HIGH MANGANESE OBSERVATIONS WITH CHEMCAM IN GALE CRATER, MARS.

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Introduction: The surface of Mars has long been considered a relatively oxidizing environment, an idea supported by the abundance of ferric iron phases observed there. However, compared to iron, manganese is sensitive only to high redox potential oxidants and when concentrated in rocks it provides a more specific redox indicator of aqueous environments. Observations from the ChemCam instrument on the Curiosity rover indicate abundances of manganese in and on some rock targets that are 1-2 orders of magnitude higher than previously observed on Mars, suggesting the presence of an as-yet unidentified manganese-rich phase. These results show that the martian surface has at some point in time hosted much more highly oxidizing conditions than has previously been recognized.

Methods: To assess the abundance and distribution of Mn detections in rock targets over the rover's traverse in the first 360 sols, the area under the Mn triple peak at 403.19, 403.42, and 404.2 nm was quantified using LIBS spectra at each target sampling location. Once peak areas were obtained, Mn abundances were modeled after the methods of [1].

Results: Mars sample results from the first 360 sols are shown in Fig. 1a, b in terms of the integrated peak areas. The distribution of the shot-averaged Mn peak areas observed by ChemCam is skewed, with a heavy tail indicating a sub-population of analyses with high Mn abundances (Fig. 1b). Sixty sampling locations are two standard deviations from the mean, containing Mn peak areas significantly higher than the majority of rocks (1750 rock sampling locations) analyzed in the first 360 sols and corresponding to Mn abundances > 1.3 wt.%. This discretionary limit represents Mn concentrations at least three times the mean in martian basalts (~0.4 wt.% MnO [2]); observations that are two orders of magnitude greater than the martian mean are also included in the > two-sigma range.

Rocks containing high Mn concentrations >1.3 wt.% MnO are generally dark, fine-grained, and relatively smooth (e.g. Fig. 2a), although this is not universal. In the target Harrison (sol 514), large, white crystal laths are observed in a dark matrix; the dark locations contain the high Mn observations (Fig. 2b). This target contains one of the highest Mn observation in the mission to date, second only to the target Caribou (sol 342; Fig. 2a). No individual grains associated with high Mn

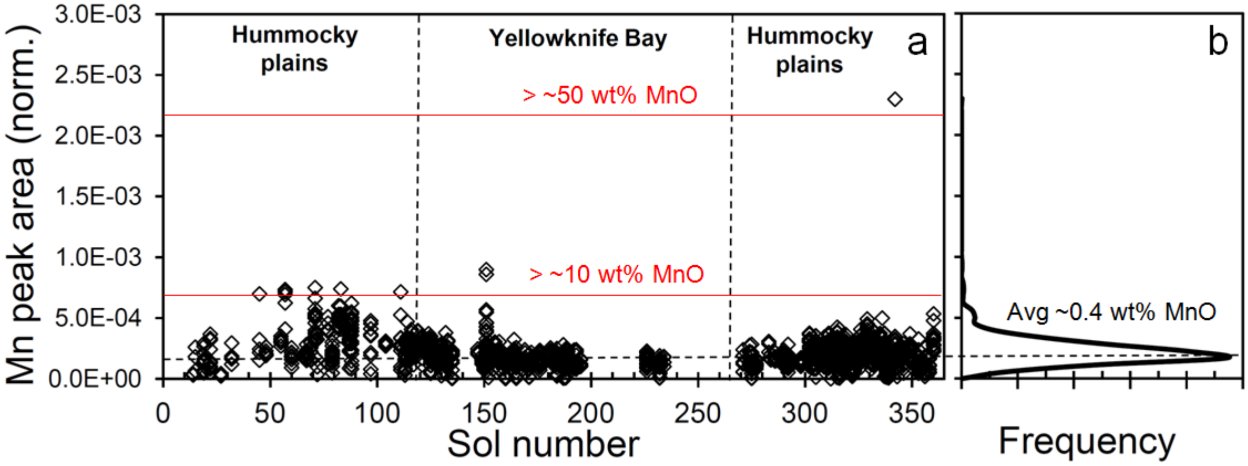

Fig. 1. Manganese peaks in martian LIBS spectra and the distribution of Mn peak areas in all martian rocks analyzed in the first 360 sols. **(a)** The triple Mn peak in the 403-404 nm range was used to determine peak areas and Mn abundance in all rocks in the first 360 sols; each sampling location is represented by the average of all shots obtained there (usually 30 shot). **(b)** The distribution of Mn abundance in rock samples indicates that most observations are low but there are a number of locations containing unusually high Mn, most notably the target Caribou (sol 342), which is above ~50 wt% MnO.

were resolvable in RMI images (e.g. Fig. 2), suggesting a typical grain size < 100 µm, which is also smaller than the LIBS laser analysis spot size of 350-500 µm in diameter. As a result, the spatially discrete high Mn abundances, both between analysis locations on a given rock and within a given sampling location, suggest that the high Mn detections are likely not due to the laser sampling single large, high-Mn grains. In particular, the well-sampled Rocknest-3 target (sols 57, 77, 82, 83, 88) contains elevated Mn in a majority of sampling locations, suggesting the presence of a broadly distributed, fine-grained Mn phase. There are no compositional trends apparent in high Mn rocks; observations containing high Mn typically show the elemental profile of the bulk rock, which is attenuated when Mn abundances are high.

