IDENIFYING POTENTIAL CHEMICAL BIOSIGNATURES IN MANGANESE MINERALS WITH LASER-INDUCED BREAKDOWN SPECTROSCOPY. N.L. Lanza[1], S.M. Clegg[1], A. Cousin[2], O. Forni[2], M.F. Kirk[3], S.N. Lamm[1,3], A.M. Ollila[1], V. Payré[4], and R.C. Wiens[1], [1]Los Alamos National Laboratory, Los Alamos, NM, U.S.A. (nlanza@lanl.gov), [2]IRAP, Toulouse, France, [3]Kansas State University, Manhattan, KS, U.S.A. [4]GeoRessources, Nancy, France.

Introduction: The newly discovered high concentrations of manganese in Gale crater on Mars indicates past episodes of strongly oxidizing conditions within an aqueous environment [1-2]. On Earth, such simultaneous conditions are almost always both habitable (potentially supportive of life) and inhabited by microbes [3]. Given its close association with life and habitable environments on Earth, manganese has long been considered a principal biosignature for Mars [e.g., 4]. However, we do not yet understand the unique Mn signatures that can distinguish Mn-rich deposits as biogenic in origin (i.e., produced by life) from altered, abiogenic Mn deposits. By studying trace element abundances and mineralogy, a clearer picture of biosignatures may be obtained. Here we discuss preliminary laboratory experiments designed to interpret trace element abundance to better identify Mn-related biosignatures from data similar to those acquired by the ChemCam laser-induced breakdown spectroscopy (LIBS) instrument on the Mars Science Laboratory rover and the future SuperCam LIBS instrument onboard the Mars 2020 rover.

Background: Manganese oxides produced by microbes have been observed to share some characteristics. Both layer and tunnel mineral structures have been observed in biogenic Mn-oxides [e.g., 5], but typical products of microbial oxidation of Mn(II) are layer-type Mn-oxides whose mineral structures are poorly crystalline and contain mostly Mn(IV) and little Mn(III) [6]. However, mineral phase alone is not a unique signature of microbial activity. We hypothesize that the presence and abundance of specific trace elements are the critical, distinguishing evidence for identifying the biogenic origin of Mn-bearing materials. Manganese oxides are well known to scavenge trace metals from water [7-8] because of their surface charge properties, which exhibit a strong dependence on the pH of the waters with which they are in contact [9]. Such scavenging has been observed even in acidic stream environments where biogenic Mn-oxides uptake Co, Ni, Zn, and other metals and thus metals are found in higher abundance in these Mn-oxides [e.g., 10]. The positive identification of terrestrial biogenic Mn minerals is an active area of research; for Mars, a thorough understanding of mineralogy, chemistry, and morphology is required to understand the origins of specific Mn-rich materials and enable association with biogenic processes.

Samples: A suite of natural rocks containing Mn-rich minerals with a range of Mn redox states were selected for analysis (Table 1). The Mn nodule sample is confirmed to have a microbial origin [11], while the rock varnish samples are likely to have some microbial involvement in their formation [12-13]. Sample provenance and mineral redox state can provide come information about whether samples are biogenic or abiogenic; biogenic Mn minerals often (but not always) have mixed valence Mn states between Mn^{3+} and Mn^{4+}. We recognize that this approach is limited because it can be difficult to confirm complete abiogenesis in natural-

Sample	Mineralogy / Stoichiometry	Origin	MnO (wt%)	Ba (ppm)	Li (ppm)	Rb (ppm)	Sr (ppm)
Marine Mn nodule	Todorokite: $(Na,Ca,K)_2(Mn^{4+},Mn^{3+})_6O_{12}$*3-4.5$(H_2O)$ Romanechite: $(Ba, H_2O)_2(Mn^{4+}, Mn^{3+})_5O_{10}$ Birnessite: $(Na, Ca, K)_x(Mn^{4+}, Mn^{3+})_2O_4$ * 1.5 H_2O	Microbial	23.3	13758	98.7	171.5	103.1
Rock varnish (4 samples)	Mixed valence Mn-oxides (Mn3+, Mn4+)	Sedimentary, microbial?	5.7	2903	28.3	32.0	303.3
Pyrolusite	$Mn^{4+}O_2$	Sedimentary, hydrothermal	22.2	1362	1.3	73.9	0.3
Psilomelane	$Ba(Mn^{2+})(Mn^{4+})_8O_{16}(OH)_4$ (mixture of minerals often containing romanechite)	Secondary alteration	27.0	38495	11.4	147.8	2464
Manganite	$Mn^{3+}O(OH)$	Hydrothermal	61.1	25.6	1.3	59.0	0.0
Hausmannite	$(Mn^{2+})(Mn^{3+})_3O_4$	Hydrothermal	15.1	1077	3.4	53.9	61.0
Rhodochrosite	$Mn^{2+}CO_3$	Secondary alteration	23.8	1.1	1.1	43.6	0.0

Table 1. LIBS elemental abundance results for Mn, Ba, Li, Rb, and Sr. Calculated abundances from each analysis location were averaged for each sample. Manganese abundance is presented as MnO (Mn^{2+}) for ease of comparison between samples.

ly formed minerals; however, we believe that it is a reasonable first approach for this initial study.

