MANGANESE TRENDS WITH DEPTH ON ROCK SURFACES IN GALE CRATER, MARS.

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Introduction: Observations on Mars of dark, shiny rocks that appear similar to varnished surfaces have led to the question of whether Mn-enriched coatings could have formed on Mars [1-6]. Here we present three martian rock targets analyzed with ChemCam—Caribou (sol 342), Little Dal (sol 151), and Peg (sol 71)—that show evidence for both high Mn on their surfaces and a decreasing Mn trend with depth, suggesting Mn enrichment on the rock exteriors. One spot on Caribou has the highest Mn abundance detected by ChemCam in the first 360 sols of the mission, which coincides with a dark-toned patch on the rock surface (Fig. 1). Terrestrial LIBS laboratory studies on a rock varnish sample show a similar systematic decrease in Mn peak intensity with depth [7-8], suggesting that these martian observations are consistent with a Mn-rich coating.

Background: Next to iron oxides, manganese oxides and hydroxides make up the most common heavy metal coatings found on Earth. The most well-known Mn-rich coating is rock varnish, which forms in arid regions all over the Earth. Because it forms on rocks that are not necessarily Mn-rich, varnish is thought to be derived from materials external to the rock such as atmospheric moisture, airfall dust, and surrounding soils [9-11]. Laboratory studies suggest that coatings formed in a similar manner could form on Mars [12]. Because of the close association between Mn minerals and microbial activity on Earth, Mn-oxides have been suggested as a potential biosignatures for Mars missions [5, 13-14], although Mn-rich coatings may also form abiotically [15-17]. On Earth, Mn coatings have been found in a variety geological settings, including caves [18], springs [19], glacial environments [20-21], streams [22], and hydrothermal systems [23]; these are all settings that have a high habitability potential.

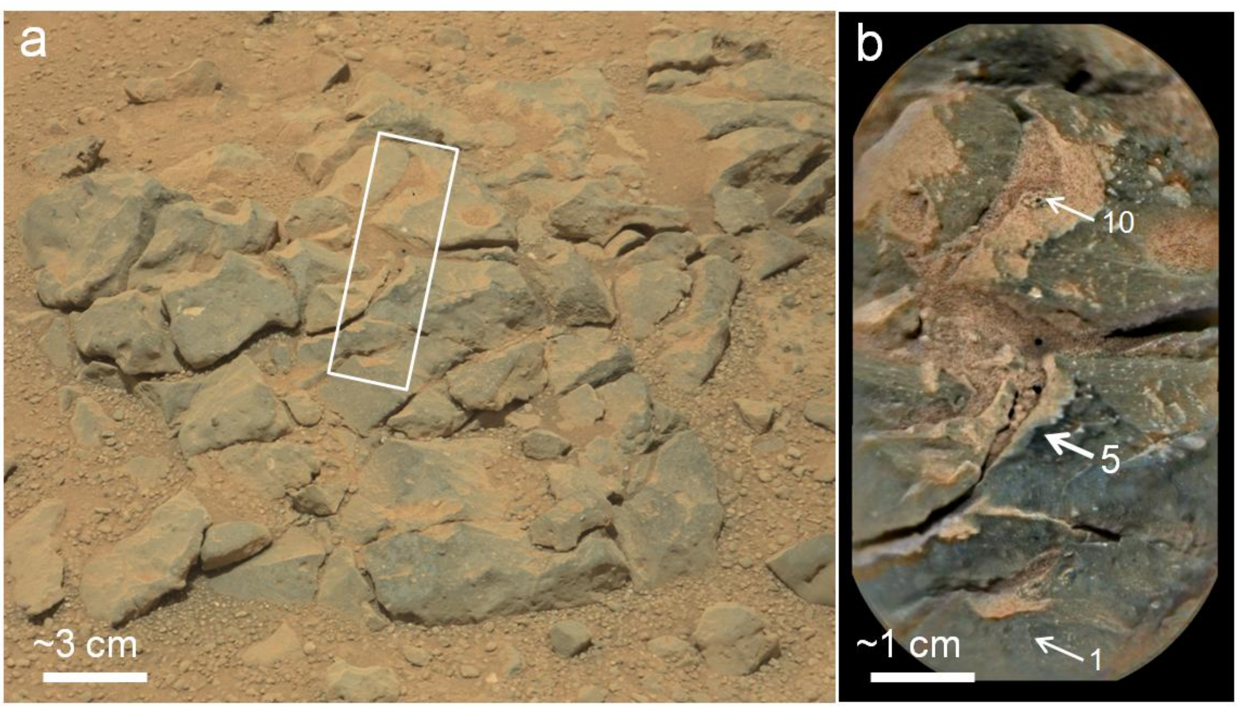

Fig. 1. The rock Caribou analyzed with ChemCam on sol 342 with a 10×1 raster with 30 shots/location. **(a)** Mastcam image of Caribou with ChemCam analysis location in white box. This rock is highly fractured and appears to have a slightly mottled coloration (Mastcam-100 image 0342MR0013820010301085E01_DWXX.IMG). **(b)** ChemCam RMI colorized with Mastcam. The high Mn analysis is at location 5, marked with a white arrow along with the first and last shots of the 10x1 raster. Location 5 appears to sample a darker section of rock than other sampling locations in the raster. Passive spectra taken in the same location suggest that this is not a shaded area but is truly dark [8].