Implications: The presence of such high Mn concentrations in and on a spatially wide range of rocks at Gale crater indicates the precipitation of Mn-mineral phases, which is only possible in a highly oxidizing, aqueous environment capable of producing sufficient concentrations of high potential oxidants to drive Mn oxidation. Thus far, the identity of the Mn-bearing materials remains unknown. The prevalence of dark-toned Mn-rich targets is consistent with a range of Mn-oxide phases like birnessite for at least some targets. Manganese oxides play an important role in environmental chemistry as powerful oxidants and strong sorbents, and can provide highly favorable substrates for microbial respiration [3]. Although the oxidizing conditions that high Mn materials indicate would not be favorable to organic preservation, the presence of Mn-oxides supports the interpretation of a once-habitable aquatic environment on Mars in Gale crater [4]. Martian surface chemistry capable of Mn-oxidation marks an era that did not occur on Earth until after the evolution of oxygenic photosynthesis, suggesting markedly different modes of planetary redox evolution.

References: [1] Ollila, A.M. et al. (2014). *J. Geophys. Res Planets.* 119, 1-31. [2] Yen, A. et al. (2007). *J. Geophys. Res. Planets*, 111 (E12S11), doi:10.1029/ 2006JE002797. [3] Myers, C.R. and Nealson, K.H. (1988). *Science* 240, 1319-1321. [4] Grotzinger, J.P. et al. (2014). *Science* 343, 1242777-1-14, doi: 10.1126/science.1242777. [5] Lanza, N.L. et al. (2014). 45th LPSC, Houston, TX, no. 2599.

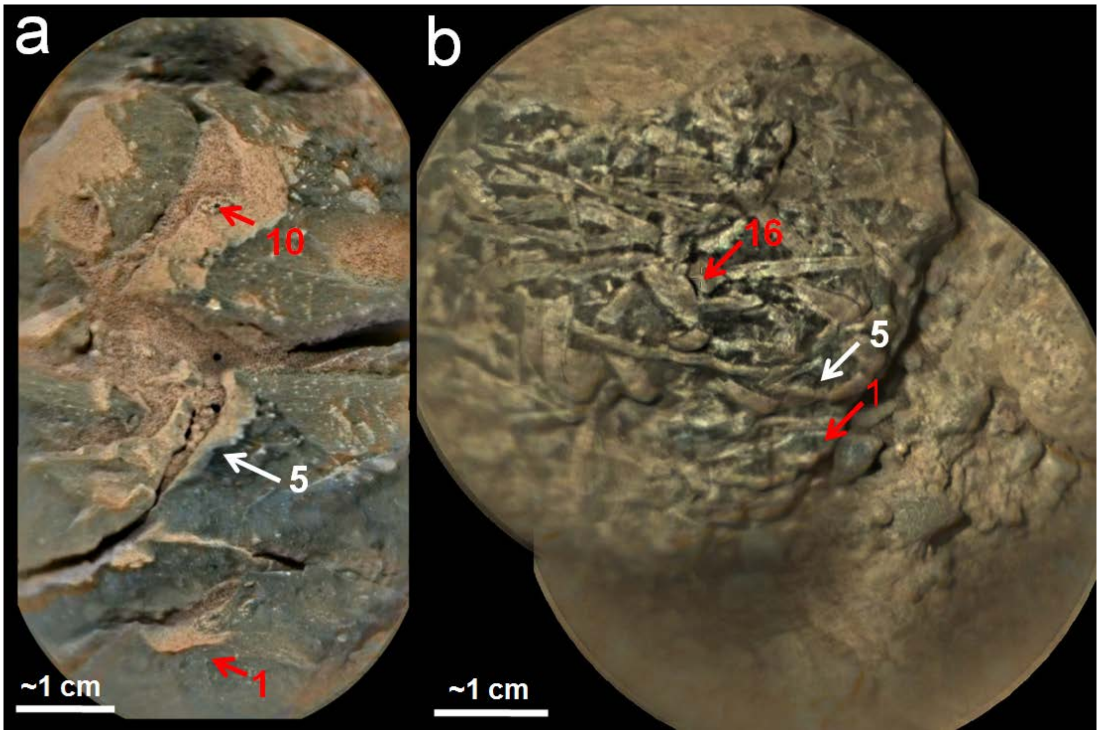

Fig. 2. ChemCam Remote Microimager (RMI) image mosaics of the two targets containing the highest Mn observations in Gale crater to date, colorized with Mastcam image data. **(a)** The target Caribou (sol 342), analyzed with a 1x10 raster (30 shots/location); location 5 contains the highest Mn observation to date. The rock surface is darker at this location and no individual grains are resolvable, although depth trends suggest that this could be a Mn-rich coating [5]. RMI from sequence ccam01342; Mastcam color image 0342MR0013820010301085E01_DWXX.IMG **(b)** The target Harrison (sol 514), analyzed with a 4x4 raster (30 shots/location); this rock contains macroscopic white crystal laths embedded in a dark matrix. The dark material is consistently higher in Mn, with location 5 containing the second highest Mn observation to date. Although the rock texture appears to be igneous, the presence of high Mn suggests that this rock has experienced at least some aqueous alteration since its formation. Similarly to Caribou in (a), trends with depth suggest that Mn is concentrated in the surface of the rock. RMI from sequence ccam02514; Mastcam color image from sequence mcam02012.