Methods: Samples were analyzed with the ChemCam engineering unit under simulated Mars conditions in a Mars environment chamber under 7 Torr CO_2 at a standoff distance of 1.6 m. Each sample was analyzed in five locations with 50 shots/location except for the Mn nodule, which was analyzed in three locations with 150 shots/locations, and the four rock varnish samples, which were analyzed in two locations with 50 shots/location. LIBS data were processed using the same methods as ChemCam data [14]. Manganese was quantified after the methods of Lanza et al. [2]. Trace elements Ba, Li, Sr, and Rb were quantified after the methods of Ollila et al. [15] and Payré et al. [16-17]. LIBS spectra were also examined for the presence of key peaks for Zn [18] and Cu [16-17]. Average Mn redox state for each sample was inferred from mineralogy and provenance.

Results and discussion: Samples with Mn in 3+ or mixed 3+, 4+ oxidation states had the highest abundances of trace elements Ba, Li, Rb, and Sr (Figure 1). No discernible Zn or Cu lines were identified in any sample. Samples with a known microbial origin (Mn nodule, rock varnish) with average Mn redox states of ~3.5+ had moderate Mn abundances >30 wt% MnO (~37 wt% MnO_2) and higher Li and Ba. Although marine samples may be expected to contain elevated Li, the presence of Li in rock varnish suggests that it may also show an affinity with biogenic Mn. These results suggest that high Mn abundance alone is not sufficient evidence of a biosignature. However, the presence of trace elements may help to infer the redox state of Mn, which may in turn point to samples that are more likely to have a biogenic origin.

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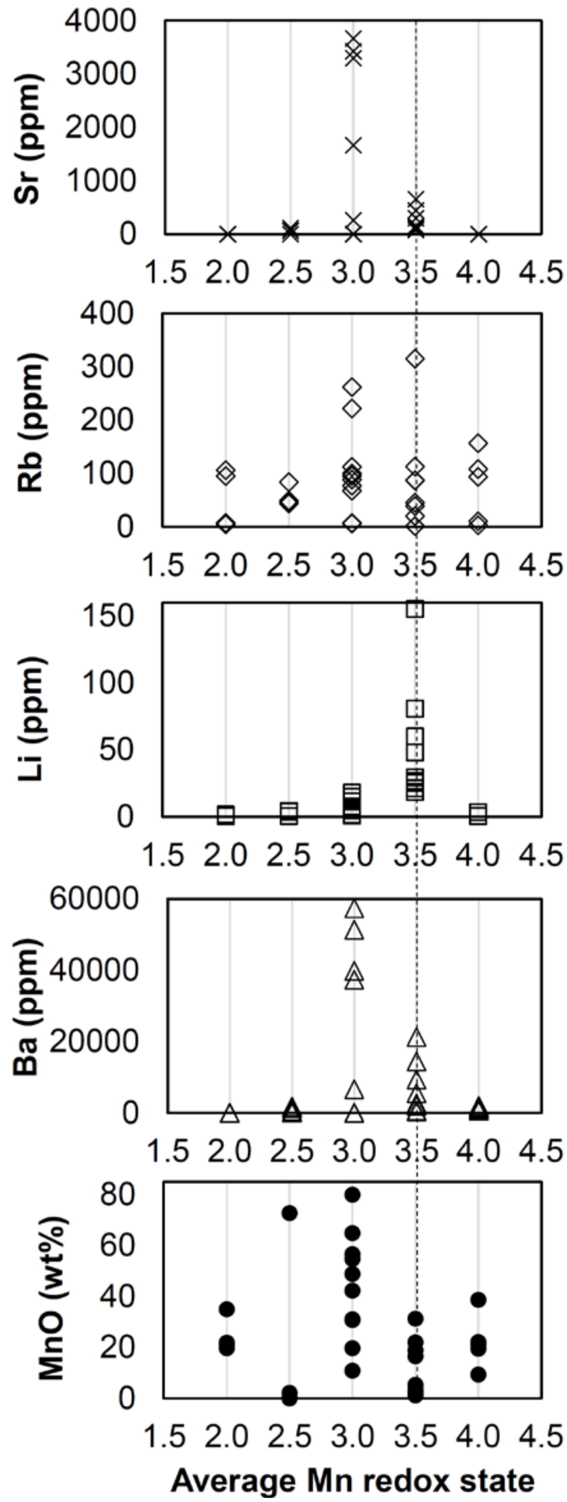

Figure 1. Abundance of Mn, Ba, Li, Rb, and Sr by average Mn redox state. Dashed line indicates biogenic Mn samples (nodule and varnish), which contain mixed valence Mn between 3+ and 4+.

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