

**VARIABLE REDOX CONDITIONS IN GALE CRATER AS INDICATED BY MANGANESE ABUNDANCE ALONG THE CURIOSITY TRAVERSE.** N. L. Lanza<sup>1</sup>, W. W. Fischer<sup>2</sup>, S. N. Lamm<sup>3</sup>, P. J. Gasda<sup>1</sup>, P.-Y. Meslin<sup>4</sup>, A. M. Ollila<sup>1</sup>, J. Frydenvang<sup>5</sup>, S. M. Clegg<sup>1</sup>, A. Cousin<sup>6</sup>, D. DeLapp<sup>1</sup>, O. Forni<sup>6</sup>, A. Reyes-Newell<sup>1</sup>, M. Salvatore<sup>3</sup>, and R. C. Wiens<sup>1</sup>, <sup>1</sup>Los Alamos National Laboratory (nlanza@lanl.gov), <sup>2</sup>California Institute of Technology, <sup>3</sup>Northern Arizona University, <sup>4</sup>Universite Paul Sabatier, France, <sup>5</sup>University of Copenhagen, <sup>6</sup>IRAP-CNRS, France.

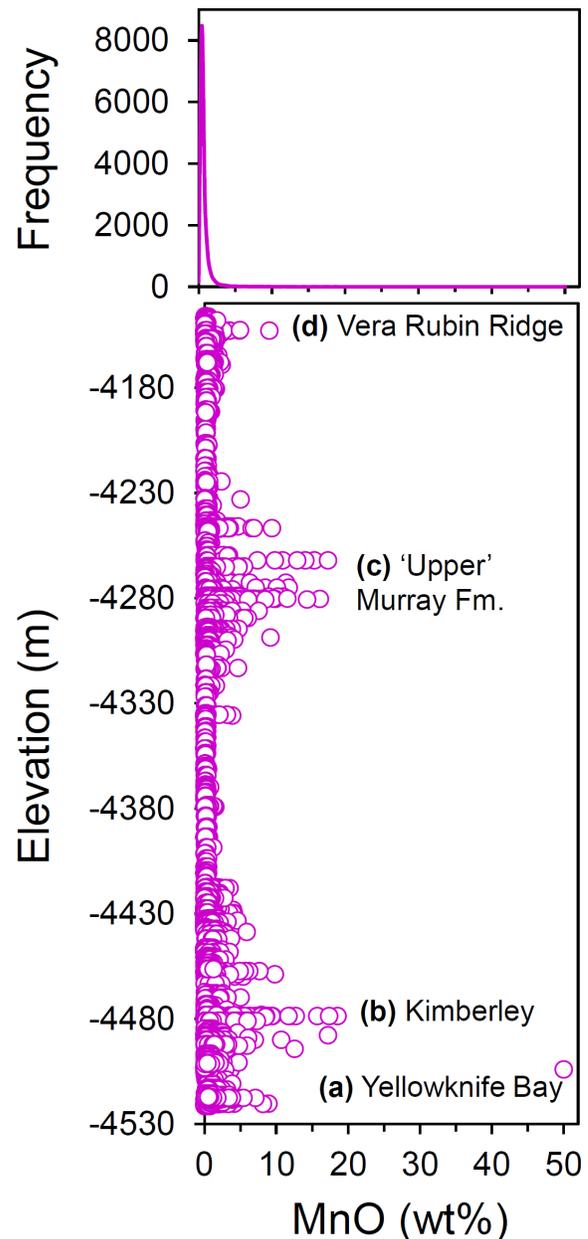
**Introduction:** Manganese abundance has varied significantly over the Curiosity traverse, and some anomalously high abundances have been observed [1-2]. To concentrate Mn in rocks and sediments requires both water and strongly oxidizing conditions (well beyond those required to oxidize iron) [3]. High manganese has been observed in a variety of geologic settings in Gale including as a surface coating [1], fracture fills [2], and embedded in fine grained sediments [4-5]. Some instances are clearly diagenetic [e.g., 2] while others may be either authigenic or diagenetic [4-5]. Here we examine the variation of Mn along the Curiosity traverse to sol 2042 using data from the ChemCam instrument.

**Quantifying Mn abundance in ChemCam LIBS data:** Previous work by [1-2] developed a univariate quantification model for Mn in ChemCam laser-induced breakdown spectroscopy (LIBS) data. Using well characterized laboratory standards, a least squares regression model of composition was made using the peak area for the manganese doublet at 403.19 and 403.42 nm. Manganese abundance in martian samples were quantified using this regression model (Fig. 1).

**Manganese abundance within the Gale crater stratigraphy:** Average Mn abundance in Gale crater is ~0.6 wt% MnO, similar to the Mars global average of ~0.4 wt% MnO [6]. However, high abundances of MnO (>4 wt%) have appeared periodically throughout the explored stratigraphy in Gale crater.

*Yellowknife Bay (Fig. 1a):* Multiple rocks containing high Mn abundances were observed in the Yellowknife Bay region, most notably the Caribou target on sol 342. Caribou is a rock target with a dark surface coating on parts its surface; one analysis location was observed to have Mn in excess of 50 wt%, the highest observed on the martian surface to date [1]. Follow up observations of Caribou were not possible because the rover was in the midst of a drive campaign when this target was analyzed. However, the apparent surface nature of the high Mn abundance suggest that it is a secondary mineral deposition.

