

AQUEOUS ALTERATION IN MT. SHARP MUDSTONES EVIDENCED BY CHEMCAM, CURIOSITY.

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Introduction: Since its landing, the Curiosity rover has traversed 15 km towards the layered rocks at Mt. Sharp (also named Aeolis Mons), spending >1600 sols (Martian days) at the surface of Mars. On sol 750, the rover entered into continuous light-toned layers named the Murray Formation marking the base of Mt. Sharp. The Pahrump Hills is the lowermost section of Murray Formation. This formation is dominated by mudstones and fine-grained sandstones, interpreted to be mostly lacustrine deposits that are locally unconformably overlain by dark-toned sandstones of the Stimson Formation deposited through eolian processes [1,2]. This study focuses on chemical variations within the Murray Formation compared to fluvial and lacustrine sediments encountered earlier in the mission, namely the Sheepbed mudstones [3], the Kimberley fine-grained sandstones [4] and the fluvial conglomerates of the Bradbury Formation analyzed along the route [5].

Method: ChemCam determines the chemistry of rocks over series of points with diameters close to the laser beam, ca. 0.3-0.5 mm. Bulk chemistry for each target can be established only by averaging several points, especially for coarse-grained targets that display strong point-to-point variations. Each target is assigned a bulk composition that is the result of the average of >5 points. Although 5 points are not sufficient for good statistics on coarse-grained rocks, mudstones and fine-grained sandstones have grain sizes smaller than the laser beam ensuring good statistics. In addition, all points corresponding to obvious diagenetic features such as light-toned veins [6, 7] are removed to obtain a composition devoid of obvious post-depositional modifications.

Indications of alteration from chemistry can be evaluated using various indexes such as the Chemical Index of Alteration (CIA), which is defined as $CIA = 100 * Al_2O_3 / (Al_2O_3 + CaO^* + Na_2O + K_2O)$ (molar). The CIA index starts to reflect the influence of chemical weathering when $CIA > 50$ for felsic rocks, and 40-45 for mafic rocks [8]. CaO^* is the CaO abundance limited to silicate minerals. While carbonates have never been observed at Gale, apatite or anhydrite could be significant contributors to the total CaO. In that case: $CaO^* = CaO - SO_3(Ca\text{-sulfates}) - 10/3P_2O_5(apatite)$ (molar).

ChemCam observed P and S locally, especially in relation with apatite and Ca-sulfates, but it cannot measure these elements at low abundance. P and S can also be linked to other cations, such as Fe/Mg-phosphates or Mg/Fe-sulfates. So, we propose to first calculate the CIA index using total CaO, which gives a lower bound because non-silicate contributions would only increase this index (Fig.1). APXS reports relatively stable P_2O_5 abundances between 0.6 and 1.2wt% in the Murray Formation and SO_3 abundances between 2 and 5% [9]. These values are inconsistent with P and S being present only as Ca-phases (anhydrite and apatite). Indeed, with 1% P_2O_5 , CaO^* drops close to 0 for many Murray targets, so other phases must explain S or P abundances. As negative values are not possible for CaO^* , we thus propose to use this value of 1% P_2O_5 for the upper bound of the CIA index, assuming it is relatively constant through targets.

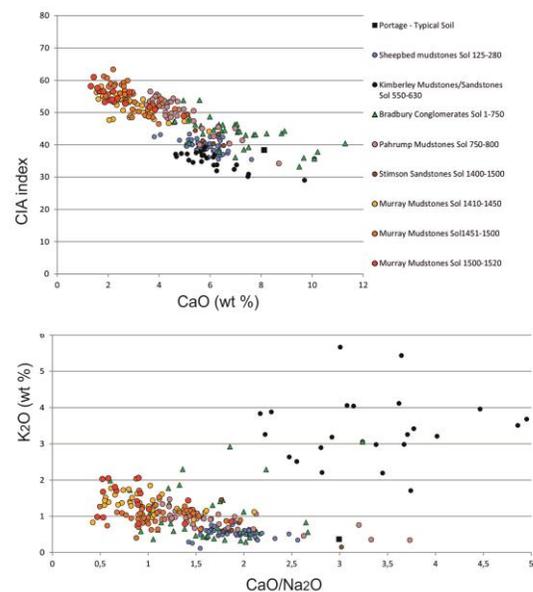


Figure 1: Diagrams of main aqueous sediments analyzed by the rover. (top) Diagram showing a decrease of CaO with an increase in CIA index for Murray mudstones (lower bound, using total CaO). (bottom) Diagram of CaO/Na_2O vs K_2O showing an increase in K_2O for low CaO/Na_2O , but with a different trend than for Kimberley rocks (black dots).

Results: The CIA index (lower bound discussed hereafter) has been below 50 for all aqueous sediments studied before Pahrump Hills, including the Sheepbed mudstones where phyllosilicates were detected [3]. Starting at Pahrump Hills, and then through the entire Murray Formation so far, values >50 are frequent, especially in the recent observations sols 1450-1520 for which the CIA index reaches 60 (Fig. 1, orange and red), a value usually suggesting a significant weathering [8]. The increase in CIA is correlated with a decrease in CaO abundance, which becomes <2% in many recent targets. This negative correlation is not found for Na₂O or K₂O. The A-CN-K ternary diagram (Fig. 2) is another way to plot the CIA index (represented as the Y-axis). It shows that the recent Murray mudstones are above the plagioclase/K-spar line limiting the presumed primary silicate minerals. This is even more the case when plotting the upper bound of the CIA index, which reaches 70 (Figure 2, bottom).