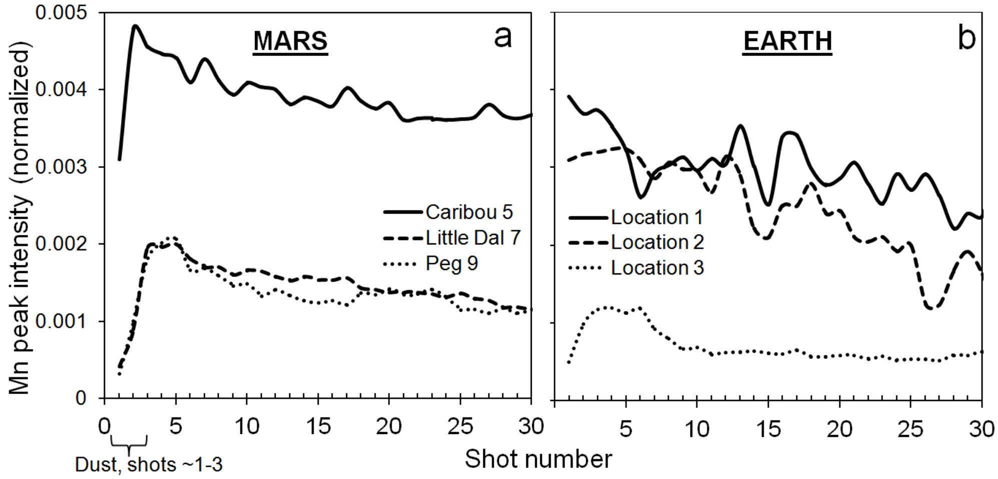

Fig. 2. Comparison of trends in Mn peak intensities (403.2 nm) with depth from selected Mars targets (a) and a terrestrial rock varnish N6B (b). **(a)** Mn peak intensity trends with depth for Caribou location 5 (Sol 342), Little Dal location 7 (Sol 151), and Peg location 9 (Sol 71). For all samples, the Mn peak intensity is observed to be high in earlier shots and decreases systematically over the 30 shot depth profile. The percent change in peak intensity for Caribou = 23%, Little Dal = 41%, and Peg = 36%. **(b)** Mn peak intensity trends with depth for terrestrial laboratory sample N6B, which is coated with a Mn-rich rock varnish. The percent change in peak intensity for location 1 = 39%, location 2 = 47%, and location 3 = 46%. The maximum Mn peak height is higher in Caribou than for those observed in N6B; both show systematic decreases in Mn peak height with depth. It should be noted that there is considerable variation in maximum Mn peak height in the terrestrial sample, suggesting a difference in coating thickness at the three sampling locations. The maximum Mn peak height in Location 3 is lower than those of Little Dal and Peg.

Analyzing coatings with ChemCam: ChemCam consists of a laser induced breakdown spectroscopy instrument (LIBS) and a remote micro-imager (RMI). The LIBS provides information about chemical composition at a microbeam scale (350-550 µm) up to 7 m from the rover while the RMI provides high-resolution (40 µrad) context images for LIBS analysis locations [24-25]. LIBS uses a pulsed laser to ablate small amounts of material from a target to form a plasma. Some material is removed from the target during each laser pulse; if multiple pulses are performed on one location, a depth profile of chemical composition is obtained. Each pulse returns a spectrum that represents the composition at a specific depth, with each subsequent shot sampling the composition at a slightly greater depth.

Observations: ChemCam analyzed ~1800 individual locations on ~400 rocks in the first 360 sols of the mission. Of these analysis locations, 15 contained large Mn peaks that showed a decreasing trend with depth in the 30 LIBS shots performed at each location. The top three highest Mn peaks with depth trends are found in Caribou, Little Dal, and Peg (Fig. 2a). For all three samples, initial shots contain a small amount of dust, which is low in Mn [26]. After the dust is removed in the first ~1-3 shots, the Mn peak intensity is high. After each subsequent shot, the Mn peak intensity decreases. This systematic decreasing trend is also observed in laboratory LIBS data of a terrestrial rock varnish (Fig. 2b). It should be noted that the Caribou Mn peak is higher than that of the varnish, suggesting a higher Mn content.

Implications for Mars: High Mn abundances in ChemCam data strongly suggest the presence of oxidized Mn minerals in Gale crater. Environments conducive to Mn oxidation and deposition such as hydrothermal systems or a freshwater lake may have existed in Gale crater shortly after its formation; however, the more recent day environment could also support Mn-depositing processes, most notably the alteration of airfall dust on rock surfaces by thin films of water and UV photolysis. While the nature of the high, trending Mn detections from ChemCam is not yet clear, the detection of Mn in excess of a typical martian basalt provides intriguing evidence for water-rock interactions in a habitable environment.

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