CHEMISTRY OF MANGANESE-BEARING MATERIALS AT THE GROKEN DRILL SITE, GALE CRATER, MARS. N. L. Lanza,[1] P. J. Gasda[1], A. Essunfeld[1], J. Comellas[1], G. Caravaca[2], E. Rampe[3], A. Williams[4], P.Y. Meslin[5], E. Dehouck[6], N. Mangold[2], W. Rapin[7], R. Hazen[8], W.W. Fischer[9], A.M. Ollila[1], C. House[10], R.C. Wiens[1]. [1]Los Alamos National Laboratory (nlanza@lanl.gov), [2]UMR CNRS 6112 LPG, Univ. Nantes, France, [3]NASA Johnson Space Center, [4]Univ. Florida, [5]IRAP/CNES, [6]LGL-TPE, Lyon, France, [7]IRAP, Univ. Toulouse, France, [8]Carnegie Institution, [9]California Inst. of Technology, [10]The Pennsylvania State University.

Introduction: In July 2020, the Curiosity rover encountered a region of bedrock that contained an abundance of layered nodular features and highly unusual Mn- and sometimes P-rich chemistries (Fig.1a) in Glen Torridon (GT), a phyllosilicate-rich mudstone to sandstone deposit [1]. This sampling location was originally targeted at a distance as a site for the Sample Analysis at Mars (SAM) instrument to perform one of its two tetramethylammonium hydroxide (TMAH) wet chemistry experiments [2] in the hopes that the new location would provide similar rocks to the previously analyzed clay-rich Glen Etive targets at approximately the same elevation [3].

Regions of high Mn abundance have previously been observed in Gale crater (e.g., [7-9]), and a relationship between Mn and P has been observed along the rover traverse at the Sutton Island member [4-6]. However, no sample of high Mn material up to this time had been delivered to either the CheMin or SAM instruments due to the occurrence of these materials as thin fracture fills and small regions containing concretions, both of which are challenging to sample with the drill. Based on the overall high Mn abundance throughout the bedrock, the unusual density of dark, often Mn-rich nodular features [10], and exciting preliminary TMAH results from the nearby Mary Anning 3 target [2], the team decided to do a drill campaign to attempt delivery of the unusual high Mn phase to CheMin [11]. Of particular interest was to determine the mineralogy and redox state of Mn, both of which have important implications for environmental conditions [e.g., 8, 12]. The selected target was dubbed Groken in reference to the Martian word "grok," [13] in the hopes that the target would provide a deeper understanding of Mars Mn mineralogy, chemistry, and redox environments. Here we describe ChemCam results from the Groken target and surrounding area obtained between sols 2829-2923.

Methods: The Groken target, drill hole, and surrounding area were analyzed with the ChemCam laser-induced breakdown spectroscopy (LIBS) instrument and spectral data were assessed for major element chemical compositions in 746 analysis locations (with 30-150 spectra per location). A new quantification model for Mn abundance in ChemCam data has been developed [14] and was applied to these data. Spectral data were examined for the presence of phosphorus after [4]. Images from the ChemCam Remote Micro Imager (RMI) and the Mastcam and Mars HandLens Imager (MAHLI) instruments were examined to categorize sampled targets as nodules, coherent bedrock, nodule-rich bedrock (where ChemCam sampled the matrix surrounding nodules), and dark-toned strata using the same methods as [10]. The fine-scale stratigraphy of nodule-bearing materials surrounding the Groken target was assessed using a photogrammetric 3D model of the surface from MAHLI images similar to [15].

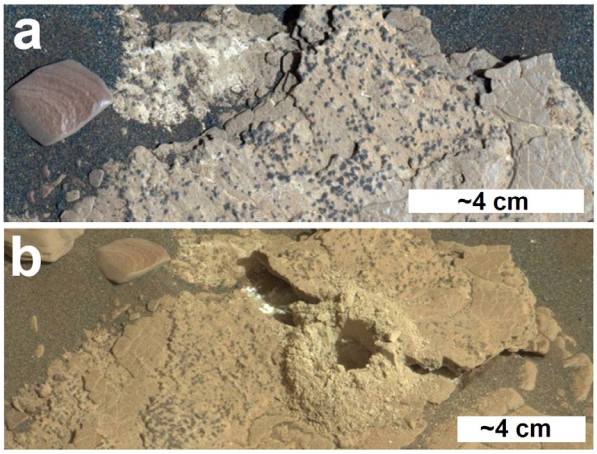

Fig. 1. (a) Groken target with dark-toned nodules (MAHLI 2906MH0002400110003483C00). (b) After drilling, the Groken slab fractured and exposed a bright-toned Ca-sulfate vein (Mastcam 2910MR0151870011300451E01).