In addition, slightly higher K₂O abundances are observed for high CIA values and low Ca/Na ratios (Fig. 1). This trend could be explained by the presence of potassium feldspars. Potassium feldspars were observed at Kimberley [4] (black dots) but Kimberley sedimentary rocks plot far beneath the alteration lines (Fig. 2). Alternatively, a higher K₂O abundance may suggest K-bearing micas, such as illite, a mineral consistent with interpretations made from coupling SAM and CheMin data in recent drill samples [10, 11]. Interestingly, the weathering trend for Murray mudstones displays a direction towards illite (Fig. 2 bottom), suggesting a link between higher K₂O and alteration.

Interpretation and discussion: Study of the chemistry of the Murray mudstones shows increased values of CIA related to low abundances of CaO (1.5-2%). Leaching of calcium is a reasonable explanation for the low CaO abundances and high CIA. Variations in provenance, from both a weathered source and a potassic source, could explain these observations, raising an interest to the origin of the weathered rocks. However, in-situ alteration of Ca-pyroxene and/or plagioclase can also explain observations very well: While both minerals were present in many rocks analyzed by CheMin so far, CheMin analyses on recent Murray rocks show only low amount of mafic crystalline phases (<5%) [12]. In addition, if the slight increase in K₂O traces the presence of illite, such an in-situ alteration would correspond to a diagenetic alteration during burial.

Overall, a leaching of CaO is an interpretation consistent with most observations, before or after deposition. Nevertheless, a similar trend should also be observed for the mobile element MgO, but MgO does not show the same decrease (average of 4-6 wt%). However,

the role of late diagenetic processes (such as Mg-rich concretions observed at Pahrump Hills [7]) is difficult to isolate from the bulk composition [13].

Leaching of calcium may also be in relation with the density of Ca-sulfate veins observed and local Ca-sulfate cements [14]. In sols 1450-1520, these veins start to display a geometry sub-parallel to bedding. This apparent enhancement of Ca-sulfate-rich deposits may be linked with the leaching of calcium. Further investigations going up in the stratigraphy will enable to refine these interpretations.

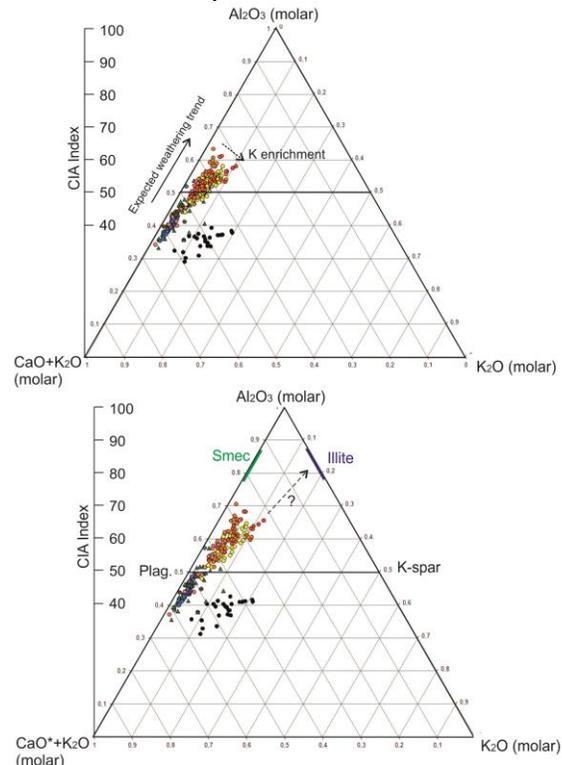


Figure 2: A-CN-K ternary diagrams (top) Diagram with total CaO reported (lower bound of CIA). (bottom) Similar diagram with an upper bound of CIA.

References: [1] Grotzinger et al. (2015), *Science*, 350, 6257. [2] Banham et al. (2016) LPSC abstract #2346. [3] Mc Lennan et al. (2014) *Science*, 343, 6169. [4] Le Deit et al (2016) *JGR-Planets*, 121, 784-804. [5] Mangold et al. (2016) *JGR-Planets*, 121, 353-387. [6] Nachon et al. (2014) *JGR-Planets*, 119, 1991-2016. [7] Nachon et al. (2017) *Icarus*, 2814, 121-136. [8] Nesbitt and Young (1982) *Nature*, 299, 715-717. [9] Thompson et al., (2017) LPSC [10] Hoggancamp et al. (2017) LPSC [11] McAdam et al. (2017) LPSC abstract [12] Bristow et al. (2017) LPSC abstract [13] Rivera-Hernandez et al. (2017) *EGU Conference*, Vienna, abstract. [14] Newsom et al. (2017) LPSC.