

LABORATORY ANALYSES OF HEMATITE-RICH MARTIAN ANALOGUES: IMPLICATIONS FOR CHEMCAM DATA AT VERA RUBIN RIDGE. G. David¹, A. Cousin¹, O. Forni¹, P-Y. Meslin¹, E. Dehouck², J. Frydenvang³, A. Fraeman⁴, P. Beck⁵, J. Johnson⁶, R. C. Wiens³, O. Gasnault¹, S. Maurice¹, J. Lasue¹, J. L'Haridon⁷, J. F. Fronton⁸. ¹Institut de Recherches en Astrophysique et Planétologie, Toulouse, France, ²LGL, Lyon, France, ³LANL, Los Alamos, USA, ⁴CIT, Pasadena, USA, ⁵IPAG, Grenoble, France, ⁶APL-JHU, Laurel, USA, ⁷LPGN, Nantes, France, ⁸CNES, Toulouse, France ; [gael.david@irap.omp.eu]

Introduction: Curiosity, the Mars Science Laboratory (MSL) rover, has been investigating Gale crater since August 2012. Its landing area was chosen partly because of its proximity to important spectral signatures from orbital remote sensing with the CRISM instrument on the Mars Reconnaissance Orbiter, including phyllosilicates, sulfates and iron oxide [1, 2]. Curiosity reached the Vera Rubin Ridge (VRR), on sol ~1800 of the mission where an orbital hematite (Fe_2O_3) signature was especially noticeable. The Rover is equipped with 2 remote science instruments: the Mastcam imager and the Chemcam instrument. Mastcam multispectral data as well as ChemCam passive VNIR reflectance spectra confirmed the hematite signature in VRR fractures [3, 4] from some distances. As seen from orbit, this unit is a ~200 m wide and ~6.5 km long distinct topographic and textural sedimentary feature, located on the lower slopes of Mount Sharp. The ridge has higher thermal inertia and is more resistant than the adjoining Murray formation, where hematite minerals were identified by X-ray diffraction measurement with the CheMin instrument [5]. But Murray, unlike VRR, shows only patchy and weak iron oxide signature from orbit [6]. The similarity between the bedding orientation measurement within the ridge and the strata above implies that the ridge strata are part of the original Mount Sharp stratigraphic sequence [7]. No stratigraphic contact between the two units was observed, which suggests continuity between the VRR and the Murray formation. In situ chemical and mineralogical investigation of the iron oxide-enriched ridge would help us understand its primary or secondary geologic deposition processes. More generally, the hematite-bearing ridge is located stratigraphically below the phyllosilicate and the sulfate units, which were thought to have been emplaced during periods of global-scale environmental changes. Constraining these different formation processes would improve our understanding of Gale's history as well as early Mars in general.

Motivation: Despite the hematite spectral signature observed from orbit or with passive spectroscopy, elemental chemistry measured with the Alpha Particle X-Ray Spectrometer surprisingly shows no significant Fe enrichment in the VRR terrain compared to the previous unit [8]. The ChemCam Laser Induced-Breakdown Spectrometer [9, 10], which mostly targeted a different set of rocks, shows a modest [11, 12], but statistically significant iron trend, as shown in the Fig. 1 in terms of ICA scores.

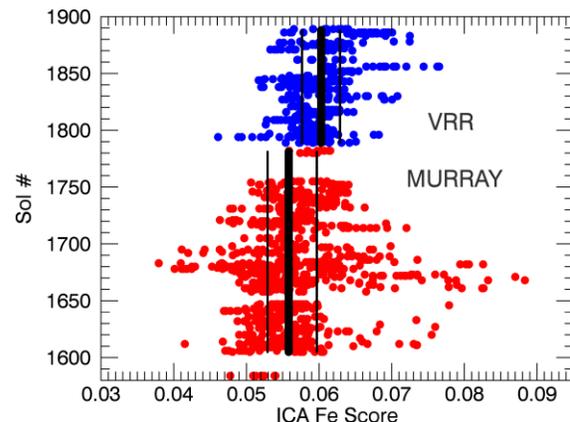


Figure 1: ICA Fe Scores of the Murray unit (since Sutton Island [13]) and the Vera Rubin Ridge bedrocks (until sol 1889). See detail for ICA in the Methods section. All spectra of calcium sulfate veins were removed. Median and lower and upper quartiles were also showed (black lines).

In this work, we explore the sensitivity of the ChemCam instrument to various iron abundances added to a basaltic matrix in order to better understand the ICA Fe scores variations in VRR. For this purpose, we investigate the iron signal of martian analogues doped with hematite to varying degrees with a laboratory setup similar to ChemCam. Laboratory observations will be then compared to the Curiosity data from the VRR.

