PRECIPITATION OF MN-BEARING NODULES IN A SHALLOW SHORELINE ENVIRONMENT IN GALE CRATER, MARS. N.L. Lanza[1], P.J. Gasda[1], E. Swanner[2], W.W. Fischer[3], A. Treiman[4], A. Essunfeld[1,5], J. Comellas[1,6], A.J. Williams[7], E.B. Rampe[8], P.-Y. Meslin[9], C.H. House[10], R. Hazen[11], & S. Schwenzer[12], [1]Los Alamos National Laboratory (nlanza@lanl.gov), [2]Iowa State Univ., [3]Caltech, [4]LPI/USRA, [5]Yale Univ., [6]Univ. Hawaii Manoa, [7]Univ. of Florida, [8]NASA Johnson Space Center, [9]IRAP/CNES, [10]The PA State Univ., [11]Carnegie Inst. for Sci., [12]The Open Univ.

Introduction: Unusually high Mn- and P-rich chemistries associated with nodule-like features were observed in the Glen Torridon (GT) region of Gale crater [1-2]. Based on chemistry, morphology, and regional geologic context, we propose that these materials may have formed in shallow lake waters in organic-bearing soft (pre-lithified) sediments at a redox interface.

Observations: *Local and regional context:* Nodules at Groken occupy thin horizons ~1.4 mm thick spaced by less nodule-dense bedrock, with the first layer exposed slightly below Groken (**Fig. 1b**, [1]). Additional nodules observed on the surrounding slab were not analyzed for thickness but appear to be an extension of the observations at Groken. Regionally the grain size is progressing from mudstone to sandstone, suggesting a transition from low-energy lacustrine deposits to a higher-energy lake margin environment [3]. There is also evidence for shallow water wave ripples in nearby stratigraphy within the Knockfarril Hill member within the GT, the same member in which Groken is found [4].

Chemistry: All 856 ChemCam analysis locations in the Groken region were analyzed for chemistry and rock type (sols 2829-2923, **Fig. 2**). Manganese abundance in and around the Groken target is typically elevated in dark nodules and bedrock containing dark nodules. Nodules were directly analyzed by ChemCam in 85 of these locations, all of which contained elevated Mn (average ~3.8 wt% MnO). The presence of P was assessed by examining the spectra after the methods of [5]. 73% of P detections in the surrounding region were within nodules. Overall, 71% of nodules contained both Mn and P, showing a strong relationship between Mn, P, and nodule morphology. An overview of diagenetic features and related ChemCam chemistry in the GT region (including the Groken slab) is described in detail in [6].

Associated organic materials: Results from the Sample Analysis at Mars (SAM) instrument at the nearby Mary Anning 3 target point to the presence of S-bearing organic molecules and high molecular weight (HMW) molecules, interpreted as potentially preserved indigenous macromolecules or remnant meteoritic infall [7-8]. Similar S-bearing organics were not detected at Groken, which may be due either to their absence or that they are in too low abundance to be detected with the elevated background in SAM after several wet chemistry experiments [7]. The wet chemistry experiments to detect HMW organics was not repeated at Groken and thus a direct comparison of results from Mary Anning 3 is not possible; however, given the close proximity of the sampling locations on the slab (within 1-2 m of each other, **Fig. 1a**), it is plausible that there is a relationship between the observed Mn-P-nodules and organic materials in the Groken area.

Mineralogy: The CheMin instrument analyzed materials from Groken and the surrounding Mary Anning slab for mineralogy. Results suggest that the high Mn and P materials are amorphous, although the observed chemistry may be consistent with initial formation as a phosphate mineral [2, 9]. Analysis by the SAM instrument detected only reduced Mn [10].

Terrestrial analogs: Mn-rich nodular features are common in terrestrial lacustrine environments. Ferromanganese concretions that are sub-mm to a few mm in diameter can form within a distinct sediment layer at or below the sediment surface in fine-grained sediments with organic carbon contents of 0.5-2 wt% [11-13]. A diagenetic formation pathway is well described in the literature for these concretions from lacustrine and coastal sediments [14-17]. In this scenario, Mn-oxides are first deposited in sediments

