QUANTITATIVE SULFUR CHEMISTRY OBSERVED ON DIVERSE SAMPLES FROM SOLS 1800-2300.

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Introduction: The diversity of sulfur chemistry observed along the Curiosity rover traverse continued on Vera Rubin Ridge. The Curiosity rover has encountered several forms of sulfur chemistry including calcium sulfate veins [1] and hydrated magnesium sulfates [2, 3]. The chemistry and mineralogy of these sulfur-containing species have been documented by the ChemCam, APXS, SAM and CheMin instruments [4, 5]. This paper focuses on the SO_3 chemical diversity observed with ChemCam along the traverse through Vera Rubin Ridge (VRR). Figure 1 contains the MastCam image of Staffa_ccam, a dark toned float rock that was part of an unusual small pile of float rocks named Bressay, encountered around Sol 2012 [6].

Quantitative LIBS calibration for SO_3 is complicated by the relatively weak sulfur emission lines and the proximity of interfering iron emission lines. Multivariate calibration of SO_3 is further complicated by correlations with other major elements such as calcium. ChemCam LIBS major-element analyses are determined with a weighted ensemble of partial least squares (PLS) and independent components analysis (ICA) [7]. These multivariate techniques identify correlations between the elemental concentrations in calibration samples and the pixel-by-pixel spectral variations. When these methods are used to quantify species with relatively weak emission lines, such as sulfur, correlations with the larger major-element peaks tend to dominate the analysis. Consequently, this SO_3 model involves the conversion of the ChemCam LIBS spectra into peak-area spectra where each of the LIBS emission lines is integrated into a single channel. This converts the 6144-channel ChemCam spectrum into typically fewer than 500 non-zero spectral channels. Figure 2 contains the processed ChemCam LIBS spectrum (top) and the peak area spectrum (bottom) used to extract SO_3 compositions for Staffa_ccam location #4,

Figure 1: The MastCam image of Staffa_ccam (ccam01015, sol 2015) from a 2.24 m standoff distance.

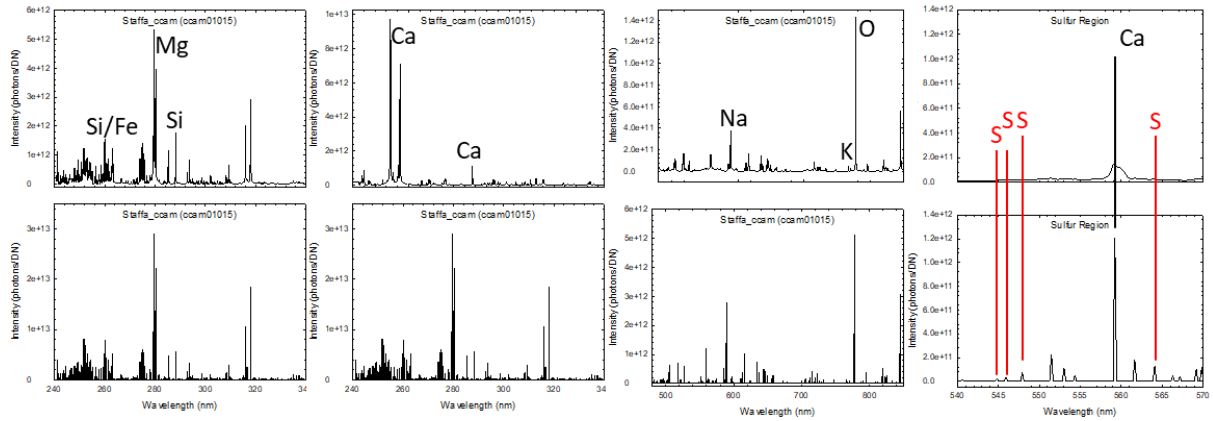

Figure 2: Sulfur compositions are extracted from ChemCam spectra (top) converted into peak area spectra (bottom) by partial least squares analysis. This figure focuses on Staffa_ccam location #4 where the CaO and SO_3 compositions suggest the presence of $CaSO_4$. The spectra to the right end of the figure highlight the ChemCam sulfur spectral region. The peak area processed data produce a significant enhancement relative to the standard ChemCam data.

where the CaO and SO_3 compositions suggest the presence of $CaSO_4$. Figure 2 also highlights the primary sulfur spectral region (543-565 nm) collected with ChemCam. The y-axes in both the standard ChemCam data (top right) and peak area processed ChemCam data (bottom right) are identical to demonstrate the significant enhancement in the peak area processing.

