the Mn-rich precipitate. Thus, is there a biosignature by which other deposits that are not as obviously biotically induced Mn-rich precipitates as the shrubs be recognized?

Amorphous Mn-oxide deposits have precipitated out of hot spring waters in Yellowstone, N.P., that have less than 0.2ppm Mn. The Mn-rich precipitates, including oncoids (bacterial coated grains), coatings on cyanobacteria, and dense laminae (Fig. 2), are composed of slightly curved

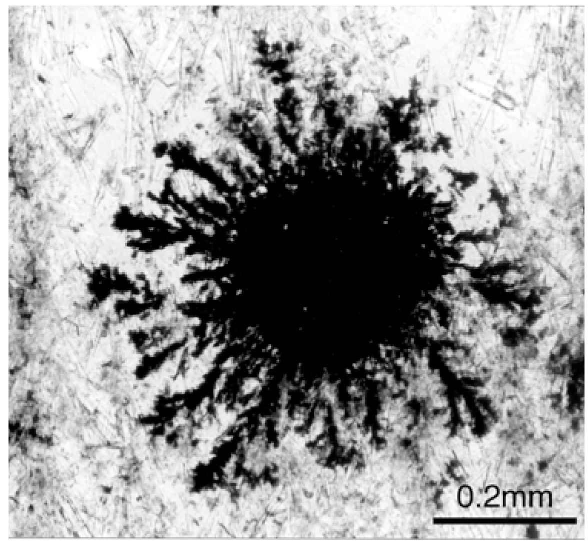

Fig 2. Photomicrograph of bacterial oncoid. Morphologically and compositionally the radially arranged appendages are essentially the same as those forming the horizontal shrub horizons (fig. 1), i.e., each are composed of bacterial fossils within curved sheets of Mn-oxides (fig. 3). Young Hopeful Geyser, Yellowstone N.P., Wyoming.

sheets in which bacterial body fossils are an abundant, conspicuous constituent. The slightly curved sheets of Mn-oxides precipitated within the lattice of bacterial bodies and stretch between and envelope the individual fossils (Fig. 3). The bacteria are rod-shaped, commonly curved and approximately 0.1μ by 1μ. The sheets of precipitate are irregular in outline, generally on the order of 5μ across and appear to be tens to hundreds of nanometers thick. The curved sheets are interpreted to be Mn-oxide replaced biofilm. It has been reported that synthetic Mn-oxides tend to have a low oxidation state, around 3, whereas Mn-biooxides have an oxidation state ≥3.4 (5). X-ray Photoelectron Spectroscopy (XPS)

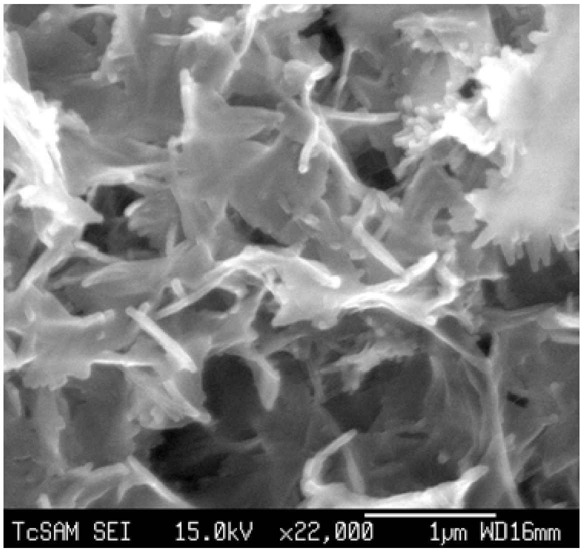

Fig. 3. SEM view of a bacterial oncoid (similar to fig. 2) shows the typical abundance of bacterial bodies within the curved sheets of Mn-oxides. this view is representative of all of the Mn-oxides, i.e., the shrubs, oncoids, dense laminae, as well as the coatings on cyanobacterial filaments. Young Hopeful Geyser, Yellowstone N.P., Wyoming.

analyses of the modern precipitates from the hot springs in Yellowstone show that the Mn-oxides are dominantly composed of Mn^{+4} with 5 to 15% Mn^{+2}, thus, supporting the early suggestion.

In order to substantiate these findings, previously studied samples from Quaternary age deposits from older inactive travertine sites in northeastern Morocco as well as deposits near Belen, New Mexico, USA (6), were also subjected to XRD and XPS analyses. These samples display all of the megascopic and microscopic attributes of bacterial shrubs (Fig. 1), i.e., they have the shrub morphology and are composed of densely packed bacterial fossils. The XRD analyses demonstrated that the Mn-oxides in these older deposits have very high oxidation states, they are mineralogically composed of pyrolusite ($Mn^{+4}O_2$), and very minor amounts of cryptomelane ($KM^{+4}{}_6Mn^{+2}{}_2O_{16}$). Corroborating the XRD results, XPS analyses of 3 shrubs from Morocco and 1 from New Mexico showed that essentially all of the Mn-oxides are in the Mn^{+4} state.

The Yellowstone precipitates and older Mn-oxide bacterial deposits from New Mexico and Morocco display oxidation states ≥ 3.7 whereas laboratory produced abiotic Mn-oxides are reported around 3.0 (6). Therefore, it is proposed that a high Mn-oxidation state is an indicator of bacterially induced precipitation, an indicator of previous life, i.e., a biosignature,.

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