*The Kimberley (Fig. 1b):* As Curiosity traveled up the stratigraphy to the Kimberley region, additional high Mn targets were observed. Here high Mn appears as erosion resistant fracture fills that have been exposed at the surface [2]. The mineralogy of these mate-



**Fig. 1.** Manganese abundance from ChemCam data across the Curiosity traverse in Gale crater. The frequency distribution (above) shows that typical MnO abundances are low (~0.6 wt% MnO); some anomalously high Mn observations are present.

rials has been inferred to be Mn-oxides due to the presence of Zn [7], Co [2], and Cu [8] in and around the fracture fill material [9]. High Mn at the Kimberley is only observed as a secondary phase filling fractures within the surrounding sandstone bedrock.

*'Upper' Murray (Fig. 1c):* After departing the Kimberley, the rover continued traversing upsection through a thick, fine grained sedimentary lake deposit named the Murray formation [10]. The Murray is periodically unconformably overlain for ~75 m by the Stimson formation, whose origins appear to be aeolian [11]. Neither the Murray nor the Stimson contain high abundances of Mn for ~100 m of stratigraphy. At ~4380 m the Stimson disappears as the Murray continues and at ~4300 m, high Mn abundances are again observed. Manganese observations in this region can be as high as those seen in the Kimberley fracture fills. However, here Mn is incorporated into fine grained sediments with no clear geological origin. High Mn in this region may be primary precipitates from lake waters, detrital grains, or grain coatings or cements [12].

*Vera Rubin Ridge (Fig. 1d):* After ~4240 m elevation, Mn abundance in the Murray again decreased to average or below average values until just below the Vera Rubin Ridge (VRR) at the "Newport Ledge" area [13]. In this region, high Mn is observed within dark toned sandstones and nodules [4,5,8], often but not always in conjunction with observations of phosphorus [5]. As before, the high Mn observed within sedimentary materials has an ambiguous origin, although an authigenic origin is hypothesized [4-5]. Once Curiosity climbed further upsection on to the VRR itself, observed Mn abundances decreased to average or below average values. However, observed Mn abundance increases at the contact between the Jura and Pettegrove Point members [14].

**Discussion:** The observations of high Mn within rocks and sediments in Gale crater provide strong evidence for strongly oxidizing, aqueous conditions [1-2]. These conditions were periodically present, likely during both primary sediment deposition within the lake [e.g., 4,15] and also post lithification of the lake sediments in groundwaters [2]. However, the notable lack of high Mn abundances in some regions coupled with observations of mixed valence iron oxides [e.g., 16] suggests that redox conditions were variable and were not always conducive to Mn deposition. Potentially authigenic Mn deposits are observed within two distinct strata in the Murray fm. (Fig. 1c, d), suggesting that conditions within the lake waters cycled between more and less oxidizing conditions as these sediments were deposited. The water column within the Gale lake may have been redox stratified, leading to more oxidizing conditions in shallow water and less oxidizing con-

ditions in deeper waters, as evidenced by the deposition of different redox sensitive mineral species [17]. Within this in mind, one possible explanation for the variation of Mn abundance within the Murray is periodic changes in water depth that could be due to either a local or overall change in lake depth or to shifting shoreline locations [4,5,8]. In terrestrial lakes, Mn is typically deposited in shallow water environments due to the increased abundance of dissolved oxygen [e.g., 4,8,13]. Such environments may also produce phosphate minerals, which may be inferred in Gale by the observations of high abundances of P, Mn, and Fe in some features [5]. In addition to Mn precipitation and deposition within the lake, Mn has also been deposited as fracture fills from groundwaters after lake sediments became lithified [2]. This Mn may have been mobilized from older authigenic deposits within the Murray or other lake sediments, although its origins have yet to be determined. The observation of a high Mn possible surface coating suggests that water-rock-atmosphere interactions may also have played a role in Mn deposition in Gale crater. Overall the highly variable Mn abundances observed across the Gale traverse point to variable redox conditions in a variety of geologic settings.

**References:** [1] Lanza, N.L. et al. (2014) GRL 41, 5755-5763. [2] Lanza, N.L. et al. (2016) GRL 43, 7398- 7407. [3] Stumm, W., & Morgan, J. J. (1996), *Aquatic Chemistry: Chemical Equilibria and Rates in Natural Waters*, 3rd ed., 1042 pp., John Wiley, New York. [4] Gasda, P. J. et al., this meeting. [5] Meslin, P.-Y. et al. (2018). 49th LPSC #1447. [6] Taylor, S. R. & McLennan, S. M. (2009). *Planetary Crusts: Their Composition, Origin, and Evolution*, 378 pp., Cambridge Univ. Press, New York. [7] Lasue, J., et al. (2016). *J. Geophys. Res. Planets*, 121, 338–352. [8] Payre, V. et al. (accepted). *Icarus*. [9] Thompson, L.M. et al. (2016). *JGR Planets* 121, 1981-2003. [10] Grotzinger, J.P. et al. (2015). *Science* 350, aac7575. [11] Banham, S.G. et al. (2018). *Sedimentology* 65(4), 993-1042. [12] Lamm, S.N. et al. (2017). 48th LPSC #2668. [13] Frydenvang, J. et al. (2018). 49th LPSC #2310. [14] Frydenvang, J. et al. (2019). This volume. [15] Gasda, P.J. et al. (2018). 49th LPSC #2483. [16] Rampe, E.B. et al. (2017). *Earth & Planet. Sci. Lett.* 471, 172-185. [17] Hurowitz, J.A. et al (2017). *Science* 356(6341), eaah6849.