CHEMCAM SULFUR ABUNDANCES IN THE KNOCKFARRIL HILL MEMBER, GALE CRATER MARS.

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Introduction: The abundance of mobile elements near the surface of Mars, like sulfur, provides insights into the planet's formation, geologic history, and evolution. Sulfur, often in the form of sulfate, is also an indicator of later episodes of diagenesis and alteration. Understanding and quantifying sulfur on Mars can lead to a greater understanding of many geologic processes related to the surface evolution, the climate history, and potential habitability of Mars.

The Mars Curiosity rover has been at Gale crater for over 10 years and has traversed across several geologically unique formations and members [1]. The sediments that have been analyzed are a complicated assemblage of materials with different origins, alteration at all scales, and interstitial deposits. Sulfur has been explored extensively with the suite of scientific instruments aboard the rover. The presence of Ca-sulfates has been detected by ChemCam and other MSL instruments throughout the traverse [2]. In general, Ca-sulfates have been associated with veins [3] and cements, which are indicators of diagenesis [4]. ChemCam has discovered evidence for Ca-sulfate cements, Fe- and Mg-sulfates, and in soils in the amorphous component [5,6]. CheMin has found Ca-sulfate minerals, including gypsum, bassanite, and anhydrite, throughout the traverse [7].

Methods: The ChemCam instrument onboard the Curiosity rover integrates remote laser induced breakdown spectroscopy (LIBS) with a remote micro-imager (RMI). LIBS uses a focused laser to ablate material from geologic targets and records the spectroscopic emission from the plasma to determine elemental compositions of the rock or soil targets [8,9]. The current calibration model uses multivariate analysis to quantify nine major elements oxides: SiO_2, Al_2O_3, TiO_2, FeO_T, CaO, MgO, Na_2O, K_2O, and MnO [10,11]. ChemCam directly measures the sample chemistry from which it can only infer the molecular structure based on the stoichiometry.

The model does not require the sum of these oxides to add up to 100 wt.%. Therefore, the total can be less than 100 percent if there are additional phases present that the ChemCam model does not report. One common example is with $CaSO_4$ veins and cements [12]. When a vein target is measured, there are qualitative sulfur peak detections in the LIBS spectra, reported as SO_3, contributing to the missing oxide total not reported by the routine techniques, as well as water that might be associated with other $CaSO_4$ species.

Several ChemCam calibration models are being developed to qualitatively report the detection of sulfur, phosphorous, hydrogen, and chlorine, or even to quantify them with ChemCam [13-17]. Often, the difficulty of detection does not come from a lack of a clear emission line in the spectra, but rather from low intensity of the emission lines or interference with close emission lines from elements like Fe and Ca in the case of sulfur [13]. This research aims to explore the relative SO_3 abundances at Gale crater with spectra collected by ChemCam using the Partial Least Squares (PLS) sub-model calibration developed by Clegg et al. [13]. This study focuses on SO_3 ranges below 20 wt.% in an attempt to understand the background abundance of sulfur in rocks of Gale crater. The model by Clegg et al. increases ChemCam's capability to quantify SO_3 throughout the traverse.

Area of Investigation: The initial investigation will be to analyze spectra taken from the Glen Etive drill location (sols 2482 to 2552) in Glen Torridon region of the Curiosity rover traverse. There were two drill holes taken to have enough sample for the CheMin and SAM instruments to analyze (figure 1).
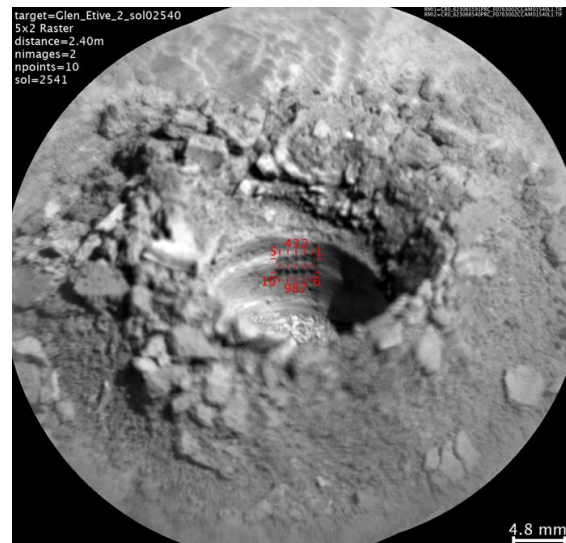

Figure 1. An image of the **_Glen_Etive_2_sol02540_** ChemCam target of the GE2 drill hole wall.

