SULFUR CHEMICAL ANALYSIS AND INTERPRETATION WITH CHEMCAM ON THE CURIOSITY ROVER. S.M. Clegg[1], R.B. Anderson[2], O. Forni[3], J. Frydenvang[1], H. Newsom[4], S. Maurice[3], R.C. Wiens[1], [1]Los Alamos National Laboratory, Los Alamos, NM, sclegg@lanl.gov, [2]USGS, Flagstaff, AZ, [3]Institut de Recherches en Astrophysique et Planétologie, Toulouse, France, 4 University of New Mexico, Albuquerque, NM.

Introduction: The Curiosity rover has repeatedly encountered many forms of sulfur including calcium sulfate veins along the traverse through Gale Crater [1]. The chemistry and mineralogy of these sulfur-containing species have been primarily documented by the APXS and CheMin instruments. A new SO_3 calibration model for the remote Laser-Induced Breakdown Spectroscopy (LIBS) technique used by the ChemCam instrument has been developed that enables the improved quantitative analysis of SO_3. In this paper, the details of this new LIBS calibration model will be described and applied to two disparate Mars samples, Mavor and Wernecke, that were also probed by the Curiosity APXS instrument.

The fundamental limitation with previous sulfur calibration models has been the relatively weak sulfur emission lines and the proximity of interfering iron emission lines. ChemCam LIBS major-element analyses are completed with a weighted ensemble of partial least squares (PLS) and independent components analysis (ICA) [2]. These multivariate techniques identify correlations between the concentrations of calibration samples and the pixel-by-pixel spectral variations. When these methods are used to quantify species with relatively weak emission lines such as S, correlations with the larger major-element peaks tend to dominate the analysis.

This new sulfur calibration model is the result of two improvements. First, the ChemCam LIBS spectrum is converted into a peak-area spectrum where each of the LIBS emission lines is integrated into a single peak converting the 6144 ChemCam spectral channels into typically fewer than 500 non-zero spectral points. Second, the PLS1 sub-model analysis developed by Anderson et al. is used segregate the sulfur calibration into three geologically relevant models [3]. The sulfur model used to analyze samples on Mars is the integration of the PLS1 sub-model technique using the peak-area calibration spectra.

Mars Samples: The ChemCam analyses of the calcium sulfate vein *Mavor* and the rock *Wernecke* are used as disparate tests of this new sulfur calibration model. These two Mars samples are also ideal targets to compare with the APXS analyses. The Mavor Remote Micro-Image (RMI) depicted in Figure 1 is a relatively wide exposure that was probed with the 1.7 cm diameter APXS sensor as well as with the sub-millimeter ChemCam analysis spots. In contrast, the Wernecke sample is a large dust covered rock as the MastCam image depicts in Figure 1. Wernecke was analyzed several times with ChemCam and APXS before and after the dust was brushed away.

Laboratory Calibration: The ChemCam instrument completed a re-calibration that is based on a significantly expanded set of standards. The original ChemCam calibration included 66 geochemical standards analyzed with the flight model prior to rover integration [4]. The ChemCam testbed at Los Alamos National Laboratory was used to collect the new LIBS geochemical database that includes more than 500 geochemical standards that are representative of the samples observed in Gale Crater [2]. The sulfur composition of these rock powder standards alone was not diverse enough to represent the range of samples probed by ChemCam in Gale Crater, so a series of doped samples containing various mixtures of calcium sulfate with the Hawaiian basalt BHVO2 are included in the

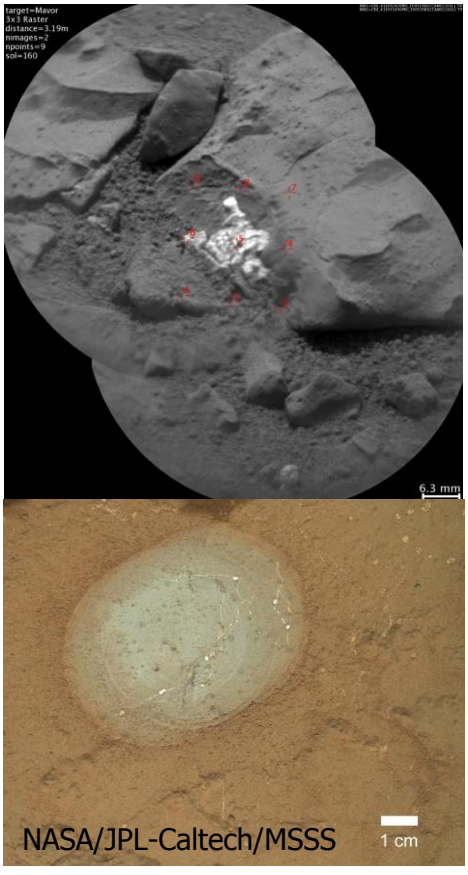

Figure 1. (Top) The ChemCam RMI of Mavor depicting the 3x3 raster locations. (Bottom) The MastCam image of the brushed Wernecke sample.

model. All of these spectra were processed as described by Wiens et al. [4].

Peak-Area Multivariate Analysis: All of the calibration spectra used in the new geochemical database were converted into peak-area LIBS spectra. Each spectral peak, independent of the identity of the elements responsible for the peak, was integrated into a single spectral feature.

