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UTILIZATION OF CHEMCAM SHOT-TO-SHOT DATA TO IDENTIFY AND DISTINGUISH CA-SULFATE CEMENTED BEDROCK FROM MIXED VEIN-BEDROCK FEATURES

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Introduction: The Mars Science Laboratory (MSL) rover, *Curiosity*, has been exploring Gale crater since its landing in 2012. Calcium sulfate veins have been an abundant diagenetic feature found throughout the rover's traverse [1], varying in abundance, in the Murray, Carolyn Shoemaker, and lower Mirador formations. While veins are often distinctly visible on the martian surface, due to their usually light-toned nature, cements are not as visually striking and typically not observed directly via imagery. ChemCam and APXS can detect the presence of cements [2]. Here, we study ChemCam depth profile data to study cements in Gale crater.

Cements are most abundant in coarser-grained materials, such as sandstone, due to the larger pore spaces available for cement formation [3]. Finer-grained materials, such as mudstones can still facilitate cement formation, but this is dependent on their porosity and, more importantly, their permeability which allows allow external fluid penetration. Terrestrial sandstone and mudstone porosity potentially range between 5% and 30% by volume, but mudstone rarely actually exceeds 15% while sandstone frequently does [4,5]. The relative maximum for pore-filling cement is ~30 wt% for Ca-sulfate [6]. Pure Ca-sulfate veins tend to have a Ca abundance exceeding 35 wt% CaO, typically averaging around 35-45 wt%, while typical Gale bedrock has a Ca abundance in the range of ~2-10 wt% [1]. This means that any ChemCam target with an average CaO abundance ranging between 10 wt% and 30 wt% may be scrutinized as a potential Ca-sulfate cement target.

This study analyzes the ChemCam shot-to-shot patterns to distinguish between different cements and mixed vein-bedrock features. ChemCam targets typically contain between 5 and 10 individual points, with the most common rasters being 5x1, 3x3, and 10x1. The LIBS laser spot size is ~400 μm in diameter and each point is shot 30 times to get an average chemical composition. Analysis of the shot-to-shot patterns can reveal that composition is not always homogeneous with depth. As the laser shoots deeper into the rock, composition of the target may vary significantly if the

laser encounters different materials from the top to the bottom of the shot profile. If the laser were to shoot near the edge of a vein and progress from pure vein material to pure bedrock, or vice versa, this creates a very heterogeneous shot-to-shot profile. Conversely, a cemented bedrock target will have a fairly homogeneous shot-to-shot profile using root mean square error prediction (RMSEP) statistical analysis. Both the mixed vein-bedrock target and the cemented bedrock target will have average CaO abundances in the moderate range of 10-30 wt%, so it becomes essential to use the shot-to-shot trends along with accompanying Remote Micro Imager (RMI) context imagery to differentiate them.

Methods: All target points with an average CaO composition between 10 wt% and 30 wt% are first separated out from the complete target list. The first 5 shots are omitted due to contamination with surface dust [7]. Targets are then separated into two categories: those with statistically homogeneous patterns and those with statistically significant heterogeneous patterns. RMSEP accuracy is derived from the MOC model [8] and each data point, whether it is an average or single shot analysis, has a corresponding RMSEP. We use the single shot RMSEP compared to the average RMSEP to determine whether there is a significant change in the CaO composition versus depth in the target. If the change of CaO with depth is greater than the sum of the RMSEP of the single shot and the average CaO value, then this is a significant change at the 2-sigma level. We define a 2-sigma variation of CaO with depth as a 'heterogeneous target.' If the change is not significant, we define it as a 'homogeneous target.' Targets with heterogeneous patterns come in several varieties, such as steadily increasing/decreasing trends (which may be gradual or very sharp), increasing/decreasing "plateau" patterns (CaO increases/decreases initially before holding a consistent composition), and a number of complex patterns (which may include bimodal or jagged patterns). All targets with moderate CaO are also analyzed using RMI context imagery and MastCam imagery (when available) to help identify visible features if possible.

