

DETECTION OF HYDROUS MANGANESE AND IRON OXIDES WITH VARIABLE PHOSPHORUS AND MAGNESIUM CONTENTS IN THE LACUSTRINE SEDIMENTS OF THE MURRAY FORMATION, GALE, MARS. P.-Y. Meslin¹, P. Gasda², J. L'Haridon³, O. Forni¹, N. Lanza², S. Lamm⁴, J.R. Johnson⁵, R.C. Wiens², L. Thompson⁶, W. Rapin⁷, O. Gasnault¹, A. Cousin¹, N. Mangold³, E. Dehouck⁸, S. Maurice¹, J. Lasue¹, J. Frydenvang⁹. ¹IRAP, UPS, CNRS (pmeslin@irap.omp.eu). ²LANL, Los Alamos. ³LPG, Nantes. ⁴Kansas State University. ⁵APL, Laurel, MD. ⁶University of New Brunswick. ⁷Caltech, Pasadena. ⁸LGL-TPE, Lyon. ⁹Univ. of Copenhagen.

Context: After exploring fluvio-deltaic strata in the Gale Crater, the Curiosity rover started to explore the basal strata of its central mountain (Aeolis Mons) around sol 780, in particular a > 300 m thick stratigraphic unit called the Murray formation, composed dominantly of finely laminated mudstones to very fine-grained sandstones deposited in a prolonged lacustrine environment, containing hematite and phyllosilicates, and a variety of diagenetic overprints (veins, concretions). The Sutton Island member of the Murray fm. presents some evidence for climate aridification, including large-scale trough cross-stratified sandstones [1], mudcracks [2] and evaporitic salts [3,4]. Here, we report on the detection with the ChemCam instrument of a variety of dark-toned features characterized by Mn- and Fe-enrichments associated with variable amounts of P and Mg, distributed over a ~160 m stratigraphic section of the Murray formation (mostly in the Sutton Island mbr), near the base of the Vera Rubin Ridge (VRR). This provides additional evidence for the presence of a more shallow, oxidizing and weakly acidic to circumneutral lacustrine environment.

Data and methods: Targets were classified according to their morphology and colour into five groups (Fig. 1): 1) dark-toned inclusions in CaSO₄-filled fractures, 2) dark-toned nodules or concretions of various sizes (a few mm to ~1 cm), dispersed along rhythmic, subhorizontal, often erosion-resistant, bedding planes, 3) dark-toned, more or less continuous subhorizontal and rhythmic laminae, 4) other diverse dark-toned diagenetic features, 5) dark-toned, coarse-grained, laminated sandstones [5]. These targets started to be detected sporadically after sol 1380 (with a small fracture-filling dark-toned inclusion in the vicinity of the Naukluft Plateau), and then more frequently after sol



Fig. 1: Representative targets of each of the 5 groups of dark-toned features.

1545, near the Old Soaker locality where mud cracks have been identified [2]. None of these features were detected on the VRR yet, except a few Fe-rich dark-toned clasts (not reported here) [6].

The chemical analysis focused on a few key elements that were found to be enriched, or strongly variable, in these targets, namely Fe, Mn, P and Mg. Because of the strong enrichments in Fe observed, for which a quantitative analysis is still ongoing, a univariate approach based on peak fitting of the LIBS spectra is followed in this study, using the Fe line at 301 nm, the Mn doublet at ~403.3 nm, and the sum of the P peaks at 255.4 and 418 nm. To better reveal possible correlations between elements, all individual spectra were analyzed (30 spectra are typically collected on each individual LIBS point).

Observations: The five groups of dark-toned features exhibit distinct chemical compositions (Fig. 2). The dark inclusions (Group 1, green) show elevated (vs. bedrock) and correlated Fe and P abundances, and no or modest Mn enrichments. The dark nodules/concretions (Group 2, blue) are characterized by strong Mn enrichments, intermediate Fe and P enrichments (between bedrock and Group 1) and a weak, scattered Mn-P correlation (the large scatter is probably in part due to the weakness of the P signal, or to a variable P/Mn ratio in these sediments). The dark laminae (Group 3, red) show more heterogeneity, and may be divided into three subgroups: (3a) similar to Group 1, (3b) similar to Group 2, and (3c) which exhibits slight or no Mn enrichment, an absence of P detection, and are strongly enriched in Fe. Group 4 (beige) mostly overlaps with group 3c, and Group 5 contains Mn-rich, Fe-rich, and

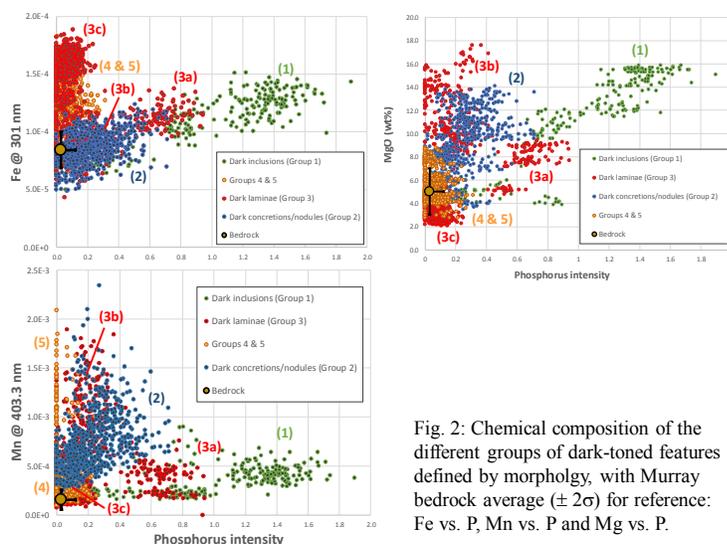


Fig. 2: Chemical composition of the different groups of dark-toned features defined by morphology, with Murray bedrock average ($\pm 2\sigma$) for reference: Fe vs. P, Mn vs. P and Mg vs. P.

