DETERMINING THE BIOSIGNATURE PRESERVATION POTENTIAL OF MANGANESE OXIDES USING LABORATORY AND SPACEFLIGHT ANALYSIS TECHNIQUES.

L. E. Judge[1], A. J. Williams[1], N. L. Lanza[2], A. M. Ollila[2], M. N. Spilde[3], V. W. Lueth[4], S. E., [1]Department of Geological Sciences, University of Florida (laurenjudge@ufl.edu), Gainesville, FL, U.S.A., [2]Los Alamos National Laboratory, Los Alamos, NM, U.S.A., [3]Institute of Meteoritics, Department of Earth & Planetary Sciences, University of New Mexico, Albuquerque, NM, U.S.A., [4]New Mexico Institute of Mining and Technology, Socorro, NM, U.S.A.

Introduction: On Earth, microorganisms almost always facilitate the formation of manganese oxides. This is because Mn-oxides require a high pH and strong oxidizing conditions to precipitate from fluids, but microbial metabolisms can create microenvironmental conditions conducive to Mn oxidation outside of these strict Eh and pH conditions. Mn-oxides recently identified on Mars indicate that alkaline and very oxidizing conditions have existed in the past in select environments [1-3]. Because of the intrinsic connection between Mn-oxides and life on Earth, research on ways to differentiate between biogenic and abiogenic manganese deposits on Mars is of the utmost importance [4-5]. Because Mars surface mission instrument payloads are restricted, it is necessary to identify biosignatures in terrestrial Mn-oxides that are detectable with current and future rover payloads. Here we focus on assessing the preservation of organic and morphologic biosignatures in natural and laboratory-precipitated Mn-oxides.

Biogenic Mn-oxides demonstrate specific trends in chemistry and mineralogy that are shared across suites of Mn-oxides. For example, poorly crystalline, layered Mn-oxides that are high in Mn(IV) and low in Mn(III) are typical of microbial oxidation [6]. However, the mineralogy alone of Mn deposits cannot distinguish the biogenicity, as many factors can affect mineralogy such as temperature, water availability, pH, and O_2 availability. Current research is focusing on multiple potential biosignatures including trace element trends [7], mineralogic structures [8], and biotextures [9]. The mineral structure of Mn-oxides may also preserve organic biosignatures in the form of organic matter from microbial communities [10], which is a large focus of this project.

Sample Suite: There are many well-studied manganese deposits of both biogenic and abiogenic origin in New Mexico, ranging from abiotic hydrothermal vein deposits [11], to active cave systems that contain biogenic manganese minerals [12-15]. Samples from these field sites will be used to determine the viability of biosignature detection in natural manganese oxide deposits with laboratory and rover payload instruments. Three natural rock samples from Mn-oxide deposits with both biogenic and abiotic origins were obtained from previously identified sites in New Mexico (Fig. 1). These samples represent a range of environments and a variety of preservation styles. MCA is from a hydrothermal deposit, and likely abiotic. TM is likely biotic and from a geothermal spring edifice and TC is from the biotic Ellis Mn deposit. Water samples were also obtained from the Snowy River Passage in Fort Stanton Cave in central NM, which has walls and ceilings covered in Mn-oxide crusts [14]. Natural waters from such cave systems can be used to determine oxidation rates of Mn in nature, as well as to learn more about the role of microbes in the oxidation process.

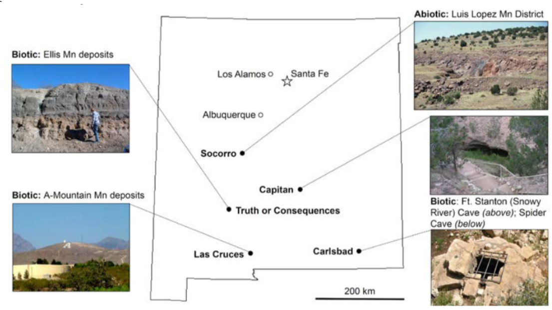

Figure 1. *Locations of high manganese deposits with both biotic and abiotic origins in New Mexico. Samples for this study were obtained from Socorro, Las Cruces, Truth or Consequences, and Capitan.*

Methods: Rock samples were cracked in half with ashed (at 500°C for 8 hours) chisels to provide a fresh surface and a dental drill with ashed drill bits was used to collect powder from the rock interior. The powder was then homogenized in a solvent-washed and ashed mortar and pestle.

GC-MS of rock samples. A solvent-washed spatula was used to load 3-5mg of ground sample into a cup. Samples were analyzed on an Agilent GC-MS coupled to a Frontier pyrolyzer. Samples analyzed for alkanes were pyrolyzed at 600°C for 0.5 minutes. The oven program ramped from 50°C to 300°C at 20°C/min with a 10-minute hold. Samples analyzed for fatty acids were subject to trimethylsulfonium hydroxide (TMSH) thermochemolysis at a ratio of 1µL TMSH to 1mg sample, with the same pyrolyzer and oven programs as for alkanes.