Glen Etive (GE) was the first drill site from the Knockfarril Hill member of the Glen Torridon region of the Carolyn Shoemaker formation. CheMin was able to characterize the mineralogy and found relatively high abundances of phyllosilicates [18]. Overall, GE was abundant in phyllosilicates and showed less diagenetic

alteration, such as Ca-sulfate veins, although minor Ca-sulfate signatures are still present. This location may possibly preserve the sulfur compositions of the residual primary depositional fluids at the time of deposition.

Results: The Clegg et al. model was run on 11 ChemCam targets associated with the Glen Etive (GE) and Glen Etive 2 (GE2) drill holes. These targets include the bedrock before drilling, the drill hole walls, the drill tailings, and the dump pile. In this case, most of the "dump pile" targets sampled more of the underlying soil. The point with the highest SO_3 content was from the GE2 drill hole wall and it was predicted to contain 18.5 wt.% SO_3 and 13.5 wt.% CaO, which likely indicates the presence of a Ca-sulfate phase. The lowest quantity of SO_3 predicted by the model was 2.99 wt.% from a bedrock target of the GE target before drilling.
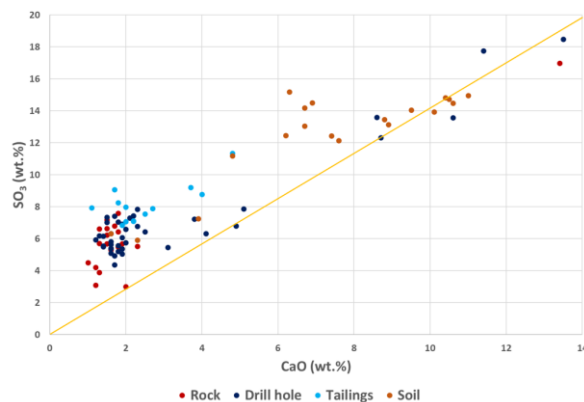

Figure 2. A plot showing the predicted SO_3 (wt.%) vs CaO (wt.%) of the 11 targets associated with the GE and GE2 drill holes. The plot illustrates the SO_3 variation by target type and the solid line represents a pure Ca-sulfate mixing trend.

The CheMin instrument detected 9.5 ± 1.3 wt.% anhydrite in GE and 3.6 ± 0.6 wt.% anhydrite in GE2 [18]. CheMin also detected 0.8 ± 1.2 wt.% bassanite in GE and 1.1 ± 0.8 wt.% bassanite in GE2 [18]. Portions of drill sample may be partly dehydrated between sampling and measurement by CheMin. There was no gypsum reported by CheMin in either Glen Etive drill hole. The SO_3 abundances measured by ChemCam were plotted against CaO (figure 2). For targets with approximately >8 wt.% CaO and >10 wt.% SO_3, the bedrock compositions are in line with the Ca-sulfate mixing trend, where the sulfate abundances are probably explained by detections of enriched Ca-sulfate, likely in the form of anhydrite or bassanite veins. However, for targets with predicted SO_3 abundances of less than 10 wt.%, the model suggests that there may be more sulfate than what can be explained by the CaO abundance. Many of these observations contain more MgO than CaO, and the

excess SO_3, if real, could be associated with $MgSO_4$, which has been detected previously along the traverse and has been suggested to make up a portion of the amorphous component of fine-grained soils [6,14].

Discussion: This investigation of SO_3 in the GE and GE2 drill holes using the calibration model proposed by Clegg et al. [13], illustrates that the model is in relatively good agreement with the qualitative techniques to identify sulfates and that multivariate analysis can be employed to quantify sulfate in ChemCam targets, especially for targets with higher SO_3 abundances. There is "excess SO_3" in some of the less SO_3 abundant targets than what can be accounted for by Ca-sulfate. Therefore, it is possible that there are additional sulfate phases, such as Mg-sulfate or Fe-sulfate, in GE that were likely below reported CheMin detection limits or in the amorphous phase.

It is important to quantify sulfur down to the lowest possible detection limits to better quantify and explain small, subtle changes in sulfate abundances throughout Gale crater. Quantifying SO_3 further constrains the "missing component" in total sum of oxides predicted by ChemCam, which may be used to better understand Cl and H abundances in ChemCam targets.

Conclusions: ChemCam sulfur calibration model for targets with lower sulfate abundances improves interpretations of sulfate compositions in regions where the rover has already traversed as well as regions like the Layered Sulfate Unit where the rover is currently exploring. The model is in good agreement with previous qualitative trends observed by ChemCam.

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