BRINY WATERS EVIDENCED BY MAGNESIUM SULFATE RICH LAYERS DISCOVERED IN SITU AT

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Introduction: Mg-sulfates are easily mobilized, due to their high solubility, and precipitate only from extremely concentrated brines. They are tracers of environments involving significant water evaporation or any processes leading to high concentation of ions in solution. Finding and studying Mg-sulfates on Mars can help delineate its significant climate evolutions. Since landing in August 2012, the MSL-Curiosity rover has explored a sequence of fluvio-lacustrine sedimentary rocks in Gale crater [1]. Earlier in the mission, Mg-sulfate was identified in centimeter-sized diagenetic features. These include dendritic aggregates that were restricted to one thin stratigraphic interval at the very base of the Murray formation [2,3], and nodules in the aeolian sandstones of the Stimson formation [4]. The dendrites are associated with Ni and Zn enrichments, which are not observed in the Stimson nodules, pointing to distinct origins or host rock compositional differences.

More recently, higher up 150 meters above the dendrites in the Murray formation, within heterolithic mudstone/sandstone stratigraphic facies [5], a series of centimeter-thick dark-toned layers were observed and which tend to be more resistant to erosion (Fig. 1). Measurements performed by the ChemCam instrument indicate significant magnesium, sulfur and hydrogen enrichments. In this study, we evaluate the abundance of Mg-sulfates (MgSO4·nH₂O) and their hydration state, as well as other possible phases associated with these materials. The presence of laterally extensive Mg-sulfate rich layers has strong implications for the deposition and diagenesis of the upper Murray sediments.

They may be linked to other diagenetic Mg-sulfates lower in the stratigraphy, and to the large bedded sulfate unit identified higher on Mt Sharp [6,7].

Methods: The dark-toned layered materials were analyzed almost exclusively by the ChemCam instrument, providing Laser Induced Breakdown Spectrscopy (LIBS) data at several locations. Major elements are quantified from the spectra using a multivariate calibration process [8]. For hydrogen, a dedicated calibration technique is applied after fitting the hydrogen emission peak to infer equivalent water content [9]. Using recent progress on understanding effects specific to the LIBS hydrogen signal [10], data quality is carefully checked before estimation of the water content. For sulfur, a second dedicated model is used for quantification [11]. The detection of sulfur peaks was also checked visually on the spectra. In addition, an APXS raster observation performed on one of the dark-toned layers, and DAN thermal neutron count rates that suggest enhanced subsurface hydrogen, will both be discussed by the time of the conference.

Results: We find that all LIBS analyses performed on the dark-toned layers are characterized by enhanced MgO content as well as sulfur detection and significant water content compared to the surrounding bedrock. Water content increases along with MgO, up to ~10 wt.% H₂O, consistent with a Mg-sulfate hydration similar to or higher than kieserite (Fig. 2). The variable water content obtained could reflect the presence of amorphous Mg-sulfates at the surface retaining variable amounts of water. These may originate from the

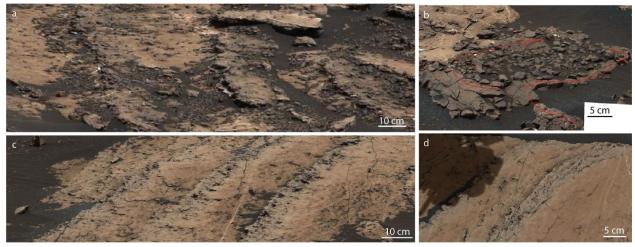


Figure 1: images of dark-toned layers observed by the Curiosity rover between sols 1677 to 1682, in the upper Murray formation. Thick, more homogeneous (a and b), thin, more heterogeneous layers (c and d), with possible polygonal ridges highlighted in red (b).

exhumation of buried epsomite-rich layers in the current climate or kieserite formed by diagenesis [12]. Figure 3 shows the specific elevation at which the dark-toned layers were observed and sampled. It highlights that a few other sparse detections of both sulfur and enhanced MgO content were observed higher in the stratigraphy. There is also a change in the bulk bedrock composition to higher MgO/SiO₂ above dessication cracks [13].

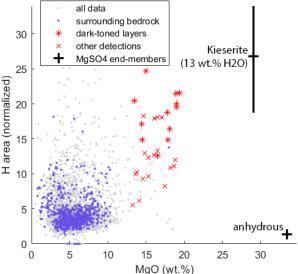


Figure 2: MgO content as a function of H signal for ChemCam data acquired on the dark-toned layers and in the vicinity. Laboratory calibration for hydrogen is used to represent kieserite end-member.

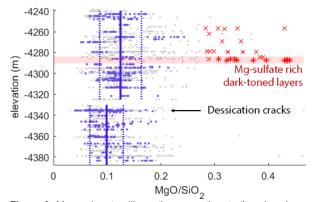


Figure 3: Magnesium to silica ratio across the stratigraphy where Mg-sulfate rich layers were observed and sampled. Bedrock average and standard deviation are shown on two sections.

Early versus late diagenesis: At least two endmember hypotheses for the deposition of Mg-sulfates in these layers exist, each with mineralization at different times relative to sediment formation and lithification (Fig. 4). In an evaporitic lake or early diagenesis scenario (Fig. 4-A), Mg-sulfate rich brines could have infiltrated the sediments, and crystallized in a subaerial setting forming polygonal growth ridges, which are possibly identified on the rock morphology (Figure 1-b). This depositional scenario implies an arid climate with only transient lakes and salt brines in the sediments. Dessication cracks below in the stratigraphy are indicative of the development of subaerial and arid conditions during the deposition of upper Murray sediments [13]; however, the preservation of Mg-sulfates would require continual arid conditions and/or lack of infilation of the upper Murray sediments by water during the formation of the overlying clay and sulfate units.

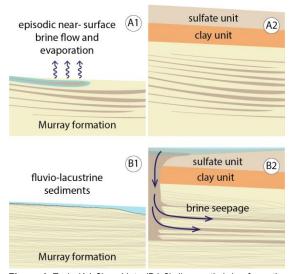


Figure 4: Early (A1-2) and late (B1-2) diagenetic brine formation scenarios for the Mg-sulfate rich layers.

An alternative hypothesis (Fig. 4-B) implies brine deep infiltration later in sedimentary diagenesis. In this scenario, a fluvio-lacustrine environment dominated the deposition of upper Murray sediments. During deposition of the overlying Mt. Sharp group, which contains the polyhdrated "sulfate-bearing unit" [6,7], dense Mgsulfate rich brines could have formed and percolated down into the buried Murray formation below. The Mgsulfate could have precipitated in layers following the paths of highest permeability. This model however implies the existence of high permeability conduits for the brine from the sulfate unit through the clay rich unit as well as impermeable horizons in the upper Murray to restrict the Mg-sulfates to certain layers. These hypotheses will be testable by the rover in the near future by documenting evidence for diagenetic brines and the relationship between the clay unit and the sulfate unit above [14].

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