

SULFUR OBSERVATIONS AND ANALYSIS BY APXS AND CHEMCAM IN GALE CRATER, MARS. V.

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Introduction: Sulfur detection and quantification carries significant implications for understanding the igneous and fluvial history on Mars. Sulfur is a major component of surface materials, as discovered by several instruments on multiple missions. In Gale Crater, S often occurs as Ca-sulfates in light-toned veins, Mg-sulfate nodules, in the matrix of bedrock, and in unconsolidated soil, sand and dust. Concentrations of SO₃ range widely from 0.6 to 45 wt%. The MSL Rover has two complimentary instruments that measure elemental compositions, the Alpha Particle X-ray Spectrometer (APXS) and the Chemistry-Camera (ChemCam). This paper discusses the detection and quantification of S on Mars by these two devices.

Methods: APXS and ChemCam use notably different methods and have vastly different sample sizes. The APXS has a field of view (FOV) of ~2cm in diameter and uses x-ray spectroscopy for identification and quantification of 16 elements, for all samples [1]. ChemCam uses Laser Induced Breakdown Spectroscopy (LIBS) to ablate, in multiple shots, a small portion (350-500 μm shot diameter) and detects emitted photons [2]. Essentially all APXS targeted areas are also measured by ChemCam, which allows for a unique opportunity to correlate and contrast results. Comparing the data from both instruments can lead to new insights, aiding in authenticating data trends and geological appraisals. Fig 1 shows a visual comparison of this difference for Mavor, a Ca-sulfate enriched target analyzed by both instruments. The APXS averages over the FOV, while the ChemCam measures multiple locations in the target area, with numerous shots per spot. The sizeable target count and high spatial resolution of the ChemCam make it an ideal candidate for analyzing narrow features.

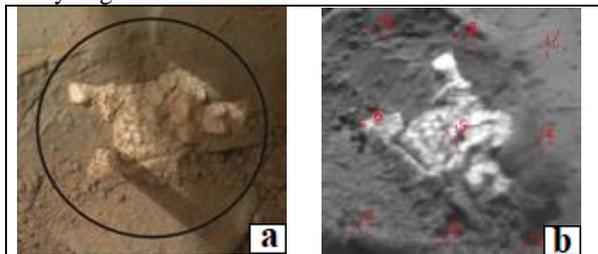


Fig. 1: Measurements on Mavor a) APXS (1.7cm FOV as indicated by circle) b) ChemCam (shots ~6.3 mm apart)

Sulfur Signal: Portions of the spectra of both APXS and ChemCam are shown in Fig. 2. The APXS spectra are from two targets analyzed during the mission that display contrasting S detections. Mavor is

highly enriched, and Wernecke is one of the lowest S values measured on Mars. The discrepancy is emphasized by the difference in signal at the labeled S peak, note the logarithmic scale. These two targets were also discussed by Clegg et al. 2017 [3]. In contrast, the distinction is less clear for the S peaks in ChemCam spectra, demonstrated in Fig. 2b with lab samples of pure gypsum, basalt and a 50/50 mixture [4]. Due to the high activation energy of S, a much dimmer LIBS emission line is produced [5]. Traditionally studied S lines are outside the ChemCam's spectrometer range, resulting in the use of lines in an unfavorably "busy" area, with several interferences and limited signal to noise ratio [5].

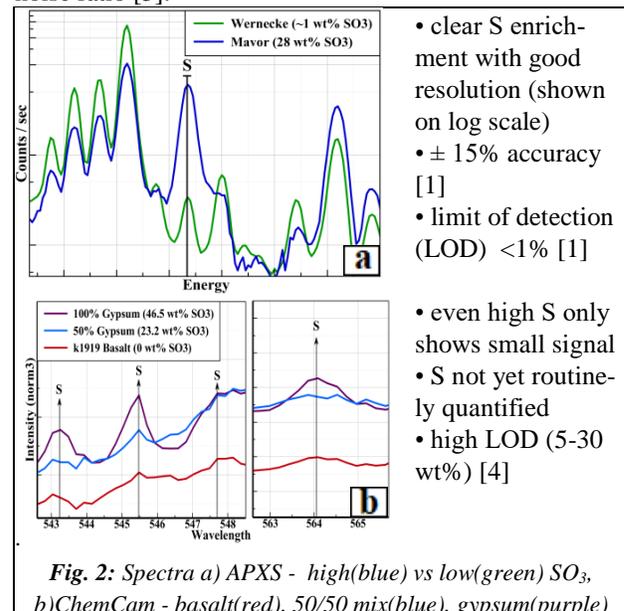


Fig. 2: Spectra a) APXS - high(blue) vs low(green) SO₃, b) ChemCam - basalt(red), 50/50 mix(blue), gypsum(purple)

Analysis: Sulfur is one of the 16 standard elements quantified by the APXS with high accuracy and precision, and low detection limits[1]. One limitation impacting S accuracy is when large S-mineral grains, e.g. Pyrite, are mixed in, resulting in matrix corrections differing significantly from sulfates. Volumetric addition of CaSO₄ or other sulfates have much less impact.

Due to the difficulty in constraining S through LIBS, quantification is not routinely reported by ChemCam. Several studies, both prior to and amid the mission phase have discussed various approaches for quantification. In this work we investigated the outcome of the multiple documented approaches. In order to quantify the sulfur signal we developed and tested various methods for peak area analysis. The suitability

of the 4 S emission lines indicated in Fig. 2b were assessed through evaluating spectra from terrestrial calibration data, on-board calibration targets, various martian samples from the PDS, and a collection of salt mixtures from [4]. The S 564nm line appeared to be the most robust and representative peak for the tested sample suite, as the other lines showed increased interference. This finding agrees with Dyar et al. 2011 [6], however is repudiated in [4] and [7], which favor the other S lines shown in Fig. 2b.

