MANGANESE OBSERVATIONS FROM CHEMCAM DURING SOLS 1650-1750: IMPLICATIONS FOR A CHANGING REDOX ENVIRONMENT.

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Introduction: The presence of high abundances of manganese in Gale [1,2] and Endeavor [3] craters on Mars suggests that the planet may have had an oxygenated atmosphere and more Earth-like environment in the past. Gale crater was once host to a stratified lake, an interpretation based on observations of fluvial deltaic deposits and finely laminated mudstones [4-5]. This study examines the lakebed deposits, informally known as the "Murray" formation, between sols 1650–1750 (Fig. 1) that the rover traversed before arriving at Vera Rubin Ridge, a location characterized as hematite-enriched from orbit [6].

Manganese is a redox-sensitive element, so its concentration and deposition provides clues about environmental conditions. On Earth, manganese-rich deposits did not appear in the geological record until the atmosphere became oxygenated by photosynthetic life. Without microbes, manganese oxides can only form if there is abundant liquid water and strongly oxidizing conditions [2]. Here, we analyze manganese abundance as tracked by the ChemCam instrument, an instrument on board the NASA *Curiosity* rover that provides the elemental composition of rocks and soils [e.g., 7]

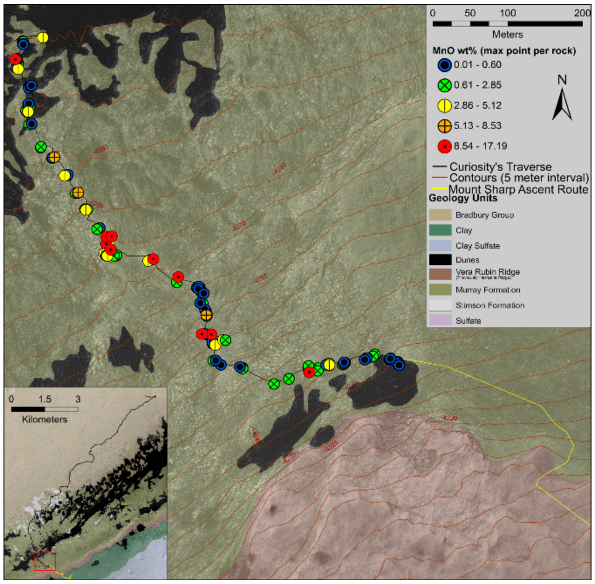

Figure 1: Spatial distribution of 151 rocks analyzed by ChemCam between sols 1650-1750 with Mn abundance indicated by color.

Methods: Compositional data for rock targets observed during sols 1650-1750 were obtained by the ChemCam laser-induced breakdown spectroscopy (LIBS) instrument on *Curiosity* [7-8]. During this time there were 151 rock targets analyzed by ChemCam with a total of 1296 sampling locations. These sampling locations were spatially mapped, assessed for manganese abundance, analyzed for relationships between Mn and major and minor elements, and categorized by geological textures and albedos. Manganese abundance was quantified using a univariate peak-area model developed by [1] covering the doublet peak at ~402–403 nm. The manganese doublet peak has little spectral interference from other emission lines, which makes it an ideal peak to use for univariate quantification. For each sampling location, Mn abundance was obtained using the peak area of the average of all 25 spectra taken after dust removal was calculated for each sampling location.

Targets were also examined for depth trends in single-shot data. Relationships between manganese and major element abundances were assessed using ChemCam data released on the Planetary Data System (PDS). Major elements are Si, Ti, Al, Fe, Mg, Ca, Na, and K. Minor elements were also assessed, including Cr, Li, Rb, Sr, and P [9]. Images of all rock targets

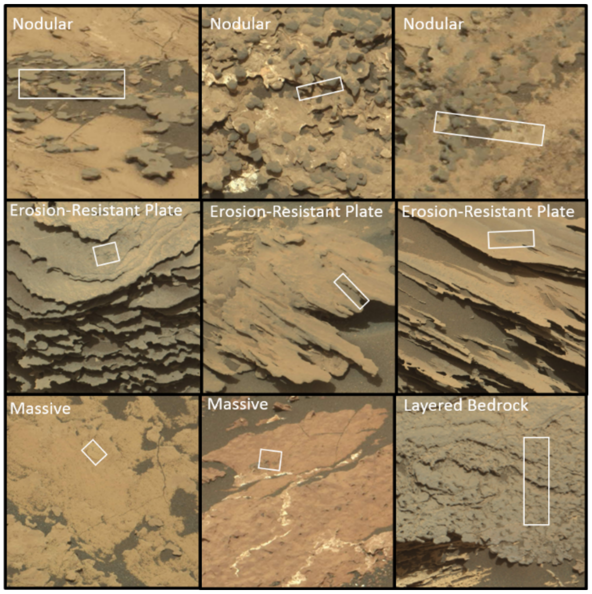

Figure 2: ChemCam targets with the highest Mn abundances in the study region. High Mn appears to be related to certain rock types and morphologies.

were analyzed for texture, albedo, and features such as veins. Targets were subdivided by rock morphology: layered bedrock, nodules, massive rocks, and erosion resistant plates (Fig. 2).