P-poor sandstones (beige, along the y-axis). Therefore, almost all of the dark-toned targets show an enrichment in Fe and Mn, but only the dark-toned sandstones of Group 5 are strongly enriched in both. All of the P detections are associated with the dark-toned features of this study, which represent 40% of all ChemCam phosphorus detections made since the beginning of the mission. The strongest P abundances are associated with Fe-rich targets, followed by Mn-rich targets. Another key observation is the correlation between P and Mg in Groups 1 and 2. The dark laminae (Group 3) show subgroups in Mg that are consistent with the heterogeneity and similarity with other groups presented above. Lastly, most dark-toned features exhibit a strong hydrogen signal compared to the bedrock.

Interpretation and implications: The strong Fe and Mn-enrichments observed in these dark-toned targets, together with the presence of a strong H signal suggest the presence of hydrous iron and manganese oxides in the lacustrine sediments. These phases are commonly formed in the top layer of marine and lacustrine sediments and accumulate above the redox boundary, to a depth at which they are reduced, dissolved, transported upward and recycled at the surface [7]. The rhythmic, subhorizontal setting of Groups 2-3 suggests the periodic onset of strongly oxidizing conditions at the water-sediment interface, possibly following variations of the lake level or variations of its vertical thermal, density or salinity profile. The enrichment in P observed in Groups 1, 2, 3a is likely due to adsorption of phosphate anions to these hydroxides, as they have a strong affinity for a variety of cations and anions. This process, together with the precipitation of apatite, is the main mechanism fixing inorganic phosphates into lacustrine sediments [8]. The Mg-P correlation observed in these targets is consistent with this interpretation. Indeed, the pH of zero-point-of-charge of Mn-oxides is ~ 2.3 and hydrous Mn-oxides are not expected to adsorb oxyanions at larger pH. But the adsorption of cations, in particular Mg^{2+} , increases their pH_{ZPC} and facilitate the adsorption of phosphate through ternary complexation [9]. The adsorption of phosphate to Mn- but also Fe-hydroxides was thus observed to be increased by the presence of Mg^{2+} and Ca^{2+} cations [8,9]. Note that most of the Fe-rich targets of Group 3c, 4 and 5 are poor in both Mg and P (Fig.2). This suggests variations with time of the concentration in phosphate anions or $[Mg^{2+}]$ in the lake waters. Nonetheless, the $MgHPO_4$ species seems to have been prevalent (vs. $CaHPO_4$). The presence of Mg^{2+} also inhibits the formation of apatite [11], which could explain why it was not detected in these sediments (alternatively, the pH may not have been high enough). The Fe/Mn-Mg-P association also provides constraints on the pH, as it controls the adsorption of phosphate anions: Mg^{2+} is not adsorbed at $pH < 4$ [9,12] and the adsorption of phosphate onto Mn-oxides in the presence of Mg^{2+} peaks for $pH = 5-7$ [10], while adsorption of phosphate to goethite is strongest for $pH 4-7$ [8,9,12]. The adsorption of P quickly decreases for larger pH, because of

competition with OH^- . Salinity, however, was not found to affect adsorption of P onto Mn-oxides [9]. Similar conditions (Eh, pH, $[Mg^{2+}]$) were probably encountered in the veins when dark inclusions of Group 1 precipitated (if not detrital), although less oxidizing conditions are required for iron oxides to precipitate.

The larger P abundance of Group 1 (Fe-rich) compared to Group 2 (Mn-rich) could also be explained by the greater affinity of Fe-oxides for phosphate anions than Mn-oxides [13], and the strongly variable P/Mn ratio of Group 2 may also be due to varying phosphate concentrations.

An intriguing observation is that some of the P-rich inclusions and laminae lack obvious Fe^{3+} signatures in the VNIR passive spectra [14]. The reduction of Fe(III)-oxides in lacustrine/marine sediments is usually accompanied by the release of P [15] and the adsorption of P to goethite protects it against reduction [16]. But it has been argued that a major part of the observed P-release could actually originate from organic, rather than inorganic P [17]. Redox-insensitive P-binding systems can also prevent P release [18], but they are unlikely in the present context. Formation of a Fe(II)-P phase (vivianite) was also shown to sequester released P [19]. Baricite $(Mg,Fe)_3(PO_4)_2 \cdot 8H_2O$ would here be a better candidate, but the H signal may then be much stronger.

The morphologies of Group 2 and 3 targets share some resemblance with the evolution pathway of phosphorite fabrics on Earth, starting with the deposition of pristine phosphate layers, which then evolve towards granular phosphorite and hard-grounds mostly by reworking and winnowing of muds under more energetic flows during periods of lowstands, and mechanical concentration of phosphate particles in nearshore lake portions [20]. Indeed, Group 3 seems to result from the deposition of lamination with chemistry distinct from the classic mudstones, and the P-rich concretions (Group 2) appear to result from the reworking of these laminae and their dispersion by transport under more energetic flows, which may trace a more shallow lacustrine environment.

Although the genetic relation between the different groups of dark-toned, Mn/Fe-rich features, and possible chemical evolution during their diagenesis remain to be understood, they collectively provide evidence for the onset of repeated oxidizing conditions at the water-sediment interface [see also 5,21] under weakly acidic-circumneutral pH. Their diversity may trace short-scale temporal or spatial variations of Eh, $[HPO_4^{2-}]$, $[Mg^{2+}]$, $[SO_4^{2-}]$ and pH conditions. The source of phosphorus remains to be identified.

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