Method: We have prepared mechanical mixtures of powders (grain size < 50 μm) between nearly pure hematite (98 wt% pristine) and basaltic BHVO-2 [14] matrix at different concentrations (0.5, 1, 2, 3, 5, 10, 15, 20, 50, 75 wt%). This basaltic martian analogue contains 12.3 wt% $\text{Fe}_2\text{O}_{3\text{tot}}$, originating from the pahoehoe lava that overflowed from the Halemaumau crater, in Hawaii. This material including only pyroxene and plagioclase [14,15], have lower iron content than any of the Gale sediments. Mixtures were compacted under 10 tons of pressure to have indurated pressed pellets hard enough to be analyzed by a LIBS beam. Their homogeneity was checked visually with binocular microscope images. LIBS analyses were done at the Institut de Recherche en Astrophysique et Planétologie (IRAP, Toulouse) with the ChemCam EQM (Engineering Qualification Model), which is very similar to the flight model. Samples are placed in a martian chamber, allowing similar martian conditions in terms of atmospheric pres-

sure (~7mbar) and composition (mostly CO₂, plus 1.6 % Ar and 2.7% N). Each pellet was probed on 5 locations with 30 shots each. The spectra obtained have been processed in the same way as the ChemCam data from Mars, except for the instrument response function [10]. The first 5 shots of each measurement were also removed. Independent Component Analysis [16] is one of the two multivariate data techniques used to quantify the ChemCam data [17]. ICA is a blind source separation which allows getting back to pristine signals in a complex signal mixing several sources, where each spectrum is considered to be a linear combination of pure sources. We considered 10 independent components (Si, Ti, Al, Fe, Mg, Ca, Na, K, H and Li). Covariance between unknown spectra and independent components gives an ICA score that reflects the elemental abundances [16]. It allows us to check differences between each spectrum, element per element, and thus to observe chemical changes which can be interpreted in some cases as mineralogical changes.

Preliminary Results: Fig. 2 shows the mean ICA scores per sample (125 shots) for the iron component. Error bars correspond to the standard deviation of the ICA scores, green lines to the confidence bands, and blue lines to the prediction bands (at 95% confidence level).

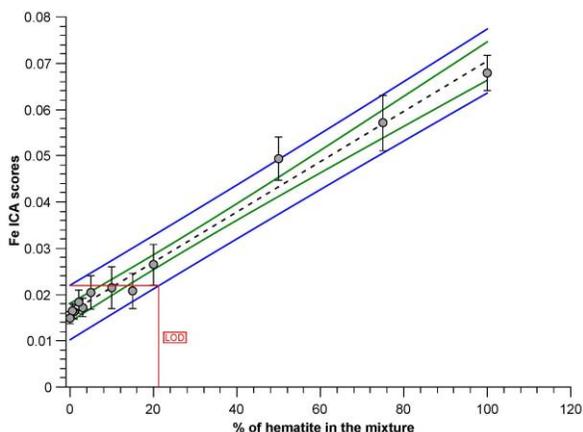


Figure 2: ICA Fe Scores as a function of the concentration of hematite added in the mixture (in wt%). Green lines correspond to the prediction bands (at 95 % confidence level) and the blue lines to the 95 % confidence bands. Limit of detection (LOD) was also plotted. R^2 is 0.98

Laboratory results show, to first order, a linear correlation between ICA Fe scores and increasing hematite concentration. However, the ICA Fe scores show a large dispersion per sample, which complicates the identification between samples with small concentrations differences. Indeed, no clear distinction can be done for low values of added hematite, such as from: 0 wt% hematite up to <5 wt%. Once the mixture contains be-

tween 5 wt% and 15 wt% of added hematite, ICA Fe scores show an increase. However these ICA Fe scores are still within uncertainty of the low values of added hematite. This result is also highlighted by the limit of detection (LOD), which corresponds to ~22 wt% of added hematite (~20 % added FeO). It means that for the analysis of a single martian rock probed with 5 points (as in our experimental conditions), 22 wt% hematite is needed to measure a significant difference (with respect to false negatives and positives). The critical level (or detection threshold at a 97.5 % confidence level) against false positives is 11 wt% of added hematite. However the LOD is expected to improve as the number of rocks analysed is increased. It is also important to mention that ChemCam is sensitive to iron signal and not directly to hematite. It means that an increase of hematite content can be potentially masked by an equivalent drop of other Fe-rich minerals.

Work to come: Our experimental model needs to be refined with additional laboratory data on hematite mixtures with high-Fe basaltic composition. In particular, we are planning to test basaltic materials with Fe contents closer to the concentration seen in Murray (~19 wt% FeO). Exploring a range of matrix with different nature would help to determine if the increase of the ICA Fe scores in VRR is really associated with an increase in FeO or linked to matrix effects, leading to a rise in the iron signal. Constraining if the mineralogy of the Fe-rich phase added can affect the ICA Fe scores will be explored as well. Characterizing the visible and near infrared spectral reflectance of our samples will also help us to understand why ChemCam passive spectra and CRISM are able to see hematite unlike ChemCam chemical measurements. It is a first order approach as our laboratory infrared spectrometer differs from the CRISM instrument (range and spectral resolution), but constraining the range of detection limit of hematite by the 2 methods could enable a better understanding of VRR's composition and formation processes.

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