Peak Analysis Method: Typical univariate LIBS analysis involves extracting a normalized peak area to calculate elemental abundance. This procedure, outlined in [7], uses a Levenberg-Marquardt (LM) least-squares optimization with a Lorentzian curve. Here, this process was reproduced with a commercial GUI, *MagicPlotPro*, that fits a Lorentzian peak on a local linear background with a LM fitting algorithm. In addition to this, a simple summation technique was applied to the same datasets. This method involves using the height of the channels that border the peak as a baseline to subtract from the summed area. A visualization of these two techniques is shown in Fig. 3a. The original peak is represented in green, the automated fit produces the blue curve after the subtraction of the blue dotted line. The summation is performed between the two solid black lines, removing the background based on the height of the points between the dotted and solid lines, producing a sum represented by the red bars. Results of both approaches agree well for the S 564nm line as seen in a plot of the peak areas found by the automated fit vs those found through the summation, as seen in Fig. 3b.

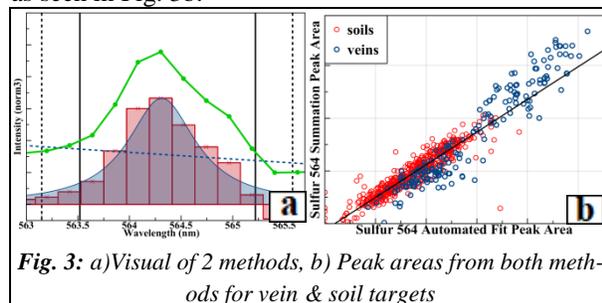


Fig. 3: a) Visual of 2 methods, b) Peak areas from both methods for vein & soil targets

Results & Discussion: The good correlation of the S 564nm peak areas in Fig. 3b led us to use the simple summation. This also bypasses the need to define an error for each channel, which is necessary for an LM-fit procedure. The results for the other 3 lines indicate that these peaks are less robust and likely overlapped by other emission lines or a high background, increasing the uncertainty. This could be a consequence of the predominance of CaSO_4 in Gale Crater and would likely change if other sulfates, such as Fe-sulfates come into play.

To check the correlation between peak area and abundance, we chose two groups of Martian target types, soils and bedrock with light-toned veins (Fig 4b). The APXS identified an average SO_3 in soils of ~6 wt% and reveals a close to ideal $\text{CaO}:\text{SO}_3$ molar ratio for bedrock. For ChemCam, the S peak area of soils and bedrock with light-toned veins was plotted against the ChemCam CaO wt%. Significantly more scatter for the high CaO values and soils indicates large uncertainties in S quantification by this univariate approach, and a higher LOD for S by ChemCam. Soils likely suffer from interferences by Fe, rendering the simplified approach invalid. Nevertheless, uncertainties will increase even if background peaks are accounted for.

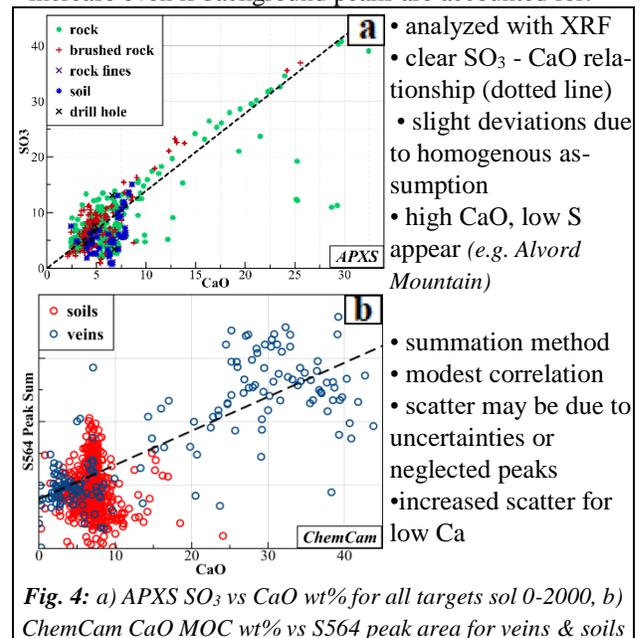


Fig. 4: a) APXS SO_3 vs CaO wt% for all targets sol 0-2000, b) ChemCam CaO MOC wt% vs S564 peak area for veins & soils

Summary:

- LIBS can detect S in much smaller spots, but has higher detection limits and uncertainties
- For this dataset, summing over a peak area with a baseline removal revealed equivalent results as a complicated fit. S 564nm was identified as the most suitable characteristic peak
- APXS can measure S with high precision, although on a larger FOV

References: [1] Gellert, Clark, (2015) *Elements*, 11(1). [2] Wiens R.C. et al. (2012) *Space Sci. Rev.*, 170, 167–227. [3] Clegg et al. 2017 LPSC Abstract #2037 [4] Anderson D. E. et al. (2017) *JGR*, 122(4), 744–770. [5] Nachon M. et al. (2014) *JGR*, 119(9), 1991–2016. [7] Dyar, M. D. et al. (2011) *Spectrochimica Acta B*, 66, 39–56. [8] Cousin A. et al. (2011) *Spectrochimica Acta B*, 66(11–12), 805–814.

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