These peak-area spectra were used to generate three overlapping PLS1 sub-models. Pure calcium sulfate veins would contain between 46.5 and 58.8 wt. % SO_3 for gypsum ($CaSO_4 \cdot 2H_2O$) and anhydrite ($CaSO_4$), respectively. Consequently, the "high" SO_3 model covers 30 – 100 wt. %. The "low" model covers 0 – 10 wt. % and represents most of the rocks and soils probed by ChemCam. The "medium" model covers the compositions between these two extremes, 5 – 40 wt. %. Finally, seamless transitions between these three overlapping models were defined as described by Anderson et al. Specifically, the low-to-medium transition covered the 5 – 10 SO_3 wt.% and the medium-to-high transition covers the 30 – 40 SO_3 wt.%.

Discussion:

Mavor: ChemCam completed a 3x3 raster of the Mavor sample as documented by the RMI in Figure 1. The RMI and resulting ChemCam chemical composition indicates that locations 5 and 6 were primarily from the calcium sulfate vein while the remaining seven locations probed the host rock. Table 1 compares the SO_3 compositions recorded by ChemCam and APXS. The ChemCam analysis of Mavor 5 and 6 suggest that these samples are representative of gypsum and bassanite. The presence the H emission in the LIBS spectrum (not shown) suggests that the sample vein is hydrated. The CaO compositions listed in Table 1 for these two locations are similar to that of pure gypsum (32.6 wt. %) and bassanite (38.6 wt. %). However, the ChemCam SO_3 compositions are between that for pure gypsum (46.5 wt. %) and bassanite (55.2 wt. %). The ChemCam chemical analysis and RMI indicate that ChemCam also sampled some non-sulfate material that is likely soil or dust. The presence of this material is likely responsible for the departure from pure compositions noted above. The presence of this material and the size of the sensor is also likely responsible for the low SO_3 composition reported by APXS compared to the ChemCam compositions and the assumed calcium sulfate chemistry.

Table 1. SO_3 compositions for CCAM Mavor locations 5 and 6 and APXS in oxide wt. %. The precision of the measurement is in parentheses.

Sample	CCAM		APXS	
	CaO	SO_3	CaO	SO_3
Mavor, 5	32.2	48.6 (1.2)	18.41	27.99 (0.47)
Mavor, 6	38.3	50.3 (1.2)		

Wernecke: The Wernecke observations provide another test of this new ChemCam SO_3 calibration model. Wernecke is a typical Sheepbed mudstone surface (Fig. 1); it was analyzed by APXS once before it was brushed and twice after it was brushed. ChemCam completed two 3x3 rasters. Table 2 summarizes the results from both ChemCam and APXS and shows that the ChemCam compositions including SO_3 are in excellent agreement with the APXS compositions after brushing. ChemCam reports slightly higher compositions for Al_2O_3 and slightly lower compositions for MgO. The ChemCam SO_3 compositions are slightly higher than the post-brush APXS analyses. The pre-brush APXS SO_3 composition is strikingly high compared to the underlying rock, suggesting the dust is significantly enriched in SO_3.

References: [1] Nachon et al. J. Geophys. Res. Planets, doi:10.1002/2013JE004588. [2] Clegg et al. Spectrochimica Acta B, 2017, in press. [3] Anderson et al. Spectrochimica Acta B, 2017, in press. [4] Wiens et al. Spectrochimica Acta B, 2013, 82, 1-17.

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Table 2. CCAM and APXS analyses of Wernecke in oxide wt%. The precision of the measurement is in parentheses. The ChemCam data represents the average composition from each 3x3 raster.

Instrument, sol	SiO_2	TiO_2	Al_2O_3	FeOT	MgO	CaO	Na_2O	K_2O	SO_3	Total
CCAM, 172 Brushed	48.9 (0.7)	0.97 (0.05)	11.4 (0.8)	18.4 (0.4)	7.74 (0.34)	5.61 (0.26)	3.38 (0.14)	0.74 (0.06)	1.24 (0.16)	98.4
CCAM, 183 Brushed	48.0 (0.5)	1.00 (0.07)	10.6 (0.6)	19.1 (0.5)	8.20 (0.24)	5.48 (0.52)	3.24 (0.09)	0.70 (0.06)	1.18 (0.06)	97.5
APXS, 168 Pre-Brush	43.31 (0.54)	0.95 (0.03)	8.41 (0.19)	20.59 (0.26)	8.61 (0.25)	6.04 (0.07)	2.66 (0.14)	0.56 (0.02)	5.65 (0.08)	96.78
APXS, 169 Brushed	46.88 (0.54)	0.91 (0.03)	8.88 (0.19)	20.50 (0.26)	9.8 (0.25)	5.4 (0.06)	3.04 (0.14)	0.62 (0.02)	0.89 (0.03)	96.92
APXS, 173 Brushed	47.57 (0.54)	0.91 (0.03)	8.90 (0.19)	19.69 (0.26)	9.76 (0.25)	5.32 (0.06)	2.98 (0.14)	0.69 (0.02)	1.04 (0.03)	96.86