

**ANALYSIS OF MANGANESE-RICH TERRESTRIAL SEDIMENTS BY LASER-INDUCED BREAKDOWN SPECTROSCOPY TO ELUCIDATE FORMATION OF MN-ENRICHMENTS IN GALE CRATER, MARS.** G. M. Ledesma<sup>1</sup>, E. D. Swanner<sup>1</sup>, N. L. Lanza<sup>2</sup>, C. A. Wittkop<sup>3</sup>, R.C. Wiens<sup>2</sup>, S. M. Clegg<sup>2</sup>, A. L. Reyes-Newell<sup>2</sup>, P.J. Gasda<sup>2</sup>, D. M. DeLapp<sup>2</sup>, <sup>1</sup>Iowa State University, <sup>2</sup>Los Alamos National Laboratory, <sup>3</sup>Minnesota State University, Mankato

**Introduction:** The NASA Curiosity rover is currently traversing through Gale crater on Mars, which is thought to have hosted an ancient lake based on sedimentological and mineralogical evidence [1]. The paleolake within Gale crater has been hypothesized to be redox stratified, although the extent and duration of the paleolake is currently debated [1,2].

The ChemCam instrument on board Curiosity has been collecting elemental data within Gale crater via laser-induced breakdown spectroscopy (LIBS). Manganese (Mn) enrichments as high as 50 wt. % MnO have been observed by LIBS in a variety of settings, compared to the Mars crustal average of 0.4 wt. % MnO [3–6].

*Significance of Manganese:* In terrestrial settings, the onset of large Mn-deposits are predominantly seen during the Great Oxidation Event, as the atmosphere accumulated sufficient oxygen in its atmosphere [7]. This is due to the significant redox potential of Mn<sup>2+</sup>, requiring a high potential oxidant to oxidize and precipitate. Although present-day atmospheric oxygen abundances on Mars can oxidize both iron and sulfur, it is insufficient to drive oxidation of Mn<sup>2+</sup>, raising questions about the formation pathway of Mn-enrichments in Gale crater and the potential atmospheric conditions required for its formation.

On Earth, sedimentary Mn-enrichments can form in well-oxygenated aquatic settings due to Mn(III, IV)-oxide formation. We hypothesize that if the observed martian Mn was precipitated as an oxide, it should be accompanied by other trace elements, as Mn-oxides strongly adsorb trace elements [8,9]. Such associations have been observed in at least one location in Gale [3]. Manganese may also precipitate from anoxic water as a carbonate after reduction of previously formed Mn-oxides [10]. These minerals are observed to form in redox-stratified lakes on Earth and would not be expected to have the significant amount of trace element enrichments that would accompany Mn-oxides. Iron carbonates have just recently been detected in Gale [11]. Although both primary Mn-oxides and secondary Mn carbonates require the oxidation and precipitation of Mn as an oxide initially, understanding the current mineralogy of Mn-rich phases provides important context for the Mn observations in Gale and may constrain the range of environmental conditions that were possible in the Gale paleolake.

To test whether the high Mn concentrations in Gale crater sediments formed due to Mn-oxide or Mn-carbonate precipitation, terrestrial analog sediments containing Mn-oxide and Mn-carbonate minerals were analyzed by LIBS under Mars conditions and by X-ray fluorescence (XRF), then compared with ChemCam data from Gale crater.

**Methods:** A set of 10 samples (*Table 1*) containing sedimentary Mn-oxide and Mn-carbonate minerals were collected from both past and present redox-stratified marine and lake environments on Earth that have analogous features to the paleolake that once existed in Gale crater. These samples were analyzed by LIBS under Mars pressure and atmospheric composition using the ChemCam engineering model at Los Alamos National Laboratory. Each sample was analyzed in 5 locations with 30 shots each, similar to analyses of martian targets. Major elemental abundances (Al<sub>2</sub>O<sub>3</sub>, CaO, FeO, K<sub>2</sub>O, MgO, Na<sub>2</sub>O, SiO<sub>2</sub>, and TiO<sub>2</sub>) were quantified after [12] and Mn was quantified after [3]. All samples were also analyzed by XRF at Minnesota State University, Mankato.

**Table 1: Sample List**

Sample	Origin	Sample	Origin
14*	Calumet MGS-8 core; Biwabik Fe-Formation, Animike Basin, MN	38*	Calumet MGS-8 core; Biwabik Fe-Formation, Animike Basin, MN
CY*	18290 core; Fe-Formation, Animike Basin, MN	MO5*	Lake Malawi, South-west Africa
Nod*	Lake Wentworth, NH	Mass*	Lake Wentworth, NH
LV*	Lake Vermillion, MN	099*	Otter Lake, MI
POX6*	Brownie Lake, MN	PAN1*	Brownie Lake, MN

\*Likely carbonates \*Likely oxides

**Results:** All samples are currently being analyzed by X-ray diffraction (XRD) to confirm mineralogy. From previous studies that involved use of these samples it was shown that sample 099 contains Fe-Mn-carbonates [13]. Sample LV comes from a lake that contains ferromanganese oxide nodules [14,15]. Sample PAN1 and POX6 are from a redox-stratified lake that contains high Mn enrichments and is predicted to thermodynamically favor precipitation of Mn-oxides anywhere oxygen is available but also has Mn(II) carbonate saturation levels at and slightly below the oxy-

gen/anoxic boundary line within the lake [16]. POX6 is from the oxic portion of the lake and therefore should contain Mn-oxides. PAN1 is from the anoxic portion however porewater may have oxidized the sample and the sample was not handled anoxically. Preliminary results suggest that samples 14, CY, 38, MO5, and 099 contain primarily Mn-carbonates and samples Nod, LV, Mass, POX6, and PAN1 contain primarily Mn-oxides.

