

IDENTIFICATION AND IMPLICATIONS OF IRON DETECTION WITHIN CALCIUM SULFATE MINERALIZED VEINS BY CHEMCAM AT GALE CRATER, MARS.

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Introduction: Diagenetic mineralized veins have been consistently observed along the Curiosity rover traverse [1,2,3], starting at Yellowknife Bay shortly after landing. Among these features, light-toned veins – primarily composed of Ca-sulfate (bassanite) [4] – are pervasive to all units and cross-cut other diagenetic features [5], thus hinting at a regional late-stage episode of fluid circulation.

Detailed chemistry is helpful in determining the nature of the diagenetic fluids occurring at the time of deposition. Such veins therefore provide insights into the diagenetic history of the sedimentary deposits during their burial.

Data processing: All data used in this study were collected by Chemcam [6], the Mars Science Laboratory (MSL) Laser Induced Breakdown Spectroscopy instrument, and the associated Remote Micro-Imager (RMI). Chemical quantifications for major elements are obtained using an updated multivariate analysis technique [7].

Chemistry: Recent observations on light-toned veins within the Murray formation show local detections of FeO_T (5-10 wt%), associated with low-to-no SiO₂ abundance, alongside the expected high CaO abundance and S emission peaks in LIBS spectra. Observations of mixed composition between the surrounding host rock and diagenetic features are not uncommon with ChemCam, because the LIBS laser spot is up to 500 μm in size. It is thus frequent to sample material from both lithologies (such as bulk rock silicate minerals and calcium sulfate in veins) if the LIBS point is located at the interface. However, shot-to-shot analysis of the LIBS data shows that FeO_T is detected in the same abundance within the bulk of the point after removal of the dust cover (first 5 laser shots), unlike SiO₂ whose abundance decreases toward zero after the first shots (Figure 1). This observation shows that iron is not associated with the silicate minerals of the host rock, and indicates a chemical composition that deviates from the 'Host rock – Ca-sulfate' mixing compositions seen so far.

Nevertheless, quantification of major elements in these diagenetic facies come with some uncertainties,

as such marginal chemical composition are not necessarily represented in the ChemCam calibrations dataset. Thus, in order to confirm these FeO_T-detections which are not correlated with SiO₂, we need to delve into LIBS spectra to compare the intensity of the iron and silica peaks, and their ratio.

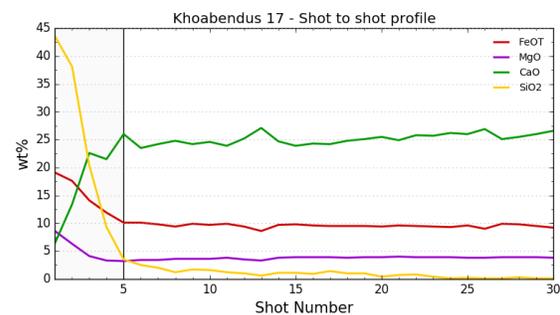


Figure 1: shot-to-shot analysis of the LIBS point 17 of the Khoabendus Chemcam target (sol 1380). The vertical line indicates that surface dust has been removed by shot #5.

Spectral analysis: A thorough investigation of the LIBS spectra of every light-toned vein observed so far by ChemCam has been conducted in order to distinguish the individual Fe detections from host rock contributions. This selection was made based on the ratio of maximum intensity between Fe (260.017 and 275.655 nm) and Si (288.242 nm) peaks deviating significantly from typical host rock ratios. A subset of light-toned veins has thus been identified (Figure 2), mainly in the last ~400 sols of the mission.

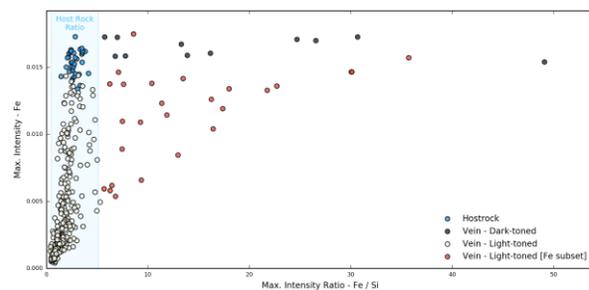


Figure 2: maximum intensity plot (Fe/Si ratio – Fe) showing the identified light-toned vein subset.

Quantification of CaO and FeO_T content in these features show that some Fe-rich light-toned vein points

tend to plot along the 'Fe-oxide – Bassanite' mixing line, suggesting that at least some of these detections may be linked to a Fe-oxide phase (Figure 3). However, a single phase cannot be implied for all of these Fe occurrences, which may in turn hint at the presence of multiple Fe-rich phases in these targets.

In addition, ChemCam recently observed darker-toned material associated with light-toned veins which display very high FeO_T abundances (Figure 3, up to ~45 wt%), associated with high MnO [8]. This metal assemblage points toward an oxide component, perhaps magnetite as passive spectra analysis suggests. These observations may be linked to the more diffuse iron detections observed within the light-toned veins and would thus support the oxide phase interpretation.

