IDENTIFYING ORGANIC BIOSIGNATURES IN MANGANESE OXIDES. 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. Shaner[1], and L. Kivrak[1], [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, the formation of manganese oxides is almost always facilitated by microorganisms. This is because Mn-oxides require a high pH and strong oxidizing conditions to precipitate. The presence of Mn-oxides on Mars indicates that alkaline and very oxidizing conditions have been present in select local environments [1-3]. However, microbial metabolisms can create microenvironmental conditions conductive to Mn oxidation. Because of the intrinsic connection between Mn-oxides and life on Earth, new research is now exploring how to distinguish between biogenic and abiogenic manganese deposits on Mars [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 identifying organic biosignatures that may be present and persist in biogenic manganese minerals. The NASA *Curiosity* rover carries the SAM instrument, which is capable of organics detection with gas chromatography-mass spectrometry (GC-MS) [6]. The ESA *ExoMars* rover will carry the MOMA instrument, which is also capable of organics detection with GC-MS [7]. The NASA Mars 2020 rover will be equipped to detect organics with the SuperCam and SHERLOC instruments that combine laser-induced breakdown spectroscopy (LIBS), Raman spectroscopy, and time-resolved luminescence spectroscopy, and UV Raman spectroscopy, respectively. By using laboratory instruments to develop a better understanding of organic biosignature preservation in Mn-oxides, we will be better able to assess the biogenicity of Mn-oxides on Mars should they be encountered by a rover.

Sample Suite: 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). MCA-2 is banded Mn-oxide and calcite from the hydrothermal deposit at the MCA mine, Luis Lopez district, Socorro County, NM [8-10]. Because this paleo-hydrothermal environment likely experienced high temperatures, this sample is most likely abiotic. TM-1 is from Tortugas Mountain (A-Mountain), and is banded Mn-oxide and calcite from a geothermal spring edifice, Dona Ana County, NM [11]. This sample is likely biotic. TC-1 is a manganese "stromatolitic" mineralization near the end of Kopra Street in T or C, from the biotic Ellis Mn deposit [12]. These samples represent a range of environments that provide different biosignature types such as alkanes and fatty acids as well as a variety of preservation styles. Water samples were also obtained from the Snowy River Passage in Fort Stanton Cave in central NM, which has walls and ceilings completely covered in Mn-oxide crusts [13]. 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.

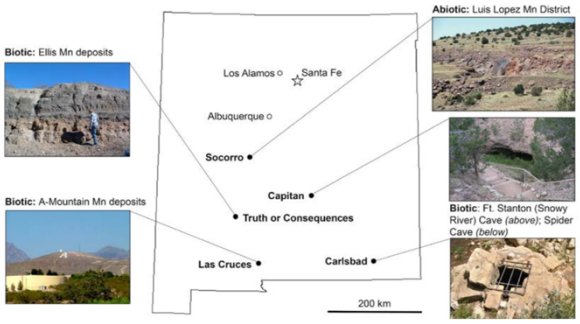

Figure 1. *Locations of high manganese deposits with both biotic and abiotic origins in New Mexico. Samples for this study were obtained from Socorro, Las Cruces, Truth or Consequences, and Capitan.*

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 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 Estes [14]. Experiments were done with unfiltered natural waters as well as filtered to remove microbes. Another set of precipitation experiments was completed with sterile

materials to precipitate abiogenic Mn-oxides for comparison. Water was placed in a sterile glass beaker at room temperature. At set intervals, the water was tested for pH and Eh. Samples from the experiment were analyzed on a UV vis spectrophotometer.

Results and Interpretations: The GCMS data for the rock samples had no alkanes detectable with whole sample pyrolysis GC-MS. A number of fatty acid methyl esters (FAMEs) were identified from all three rock samples. FAMEs from C8 to C22 were detected in all three samples, with some variation in abundance and number of FAMEs. The abiotic sample MCA-2 showed FAMEs C8 to C24, with very low abundance in FAMEs C20 to C24. Biotic sample TM-1 had FAMEs C6 to C22 with similar abundance to MCA-2 (Fig. 2). In biotic sample TC-1, FAMEs C8 to C27 were identified, with extremely low abundance compared to the other two samples (Fig. 3). Overall, no significant difference is noted in FAME presence between rock samples. This suggests that there could be sub-modern or modern organisms living on these rocks that are being detected, instead of organics preserved within the mineral structure of the samples.

