

CHEMCAM SULFUR QUANTITATIVE ANALYSIS OF THE ASKIVAL ALTERED FELDSPATHIC CUMULATE TARGET, GALE CRATER, MARS. S.M. Clegg¹, R.B. Anderson², W. Rapin³, B.L. Ehlmann³, D.E. Anderson³, N.H. Thomas³, P. Gasda¹, J. Frydenvang⁴, O. Forni⁵, H. Newsom⁶, D. Blaney⁷, W. Goetz⁸, S. Maurice⁵, R.C. Wiens¹, ¹Los Alamos National Laboratory, Los Alamos, NM, sclegg@lanl.gov, ²USGS, Flagstaff, AZ, ³California Institute of Technology, Pasadena, CA, ⁴Univ. of Copenhagen, Copenhagen, Denmark, ⁵Institut de Recherches en Astrophysique et Planétologie, Toulouse, France, ⁶University of New Mexico, Albuquerque, NM, ⁷Jet Propulsion Laboratory, Pasadena, CA, ⁸Max-Planck-Institut für Sonnensystemforschung, Göttingen, Germany.

Introduction: The Curiosity rover has encountered many forms of sulfur including calcium sulfate veins [1], and hydrated magnesium sulfates [2] along the traverse through Gale crater. The chemistry and mineralogy of these sulfur-containing species have been primarily documented by the APXS, SAM and ChemMin instruments [3]. A ChemCam multivariate analysis method along with an expanded calibration database has enabled quantitative SO_3 analysis by remote Laser-Induced Breakdown Spectroscopy (LIBS). In this paper, variable SO_3 compositions from the chemically heterogeneous Askival target (ccam03015, sol 2015) are examined. Shown in Figure 1, Askival is a hydrothermally altered feldspathic cumulate [4].

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) [5]. 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

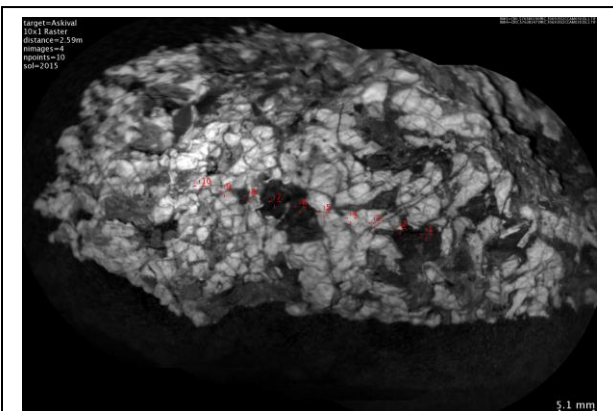


Figure 1: The remote micro-image of Askival from a 2.95 m standoff distance.

peaks tend to dominate the analysis.

This SO_3 model involves the conversion of the ChemCam LIBS spectrum into a peak-area spectrum 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 Askival location #2, the location with the highest