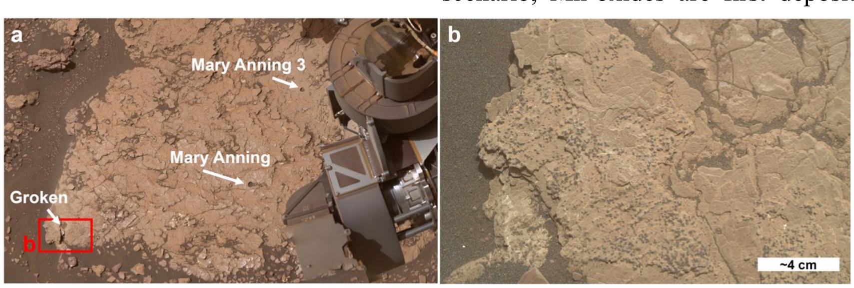

Fig. 1. (a) Mastcam overview image of the Mary Anning/Groken slab, with the locations of the three drill holes labeled; red box indicates the approximate location of (b) (PIA24173-1600). (b) Closer MAHLI view of the Groken sampling location (pre-drill) showing multiple thin layers of dark nodules within a fine-grained bedrock matrix (MAHLI 2906MH0004650011003489C00).

where oxygen is absent below the top layer. The oxides then dissolve by reduction with organic carbon to form Mn^{2+}, which diffuses upward to the oxidizing interface and re-precipitates as Mn-oxides along a thin horizon. Due to the slightly lower redox potential of Fe^{2+}, Fe-oxides and peak concentrations of dissolved Fe^{2+} are found just below the Mn-oxides. Amorphous Mn and Fe oxides have been shown to sorb P if it is available in solution [18-19].

A similar diagenetic pathway may be applicable to the mm-scale Mn nodules that outcrop on the sediment surface at Groken. Nearby evidence for shallow water [3-4] suggests a near-shore environment where groundwaters, lake waters, and atmosphere would interact. Nodules form within linear zones, as would be expected at a redox interface. Organic material has been detected in close proximity [7-8]. Manganese does not appear to be in an oxidized form, and siderite has been detected nearby [10, 20], consistent with the diagenetic formation of carbonate minerals. Although Mn-phosphate minerals have also been suggested [5, 9], they appear unlikely to have formed in abundance [21].

Discussion: Numerous aqueous interfaces could have existed within Gale lake to allow for deposition of minerals from water, formation of minerals within sediments, and/or due to early diagenetic processes that produced sedimentary Mn enrichments. Based on the current observations, we favor a model in which Mn enters the system dissolved in groundwater, where it accumulates within the water column. To stabilize a lake within Gale crater, between 39–47% of the total water influx to Gale would have had to be groundwater [22]. The groundwater chemical composition would have been anoxic and alkaline based on what is expected when meteoric water reacts with basalt under a similar climate regime (e.g., Iceland) [23-24]. Mixing of lacustrine and groundwater fluids beneath the lake may broadly explain the observed mineralogies in GT [20]. The conditions within the lake are inferred to have been mildly saline, pH-circumneutral, and CO_2-bearing [24-25]. Waters of distinct chemical composition likely existed at different depths within the lake water (i.e., chemical stratification) [26]. This interpretation is based on the stratigraphy of hematite (oxidized ferric iron; Fe^{3+}) and magnetite (mixed-valent Fe^{2+} and Fe^{3+}) minerals within the Murray formation, although this stratigraphy could also be diagenetic [27]. Such "redox stratification" of abundant dissolved and reduced Fe^{2+} in deep, anoxic water commonly co-occurs with abundant dissolved Mn^{2+} due to their similar redox potential [28]. Such chemical gradients can be the site of hydrogenetic mineral formation (minerals that precipitate within a water column and deposit as sediments), including Mn-oxides [29] and Mn-carbonates [30]. Within a near-shore environment, redox stratification may extend into sediments, with oxic shallow waters in communication with the atmosphere overlaying sediments containing a redox front at some depth where the environment transitions from reducing at depth to oxidizing. The chemistry of sedimentary porewaters is expected to evolve due to diagenetic reactions, which on Earth comprise water-rock interactions, microbial activity, and compaction. Sedimentary diagenesis produces porewaters with chemical compositions that are distinct from overlying water, from which new minerals can precipitate prior to lithification, including minerals that are not thermodynamically favored to form in the overlying water. Thus, dissolved Mn present within porewaters may reprecipitate in layers within sediments at depths where conditions are sufficiently oxidizing.

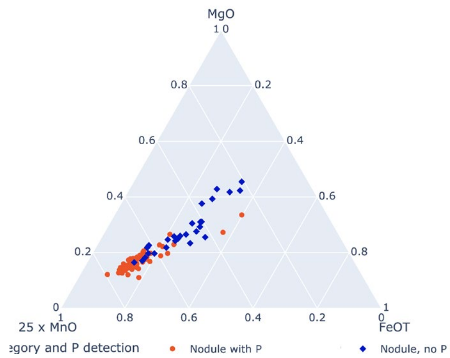

Fig. 2. ChemCam chemistry of Groken area nodules.

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