Results: Manganese abundance increased from Gale average (0.6 wt% MnO) in rock targets between sols 1650–1750 (Figs. 3, 4). Of all rock targets analyzed 7% (94 samples) have Mn abundances $\geq$2.9 wt% MnO, which is 2-σ above the Gale mean and thus are considered to have "high" Mn abundance in this study. The maximum MnO observed was 17.2 wt% MnO in target East Point (Sol 1718), which sampled a nodular texture (Fig. 2). Thirteen sampling locations had very high Mn abundances >10 wt% MnO. Overall there was an increase of Mn, Fe, Mg, and P abundances as the rover moved upsection towards Vera Rubin Ridge [10]. While the abundances of all four of those elements were increasing, they were not correlated with one another. There was no clear association with Mn or any other element assessed (Fig. 5). 63% of high Mn targets ($\geq$2.9 wt%, 2σ > Gale avg) were found in dark-toned areas with low albedo.

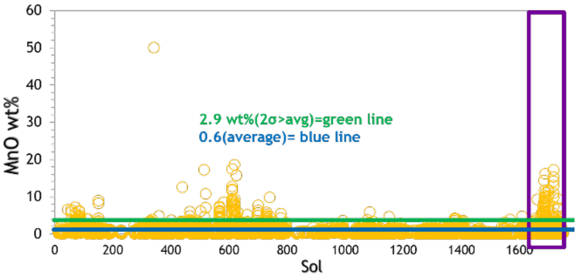

Figure 3: MnO wt% by sol for the traverse to sol 1750. All sampling locations on rocks were plotted. The purple box indicates the period of time analyzed for this study. Blue line = Gale average, green line = MnO wt% 2-σ above average

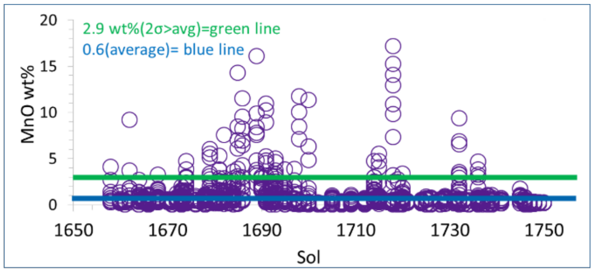

Figure 4: MnO wt% by sol for the study period. Blue line = Gale average, green line = MnO wt% 2-σ above average

Discussion: Without a clear association between Mn and any other element, we hypothesize that the Mn-bearing phase is likely in an oxide phase rather than associated with other major or minor elements. Some high Mn targets also contain P, which can be scavenged by Mn oxides [e.g., 9]. High abundances of Mn were not strongly associated with rock type or albedo. Overall our results do not point to a single formation mechanism for Mn deposits in the Murray; these high Mn materials may be primary, detrital, or diagenetic (or a combination of the three). However, the general presence of high abundances of Mn in this region suggest that this portion of the lake experienced a change in redox conditions that allowed for the precipitation and preservation of high Mn sediments. The highly oxidizing conditions in this area could point to a change in depositional environment, for example, in shallow water or lake shoreline deposits connected to periodic changes in lake level [e.g., 9, 11]. However, high manganese can also be the product of highly oxidizing groundwater permeating through the bedrock post-lithification [e.g., 1].

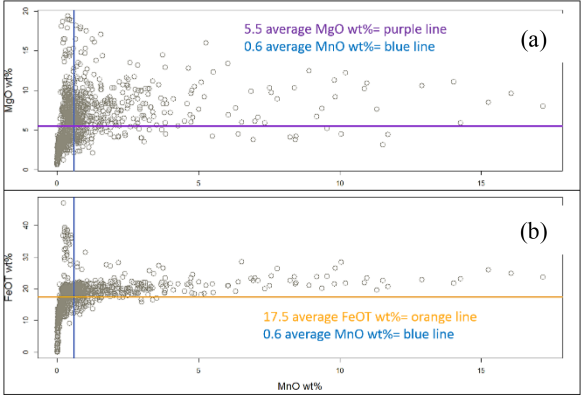

Figure 5: Relationship between (a) Mn and Fe abundance and (b) Mn and Mg abundance for all sampling locations in this study; average compositional values are for full traverse.

Conclusions: *Curiosity* observed high Mn sediments with the ChemCam instrument in the region between sols 1650-1750. Our analysis of the bedrock morphologies and elemental abundances of other elements measured by ChemCam show no clear correlation between Mn and any particular rock type. Thus, we conclude that Mn is primarily in the oxide phase. Furthermore, the Mn oxides must have formed in wet and highly oxidizing conditions, either primarily in the lake or during a secondary diagenetic process.

References: *[1] Lanza N.L. et al., (2014) Geophys. Res. Lett., 41, 5755–5763. [2] Lanza N.L. et al., (2016) Geophys. Res. Lett., 43, 7398-7407. [3] Arvidson R.E. et al., (2015) J. Geophys. Res. Planets, 120. [4] Grotzinger et al., (2015) Science, 350. [5] Hurowitz et al., (2017) Science, 356. [6] Fraeman A.A. et al., (2013) Geology, 41, 10, 1103-1106. [7] Wiens et al., (2012) SSR, 170, 167–227. [8] Maurice et al., (2012) SSR, 170, 95–166. [9] Meslin P.Y. et al., (2018) this meeting. [10] Frydenvang J. et al., (2018) this meeting. [11] Gasda, P.J. et at., (2018) this meeting.*