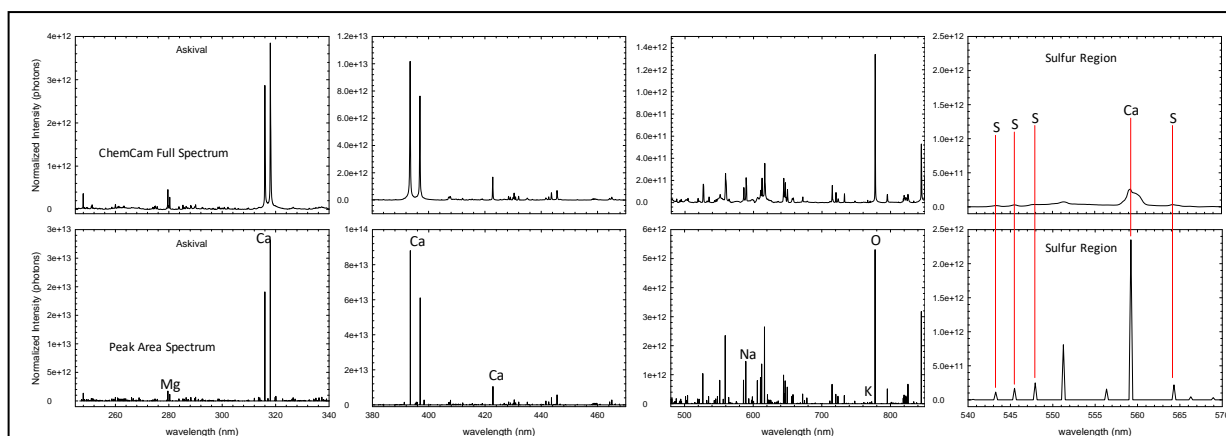


Figure 2: Sulfur compositions are extracted from ChemCam spectra (top) converted into peak area spectra (bottom) by partial least squares analysis. This figure focuses on Askival location #2 where the CaSO_4 composition is the highest among the 10 locations probed. The spectra to the right end of the figure highlight the ChemCam sulfur spectral region. The y-axes in both the standard ChemCam data (top right) and peak area processed ChemCam data (bottom right) are identical. The peak area processed data produce a significant enhancement relative to the standard ChemCam data.

SO₃ composition. 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.

The PLS1 sub-model analysis developed by Anderson et al. is used to segregate the sulfur calibration into three geologically relevant models [6, 7]. The sulfur model used to analyze samples on Mars is the integration of the PLS1 sub-model technique using the peak-area calibration spectra.

Laboratory Calibration: 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 [5]. A series of doped samples containing various mixtures of CaSO₄, MgSO₄, and Fe₂(SO₄)₃ with either BHVO2 or K1919 were added to the database [8-10]. All spectra were processed as described by Wiens et al. [11] and then converted into peak-area spectra.

Multivariate Analysis: Following [6], three overlapping PLS1 sub-models were generated with these peak-area spectra. The “high” SO₃ model covers 30 – 100 wt. %. The “low” model covers 0 – 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. [6].

Discussion: ChemCam analysis of the Askival target documents a chemically heterogeneous target. Quantitative SO₃ compositions were extracted from seven of the ten locations probed. Locations 1, 2, and 8 contained elevated SO₃ compositions that coincide with elevated CaO suggesting the presence of CaSO₄.

All remaining locations analyzed by LIBS contain < 2 wt. % SO₃. Locations 3-5, 9 and 10 are light-toned materials as depicted in the RMI and contain elevated SiO₂ (< 63 wt. %). Locations 4, 5 and 10 do not contain quantifiable SO₃ compositions using this analysis method. Finally, locations 6 and 7 are dark-toned materials that contain < 2 wt. % SO₃.

The APXS instrument also analyzed the Askival target three times and obtained SO₃ compositions that are in agreement with the average ChemCam SO₃ composition. The APXS compositions for the three analyses were 7.65 ± 0.25 , 9.72 ± 0.1 , and 9.8 ± 0.28 wt. % SO₃. The average ChemCam SO₃ composition is 10.44 wt. %.

Conclusion: The Askival target analysed by ChemCam on sols 2015-2020 is a chemically heterogeneous target. This target proved to be an interesting target to further test ChemCam SO₃ quantitative analysis using the peak-area PLS method. A single multivariate ChemCam model extracted SO₃ compositions from seven of the ten locations analyzed while the remaining three locations were below the quantitative limit of this model. Four of the seven locations contained low SO₃ compositions (< 2 wt. %). Finally, the same model extracted relatively high SO₃ compositions for the three locations that appeared to contain elevated CaSO₄ even though a discrete vein is not observed in the RMI image.

References: [1] Nachon et al. J. Geophys. Res. Planets, doi:10.1002/2013JE004588, [2] Rapin et al. 2018 LPSC Abstract, [3] Vaniman et al, 2018 American Mineralogist, doi:10.2138/am-2018-6346, [4] Bridges et al. 2019 LPSC (this conference), [5] Clegg et al. Spectrochimica Acta B, 129 (2017) 64–85, [6] Anderson et al. Spectrochimica Acta B, 129 (2017) 49–57, [7] Anderson et al. 3rd Planetary Data Workshop, abst. 7061, 2017. [8] Clegg et al. 2017 LPSC Abstract #2037, [9] Clegg et al. 2017 AGU Abstract P31A-2796, [10] Anderson JGR Planets, 2017, 122, 744–770, [11] Wiens et al. Spectrochimica Acta B, 2013, 82, 1-17.

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