MINERAL PRECIPITATION BY MN-OXIDIZING MICROBES: COMPARING NATURAL AND CULTURED MN-MINERALS. M.N. Spilde¹, P.J. Boston¹, R. T. Schelble³, and J.J. Papike¹, ¹ Institute of Meteoritics, University of New Mexico, Albuquerque, NM 87131 (mspilde@unm.edu), ² Department of Biology, University of New Mexico, Albuquerque, NM 87131 (pboston@complex.org), ³ Department of Earth and Planetary Sciences, University of New Mexico, Albuquerque, NM 87131.

Introduction: Microbial oxidation of Mn is common in the terrestrial environment and can be found in deep marine, lake sediment, and hot springs environments. We have cultured microorganisms from Luruguilla and Spider Caves in Carlsbad Caverns National Park, New Mexico where Mn-oxides are abundant on cave surfaces and present even on some speleothems. Mn-minerals are often associated with Al and Al-minerals including goethite, hematite and nordstrandite. Amorphous Mn and Fe oxyhydroxides are also present. Prior work has shown that these deposits are microbially influenced [1]. DNA analysis yields a community of microorganisms, including Mn-oxidizers [2].

Biotically precipitated Mn-oxides are initially amorphous or poorly crystalline oxides. The exact mechanism of precipitation and metabolic pathway is poorly understood, as is the path by which the amorphous material organizes into crystalline minerals.

Methods: Liquid and agar plate media were enriched with 0.1 % wt/vol of MnO, MnCl₂, MnCO₃, Mn₂O₃, or Mn(NO₃)₂. In addition, a full suite of media contained low carbon (0.1%) to identify Mn-oxidizing chemolithotrophs (need organic carbon), while another suite contained no carbon to identify Mn-oxidizing chemoorganotrophs (Mn oxidation as sole energy source). Both live and killed cultures and controls were examined by optical microscopy, SEM/EDX and XRD at intervals of 2 weeks, 1, 3 and 8 months.

Results: At least two different organism strains have been isolated on the two different media types. Both precipitate Mn, one requiring low organic carbon and the other requires little or no organic carbon to be present. Cultures only a few weeks old exhibit visible growth of dark Mn-rich material, while un-innoculated control samples shown no visible growth. XRD analysis indicates that young cultures produce only amorphous phases (Fig. 1a). After 3 months, weak crystalline peaks are visible in XRD (Fig. 1b), and as the cultures age, crystallinity increases. At 8 months, XRD peaks have grown in number and intensity (Fig 1c). To test whether microbial activity has an influence on the degree of crystallinity, a live culture was killed and fixed at 1 month, stored at room temperature, and then examined at 8 months. This fixed culture showed no development of crystalline peaks in XRD indicating that the amorphous Mn precipitates do not undergo auto-crystallization.

Both the liquid and plate cultures precipitate identifiable Mn-oxides: buserite, Na₄Mn₁₄O₂₇·7H₂O (a poorly-crystalline 10-angstrom manganate); birnessite, (Na,Ca)₆₃Mn₆O₁₃·1.5H₂O; and vernadite, MnO₃(Mn,Fe,Ca,Na)(O,OH)₆·nH₂O. Buserite is present initially in XRD patterns, but birnessite and vernadite peaks become visible at 3 months. Phosphate is added to the media to ensure adequate basic nutrients; as a result, the most abundant Mn mineral that forms in the agar plate cultures is switzerite (Mn₆(PO₄)₆·7H₂O).

SEM imaging indicates that the oxides are present near the surface of the plates in grape-like clusters of sub-micrometer spheres, which may be incrusted microbial bodies. Optical examination of the plates, however, confirms that the Mn precipitate extends deep into the agar, forming nodules interconnected with dark filaments. The switzerite forms 20 - 50 µm starburst-like disks at the surface.

Discussion: The natural samples from Lechuguilla and Spider Caves contain significant amounts of Fe and Mn-oxides, microbially leached from the altered bedrock [3]. The principal Mn-oxide is todorokite (Fig. 2), ± birnessite and feitknechite, along with varying amounts of amorphous Mn-oxhydroxides. Previous work indicates that the oxidation state of Mn ranges from 2⁺ to 4⁺ [4]. The culture samples seem to parallel the natural samples where a range of both crystallinity and oxidation state are present. Buserite and birnessite host variable oxidation states of Mn, and vernadite is predominantly 4⁺. The 10-angstrom manganate mineral probably consists of loosely bound sheets of Mn-octahedra, resulting from initial crystallization of the amorphous Mn-oxide. Over time these sheets become organized into birnessite and todorokite, both of which contain channel- or tunnel-like arrangements of Mn-octahedra. Therefore the 10-angstrom manganate in the cultures represents a precursor to todorokite, which is present in the natural samples.

Figure 1

Figure 2