Laboratory Calibration: The PLS1 sub-model analysis developed by Anderson et al. is used to segregate the sulfur calibration into three geologically relevant models [8, 9]. The sulfur model used here to analyze samples on Mars is the integration of the PLS1 sub-model technique using the peak-area calibration spectra.

The ChemCam testbed at Los Alamos National Laboratory was used to collect the LIBS geochemical database that includes more than 500 geochemical standards [7]. A series of doped samples containing various mixtures of $CaSO_4$ and $MgSO_4$ with BHVO2 were added to the database [10, 11]. All spectra were processed as described by Wiens et al. [12] and then converted into peak-area spectra.

Multivariate Analysis: Following [8], three overlapping PLS1 sub-models were generated with these peak-area spectra. The "high" SO_3 model covers 30 – 70 wt. %. The "low" model covers 1 – 10 wt. % and represents most of the bedrock and soils probed by ChemCam. The "medium" model covers the compositions between these two extremes, 5 – 35 wt. %, and could represent various sulfate structures such as calcium sulfate cemented sandstones. Finally, seamless transitions between these three overlapping models were defined as described by Anderson et al. [8].

Discussion: Figure 3 contains a plot of the CaO vs. SO_3 compositions for Bressay, Pettegrove Point concretions, float rocks, and soils observed on VRR. The red line and data points highlight the pure gypsum, bassanite, and anhydrite compositions and mixtures therewith. As the calcium concentration increases to >8 oxide wt. %, the sulfur compositions generally follow the $CaSO_4$ trendline and nearly all were observed in the Bressay

Most of the Bressay compositions are close to the $CaSO_4$ trendline, which suggests the presence of $CaSO_4$. However, some of the Bressay float rocks, Pettegrove Point concretions, and the soils also contain excess SO_3 requiring another sulfur-containing phase not depicted in Figure 3. This missing phase could include iron or magnesium sulfate, both of which have been observed along the traverse.

Ardgour location 9 (ccam01018) is the single Bressay observation with 27.5 wt. % SO_3 and 2.0 wt. % CaO that is well above the $CaSO_4$ trendline. This ovservation contains only 6.9 wt. % MgO suggesting

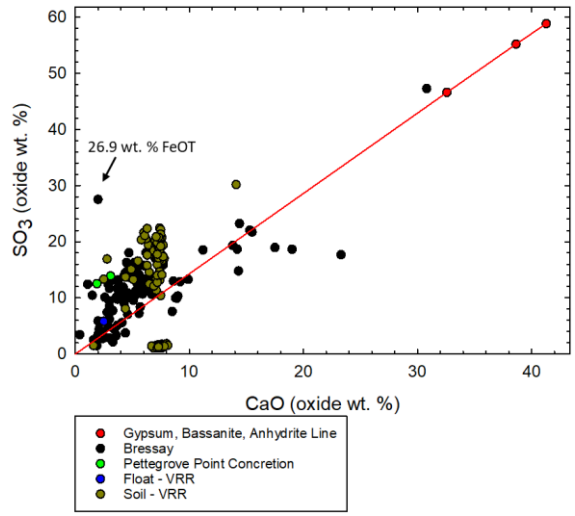

Figure 3: A plot of the CaO vs. SO_3 compositions ovserved in several of the Vera Rubin Ridge features. The red data points and line define the $CaSO_4$ trendline and include pure gypsum, bassanite, and anhydrite.

this could contain a limited amount of $MgSO_4$. However, Ardgour location 9 contains 26.9 wt. % FeOT, inferring that there could also be some form of iron sulfate.

Conclusion: ChemCam is fundamentally a chemistry instrument from which molecular or mineralogical correlations can be inferred. Most of the SO_3 observations made by ChemCam recently appear to contain some $CaSO_4$. The excess SO_3 also suggests additional the presence of phases that could include iron and magnesium sulfate, as these have been observed along the traverse.

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