Results & Discussion: Analysis through sol 2003 has identified over 1200 candidate targets with moderate CaO composition. The large majority, ~80%, of these moderate CaO targets exhibited a homogeneous shot-to-shot trend indicative of Ca-sulfate cemented bedrock (**Figure 1**). Heterogeneous shot-to-shot patterns indicative of mixed vein-bedrock targets (**Figure 2**) and other irregular targets are therefore fairly infrequent in comparison. The abundance of targets with moderate CaO with homogeneous shot-to-shot trends indicates that cemented bedrock is abundant in Gale, particularly in coarser sandstone rock accounting for at least 20% of bedrock where Ca-sulfate intrusion was abundant. Formations, such as the Murray, which feature abundant sandstone and abundant intrusion of calcium sulfate, may therefore feature abundant calcium sulfate cement.

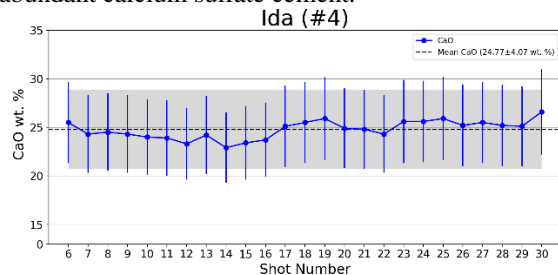


Fig. 1: Homogeneous shot-to-shot trend indicative of cemented sandstone with average CaO of ~25 wt%.

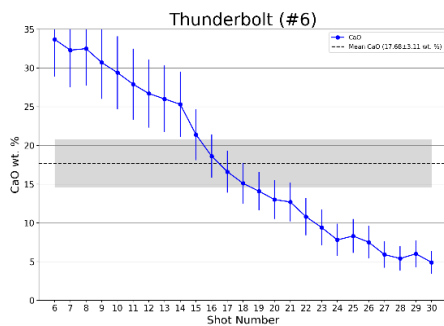


Fig. 2: Heterogeneous shot-to-shot trend of target hitting mixed bedrock-vein across depth profile with average CaO of ~20 wt%.

There have been numerous fluid events in Gale crater [9-11], including those that introduced the calcium sulfate veins. The fluid that formed the cement may have formed prior to, concurrent with, or after the formation of the veins or other cements, but this is poorly understood. Cement formation before or after would indicate multiple fluid events enriched calcium sulfate. Concurrent formation could occur as veins were forming along cracks, while excess fluid permeated into the pore space of surrounding bedrock forming the cement.

Conclusion and Future Work: This study shows that analysis of shot-to-shot data may be necessary for differentiating features with similar average chemical compositions. There are abundant ChemCam LIBS targets which contain moderate CaO. These targets can be separated using statistical analysis of their shot-to-shot patterns into homogeneous cemented bedrock targets and heterogeneous targets including mixed vein-bedrock targets and other irregular targets. Cemented bedrock targets are abundant in Gale crater and are most easily identified by using shot-to-shot analysis. The presence of calcium sulfate cements indicates that fluid infiltration was not limited to vein intrusions. A calcium sulfate rich groundwater was able to permeate into the coarser Gale bedrock and deposit cement material into available pore space. This provides additional insight into the groundwater history of Gale, specifically on when and where it was able to more easily infiltrate the bedrock.

Future work will include analysis of moderate CaO targets to current sols in the mission. This will allow analysis of the rest of the traverse to determine if calcium sulfate cement continues higher up in the Gale stratigraphy. The GINI index will also be used to identify the grain size of targets within each formation, correlate the amount of targets containing Ca-sulfate, and then calculate the proportions of cement-bearing rock types [12]. In the Sutton Island member of the Murray, as well as higher in the stratigraphy in the sulfate unit, when magnesium sulfates are present or dominate over of calcium sulfate, this study will look to determine if the cement composition changes accordingly [13]. Lastly, as LIBS sulfur calibration improves, it will be essential to compare estimated sulfur compositions to verify moderate CaO detections correlate with Ca-sulfate.

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