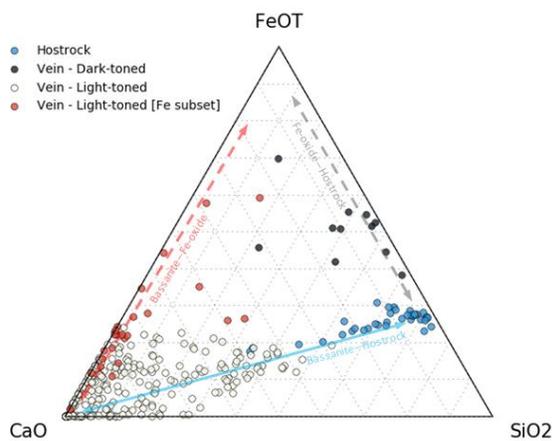


Figure 3: $\text{CaO}/\text{FeO}_T/\text{SiO}_2$ ternary diagram (normalized wt%), illustrating the 'Bassanite – Host rock', 'Bassanite – Fe-oxide' and 'Fe-oxide – Host rock' mixing lines.

Texture: Fe-rich light-toned veins are often associated with a branched texture and 'dirty' aspect (i.e. displaying darker areas within the vein), as opposed to the massive texture and 'pristine' aspect of the pure Ca-sulfate veins (Figure 4). These detections are also heterogeneous within the light-toned veins, with several LIBS points showing the Fe-rich signature, whereas neighboring points display a typical Ca-sulfate signature. These observations highlight a chemical heterogeneity within the identified subset of light-toned veins.

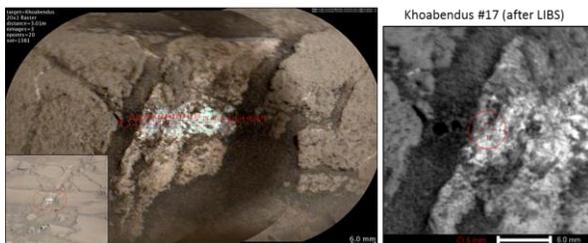


Figure 4: Khoabendus target (ccam03380) presenting Fe detections on points 17 (zoomed in).

Interpretation and discussion: At this stage, identification of the Fe-bearing mineral phase(s) proves to be rather difficult. Although the iron is likely present within a non-silicate phase, discriminating between either sulfates, oxides or other Fe-rich minerals solely based on Chemcam data is challenging due to the fact that potential diagnostic elements such as Ti, Mn and other metallic minors and trace elements are often either below detection limit or poorly constrained for the amount of Fe detected. Additional information from CheMin and APXS instruments, and recent calibration efforts for minor elements with ChemCam could help to better constrain the chemistry of these Fe-phases and identify their mineralogy. At present and based on ChemCam observations, an Fe-oxide phase seems to account for at least some of these detections, but other phases such as Fe-sulfates may also be present, and cannot be discarded without further studies.

The presence of Fe in recent Ca-sulfate veins sheds new light on our understanding of late diagenesis events occurring in Gale crater. Heterogeneities within the veins seemingly unrelated to the average local host rock composition, indicates a complex deposition process with lateral and horizontal variations, potentially linked to the fluid chemistry.

The observed changes in light-toned vein chemistry may be influenced by the nearing proximity of the hematite ridge [9] and the sulfate layers observed from orbit [10] farther up the slopes of Mount Sharp, as the rover continues its ascension. Fe-sulfates would indicate an authigenic origin probably linked with a more acidic diagenetic fluid composition. Fe-oxides could point toward an oxidizing and acidic environment or instead, toward reducing conditions depending on the oxidation state (Fe^{3+} and Fe^{2+} respectively) of the iron during its transport within the fluids.

Further on-going work within the MSL team with respect to vein texture and relationships with other diagenetic features and their distribution within the local stratigraphy will provide more information to better constrain the settings linked to the emplacement of these veins.

References: [1] Nachon, M. et al. (2014), *JGR Planets*, 119, 1991–2016. [2] Nachon, M. et al. (2016), *Icarus*, 281, 121. [3] L veill , R. J., et al. (2014), *JGR Planets*, 119, 2398–2415. [4] Rapin W., et al. (2015), *submitted*. [5] Kronyak, R. et al. (2015), *AGU abstract*. [6] Wiens, R.C., et al. & Maurice, S. et al. (2012), *Space Sci. Rev.*, 170. [7] Clegg et al. (2017) *SCAB*, *accepted*. [8] Forni, O. et al. (2017), LPSC (this meeting). [9] Fraeman, A. et al. (2016), *Fall AGU, San Francisco*. [10] Anderson, R. et al. (2010), *Mars J.*, 5, 76–128.