Precipitation of Mn-oxides. Samples of natural waters from the Snowy River Passage in Fort Stanton Cave in New Mexico were used to precipitate Mn-oxides to assess biotic Mn oxidation rates as per [10]. Precipitation experiments were performed with unfiltered natural waters as well as water filtered through a 0.1µm filter to remove microbes. Another set of precipitation experiments was completed with sterile materials to create abiogenic Mn-oxides for comparison. Water was placed in a sterile glass beaker at room temperature and pH and Eh were monitored periodically. Samples were analyzed on a UV vis spectrophotometer.

Trace Element and TOC Analysis. Trace element (TE) data were collected from the three New Mexico Mn oxide samples with ICP-MS bulk dissolution analysis. These samples were compared with two biotic deep-sea Mn nodules (Nod-P and Nod-A). Total Organic Carbon (TOC) was determined by measuring Total Carbon (TC) and Total Inorganic Carbon (TIC) and subtracting TIC from TC.

Solvent Washing. A subset of each rock sample was solvent washed to remove any surface organics using progressively more polar solvents and a sonicator.

Results: GC-MS data of the rock samples had no alkanes detectable with this method in both solvent washed and unwashed sample sets. A number of fatty acid methyl esters (FAMEs) were identified from all three rock samples. FAMEs from C_8 to C_{22} were detected in all three samples, with some variation in abundance and number of FAMEs (Fig. 2).

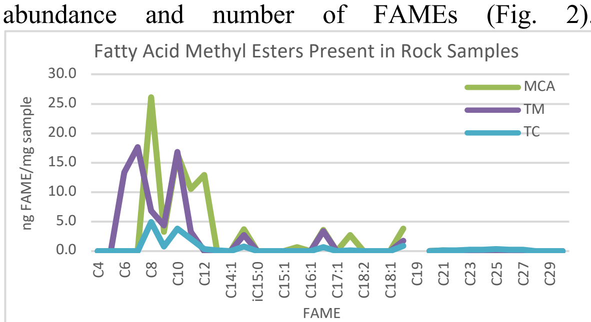

Figure 2. GC-MS data for FAMEs present in the three, non-solvent washed rock samples from New Mexico. TC has the lowest abundance of FAMEs.

TOC data suggest that two of the samples (MCA and TM) have high amounts of inorganic carbon. TC had the lowest amounts of TIC, but also the lowest amounts of TC. Overall, sample TM showed the highest amount of TOC (Table 1).

Sample	wt % TC	wt % TIC	wt % TOC
MCA-SW	11.27	11.21	0.06
TC-SW	0.45	0.24	0.21
TM-SW	10.07	9.56	0.51
MCA-NW	11.25	11.15	0.10
TC-NW	0.39	0.04	0.35
TM-NW	9.79	9.12	0.67

Table 1. TC, TIC, and TOC data for rock samples, both solvent washed (-SW) and not washed (-NW). TOC was calculated by subtracting TIC from TC.

Trace element data for the three rock samples were compared to TE data from two biotic deep-sea nodules. TC showed the most similarity in TE trends to the nodules, while TM and MCA both showed differences in both elements present and abundance of elements (Fig. 3).

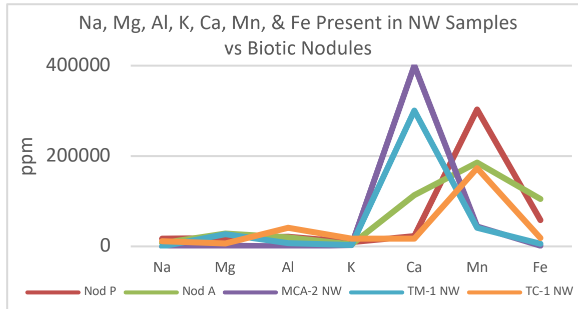

Figure 3. Select TE data for Mn-oxide samples compared to two biotic deep-sea nodules, focused on Ca, Mn, and Fe trends.

Discussion & Conclusion: Abiotic and biotic samples show similar numbers of FAMEs at varying abundances. MCA appears to have the lowest wt % TOC, while TM has the highest. Both MCA and TM also showed high wt % of TIC, due to the calcite layers present in these samples. Sample TC shows TE trends similar to two biotic deep-sea nodules, while MCA and TM show significant differences to the nodules, suggesting that TC is biotic and the other two samples are not. This will be compared with paleoenvironmental information for each sample to determine if the TE trends match expected biogenicity. These techniques, which are translatable to rover instruments, are promising for elucidating the biogenicity of Mn-oxides on Mars.

Ongoing and Future Work: Precipitation is underway, with results are forthcoming.

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