As discussed before, Mn-oxides strongly adsorb trace elements and samples containing Mn-oxides should theoretically be accompanied by a larger amount of trace elemental enrichments compared to Mn-carbonates. Elements Ba, Ni, Cu, Zn, and Pb have previously been observed as trace element associations in terrestrial Mn-oxides and Mn-nodules [14,17].

If the samples that are hypothesized to contain primarily Mn-oxide and/or Mn-carbonate samples are correct, then XRF data (Table 2) shows that oxides are more likely to be associated with the selected trace elements than are Mn-carbonates.

From XRF data, the proposed samples with predominantly Mn-oxides showed 60% of samples had trace amounts of NiO, 100% had trace amounts of Zn, 40% had trace amounts of Ba, 20% had trace amounts of Pb, and 60% had trace amounts of Cu. The samples thought to contain predominantly Mn-carbonates had 0% had trace amounts of Ni, 80% had trace amounts of Zn, 40% had trace amounts of Ba, 0% had trace amounts of Pb, and 0% had trace amounts of Cu.

**Table 2: XRF data of trace elements in wt. %.**

Sample	BaO	NiO	CuO	ZnO	PbO
14*	0	0	0	0.0119	0
38*	0	0	0	0.0101	0
CY*	0	0	0	0	0
POX6 <sup>+</sup>	0	0.0093	0.0103	0.0419	0
PAN1 <sup>+</sup>	0	0.0094	0.0206	0.0999	0
MO5*	0.0491	0	0	0.0090	0
099*	0.0703	0	0	0.0070	0
Nod <sup>+</sup>	0	0.0210	0.02375	0.0227	0.06907
Mass <sup>+</sup>	2.698	0	0	0.1374	0
LV <sup>+</sup>	1.533	0	0	0.0363	0

\*Likely carbonates    <sup>+</sup>Likely oxides

From XRF data, trace elements seem to be associated more with samples that predominantly contain Mn-oxides, pending XRD data. Specifically Ni, Pb, and Cu seem to only be detected in samples which likely contain Mn-oxides.

**Future Work:** ChemCam has previously detected Ba, Ni, Cu, and Zn within LIBS spectra [18–20]. Using the ChemCam Quick Element Search Tool (C-QuEST)

[21], a set of wavelengths that correspond to the most diagnostic emission lines for Ba, Ni, Cu, Zn, and Pb can be determined (Table 3). LIBS spectra produced from the 10 terrestrial samples at these wavelengths will be observed to assess if they contain diagnostic peaks for these trace elements. The spectral data at these wavelengths will then be analyzed using a multivariate analysis technique which might distinguish Mn-oxide and Mn-carbonate samples. This approach can then be utilized for comparison between Earth lake sediments and Mn-rich Gale crater samples. Results are forthcoming.

**Table 3: Trace elements and wavelengths corresponding to highest emission peaks from C-QuEST.**

Element	Wavelength Range Being Used (nm)
Ba	454-456; 552-554; 648-650
Ni	300-302; 309-311; 439-441; 509-511
Cu	323-325; 514-516; 519-522; 808-810
Zn	279-281; 329-331; 333-335; 467-469
Pb	404-406; 423-425; 437-438

**Conclusion:** On Earth, Mn deposits have served as a paleo-indicator in geologic history of rising oxygen in the atmosphere. Discovering Mn enrichments within Gale crater opens up questions of duration and extent of possible atmospheric oxygen on Mars, and the occurrence of redox-stratified lakes. Determining the current mineralogy of Mn enrichments provides key information about the environmental conditions present in the Gale paleolake.

**References:** [1] J.P. Grotzinger et al., *Science*, 2014, 343, 1. [2] J.A. Hurowitz et al., *Science*, 2017, 356. [3] N.L. Lanza et al., *Geophysical Research Letters*, 2016, 43, 7398. [4] N.L. Lanza et al., *Geophysical Research Letters*, 2014, 41, 5755. [5] P.J. Gasda et al., 49th Lunar and Planetary Science Conference, 2018, 2018, Abstract #2483. [6] G.J. Taylor, *Chemie der Erde*, 2013, 73, 401. [7] J.E. Johnson et al., *Geochimica et Cosmochimica Acta*, 2016, 173, 210. [8] E. Goldberg, *The Journal of Geology*, 1943, 62, 249. [9] B.M. Tebo et al., *Annual Review of Earth and Planetary Sciences*, 2004, 32, 287. [10] E. Kristensen, K.D. Kristiansen, M.H. Jensen, *Estuaries*, 2003, 26, 690. [11] D. Archer et al., this meeting [12] S.M. Clegg et al., *Spectrochimica Acta - Part B Atomic Spectroscopy*, 2017, 129, 64. [13] C. Wittkop et al., *Chemical Geology*, 2014, 389, 153. [14] C.A. Asikainen, S.F. Werle, *Proceedings of the National Academy of Sciences of the United States of America*, 2007, 104, 17579. [15] M.G. Sommers, M.E. Dollhopf, S. Douglas, *Geomicrobiology Journal*, 2002, 19, 407. [16] N. Lambrecht et al., *Journal of Geophysical Research: Biogeosciences*, 2018, 123, 3403. [17] A.H.F. Robertson et al., *Sedimentary Geology*, 2019, 385, 126. [18] J. Le DeLasue et al., *Journal of Geophysical Research: Planets*, 2016, 121, 338. [19] V. Payré et al., *Icarus*, 2019, 321, 736. [20] V. Payré et al., *Journal of Geophysical Research: Planets*, 2017, 122, 650. [21] A. Cousin et al., *Spectrochimica Acta - Part B Atomic Spectroscopy*, 2011, 66, 805.