Results: Manganese abundance in and around the Groken target is typically elevated in dark nodules and bedrock containing dark nodules as compared to the overall coherent bedrock and the majority of dark-toned strata targets (Fig. 2), with nodules containing ~4-6 wt% MnO. Phosphorus is detected in 33% of dark nodules analyzed, compared to 7% of targets in nodule-rich bedrock and 2% of targets in dark-toned strata. Nodule-rich bedrock is typically higher in Mg, while dark-toned strata are typically higher in Fe. There is an association between Mg abundance and H, suggesting a hydrated phase or phases. The majority of dark nodules are not enriched in Mg or Fe as compared to either nodule-rich bedrock or dark-toned strata. Dark-toned strata targets show significant variation in Mn abundance, with some observations containing high Mn abundances similar to

those found within nodules. Some nodules are associated with enriched Ca [10, also see Fig. 1b]. Analysis of the MAHLI 3D model suggests that there are 2-3 distinct nodule-rich layers that are ~1.4 mm thick, spaced by less nodule-dense bedrock, with the first layer exposed slightly below Groken (Fig.1a).

Discussion: ChemCam results suggest the presence of a high-Mn, sometimes P-bearing phase or phases present within the Groken dark nodules. Manganese is also present in higher abundances in the surrounding bedrock where nodules are present, suggesting a relationship between nodules and bedrock. The Groken drill site exposed a light-toned vein that appears to be Ca-sulfate (Fig.1b, [10]), which may account for the increase in Ca observed in some nodular and otherwise high-Mn materials due to mixing, an interpretation that is supported by chemistry results from the Alpha Particle X-ray Spectrometer (APXS) [16]. At first glance, the morphologies of the nodule features are suggestive of diagenetic concretions [10, 17], which on Earth are deposited as a cement by Mn-bearing groundwater moving through fractures and pore spaces, typically as Mn^{4+} oxides (although such deposits, when ancient, are typically reduced to Mn^{2+} [12]). However, MAHLI images show morphologies suggestive of prismatic crystal habits and potential twinning, which may be indicative of the current mineral phase or show an initial phase that has since been replaced. Results from the SAM TMAH experiment at the nearby Mary Anning 3 target point to the presence of high molecular weight (HMW) organic molecules [2, 18]; on Earth, HMW molecules are preserved in biogenically produced Mn-oxides [19].

While the observed morphologies and overall high regional Mn abundances are consistent with a model of Mn deposition as a cement, results from other rover instruments are not consistent with the presence of a 3/4+ Mn-oxide mineral at Groken. Results from the SAM instrument suggest that the Mn present in Groken is likely to be in the 2+ oxidation state [20]. Results from the CheMin instrument suggest a Mn-bearing phosphate mineral in the jahnsite-whiteite group, which on Earth is associated with alteration of preexisting Fe-, Mn-, and P-rich deposits [11]. There are several possible interpretations for the combined observations at Groken. We favor a diagenetic origin for the dark nodules based on their overall morphology and their occurrence along planar zones of increased permeability in the bedrock, as well as widespread evidence for multiple episodes of diagenesis throughout the GT region [10]. The CheMin detection of a jahnsite-whiteite group mineral at Groken suggests that the dark nodules may represent an unusual diagenetic occurrence of this mineral group [e.g., 11]. ChemCam results are

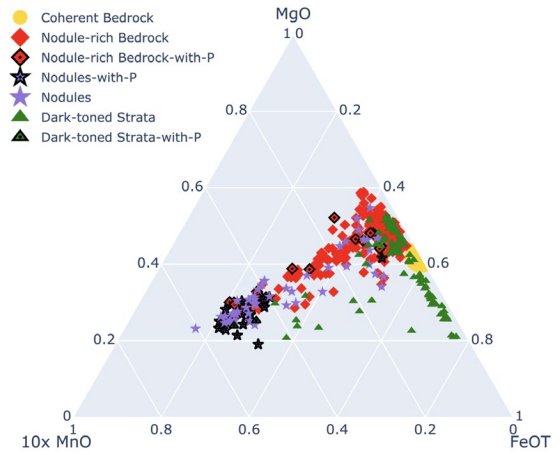

Fig. 2. ChemCam chemistry of the Groken region.

broadly consistent with the presence of a Mn- bearing phosphate within the Groken nodules. Alternatively, the CheMin Groken sample may not have included a significant fraction of dark nodular material, in which case the nodules may not be the source of the mineralogical detection of phosphate. ChemCam analysis down the Groken drill hole suggests that nodular material is less abundant in the drill hole at the depth at which CheMin and SAM obtain samples. The overall high abundance of Mn within the Groken slab along with the distribution of P suggest that Mn-and P-bearing phases are present both within and outside of nodules. Thus, the observed Mn-bearing phosphates could be present within the bedrock alongside nodules that represent a different diagenetic event. Weathering of preexisting Mn-bearing phosphates could have produced Mn-oxide nodules that scavenged P. Regardless of the exact process by which these high-Mn materials were emplaced, the observations at the Groken slab are consistent with the past existence of oxidizing aqueous environments at Gale and the presence of unusual source materials that have yet to be fully understood.

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