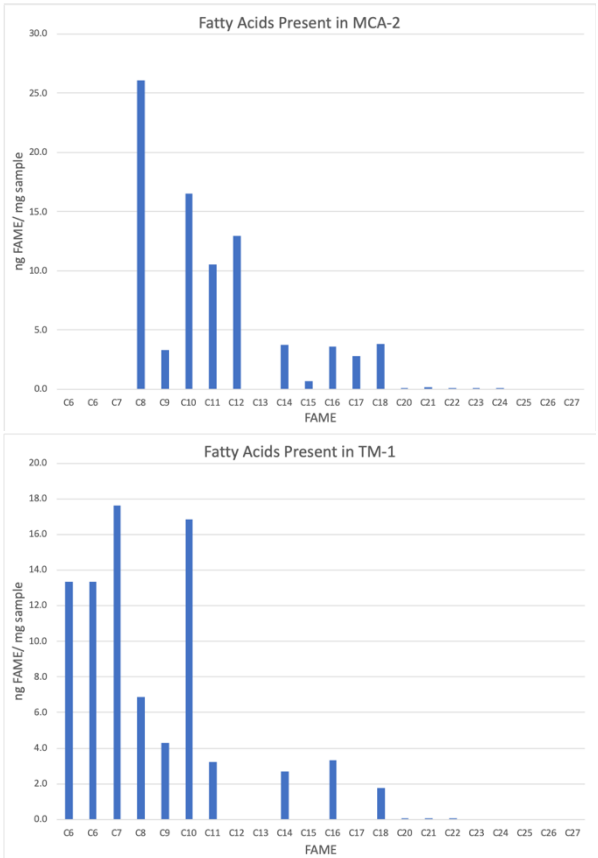

Figure 2. *Total ng of lipid per mg of sample with FAMEs on the x-axis for abiotic sample MCA-1 and biotic sample TM-1.*

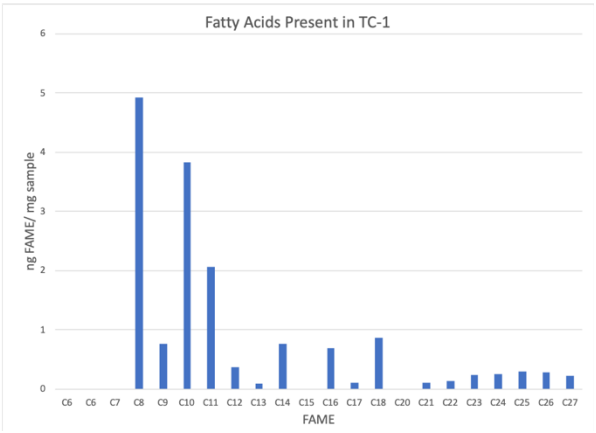

Figure 3. *Total ng of lipid per mg of sample with FAMEs on the x-axis for biotic sample TC-1.*

Ongoing Work: The precipitation experiments are underway and results are forthcoming. In order to mitigate the potential effects of modern organisms, rock samples will be solvent washed to remove external organics. Powdered samples will be placed in a 100mL beaker, covered with methanol, and sonicated for 10 minutes. Excess methanol will be decanted and the process repeated with DCM (dichloromethane). Excess DCM will be decanted, and the process will be repeated with DCM with 5 minutes of sonication until no suspended particles are observable in the solvent. Samples will be stored in solvent washed vials in the refrigerator. The removal of external organics will allow us to analyze organics within the mineral structure of the samples.

Conclusions: Abiotic and biotic samples show similar numbers of FAMEs at varying abundances. The organic molecules present in these samples are likely surface organics due to these similarities. Mn oxides are not detrimental to organics detection with pyrolysis GC-MS. Future work will establish whether there are organic signatures in Mn-oxides that can be used to identify biogenic materials.

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