

# COMPARISON OF THE IRON-MANGANESE RATIO DISPERSION IN MARTIAN SOILS WITH THE MARS SCIENCE LABORATORY APXS AND CHEMCAM. B. Wilhelm<sup>1</sup>, R. Gellert<sup>1</sup>, V. Flood<sup>1</sup>, S. VanBommel<sup>2</sup>, and J. Hanania<sup>1</sup>, <sup>1</sup>University of Guelph, Guelph, ON, <sup>2</sup>Washington University in St. Louis, St. Louis, MO.

**Introduction:** The Alpha Particle X-ray Spectrometer (APXS) onboard the Mars Science Laboratory (MSL) rover *Curiosity* uses a combination of Particle-Induced X-ray Emission (PIXE) and X-ray Fluorescence (XRF) to determine the abundance of Fe and Mn with high precision and accuracy (<10%) [1]. *Curiosity*'s payload also includes the ChemCam laser-induced breakdown spectroscopy (LIBS) instrument [2], where photons emitted by a pulsed plasma are detected wavelength dispersive with three spectrometers ranging from the ultraviolet to near infra-red, detecting element specific emissions for quantification of Fe and Mn.

Both instruments detect and quantify Fe and Mn, two undoubtedly significant geochemical elements, but on a vastly different volume scale and with very different methods. Each instrument and method have their advantages and disadvantages.

In this work we use ChemCam spectra and try to understand and partially reproduce the analysis presented by the ChemCam team in dedicated papers [3]. This work is done to get a better idea of the analysis and related uncertainties and the possible impact of matrix effects. We compare our preliminary results with published Mn peak areas and apply simple consistency checks comparing the wealth of ChemCam data available in the raw data set with trends we see in published APXS data using the Fe:Mn ratio.

**Methods:** The APXS measures a sample of ~20mm diameter with element specific information depths ranging from 2-5  $\mu\text{m}$  for low z elements to ~50  $\mu\text{m}$  for high z elements like Fe and Mn. A homogeneous sample is assumed to correct for XRF matrix effects, which limits the accuracy to ~10% for Fe and Mn. To date the MSL APXS has measured ~700 samples.

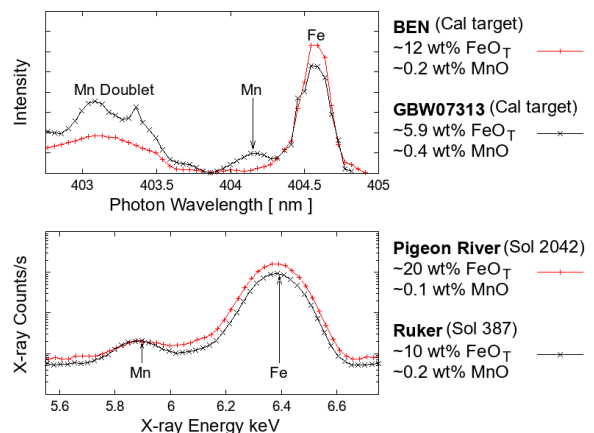
ChemCam measured more than 2500 samples, each with typically 30 shots and 5-10 distinct spots, representing millions of spectra of ~0.5mm spot sized targets that ablate ~1-3 $\mu\text{m}$  per shot. Analysis is done using multivariate methods for major elements [4] and typically univariate (peak area) approaches for minor or trace elements like Mn [3].

**Motivation:** Mn is undoubtedly a geochemically important element. The APXS with its large sample volume has significant limitations when the Mn minerals are distributed in millimeter sized grains and heterogeneous in depth. However, anomalous high APXS MnO concentrations like in Jones Marsh with ~4%, more than 10 times above the surrounding Mur-

ray bedrock, where the APXS homogeneous assumption works well, coincide with localized, very high Mn quantifications by ChemCam. Mitigations for this APXS limitation are rasters, covering different parts of the sample, like done on Stephen, where good correlations of Mn with Cu, Ni and Zn were used as evidence for certain Mn minerals [5].

The ultimate goal of this work is to try to use ChemCam point data to compare against the APXS large volume data for homogeneous samples and to possibly use ChemCam derived minerals for APXS modelling without the homogeneous assumption. Work like this will also be important in case MSL will ever encounter Mn enriched features big enough to drill ~5cm<sup>3</sup> sample for in detail analysis with CheMin and SAM.

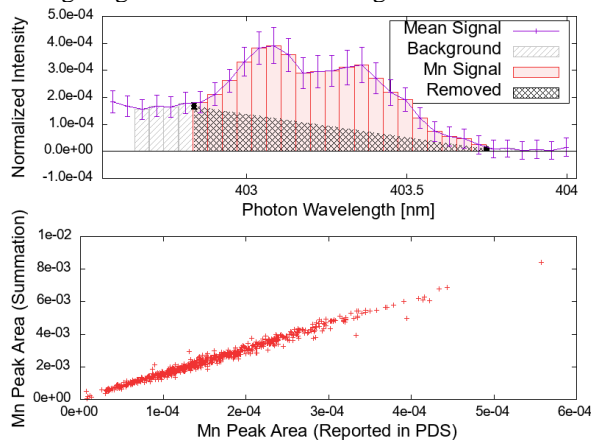
**Data Sets and Analysis:** Peak areas of the characteristic X-ray lines in APXS spectra increase linearly with abundance, adjusted for an assumed homogeneous matrix accounting for matrix effects. Figure 1 (bottom) captures Fe and Mn peaks in Mars spectra. The Fe and Mn peaks correspond to a weighted-average contribution across the APXS field of view.



**Figure 1:** Spectra from the ChemCam (top, linear plot) and APXS (bottom, semi-log plot) in the energy range relevant to Fe and Mn (relative).

In LIBS spectra, the main Mn lines and a neighboring Fe line are shown in Figure 1(top). In the analysis, 8 major elements are quantified using a multivariate approach with PLS. Fe has an additional empirical ICA correction, indicating significant dependence of the emitted Fe lines from the matrix [4]. Minor elements like Mn are usually quantified by an univariate model where the peak area, normalized to all counts of the spectrometer, is transferred into abundance [3].

For Mn, only a subset of peak areas and no Mn abundances are available on the PDS. Therefore a simple summation approach was developed to quantify the Mn signal, as illustrated in Figure 2 (top). The signal to noise is often low relative to nearby emission lines in the visible spectrometer region, requiring the removal of a linear background determined by the intensity of the neighboring channels. The summation method agrees favorably with Mn area data published in the PDS (Figure 2, bottom). Outliers deviating ~40% indicate that for some samples, additional background or peaks need to be accounted for. We are investigating various methods to flag these cases.



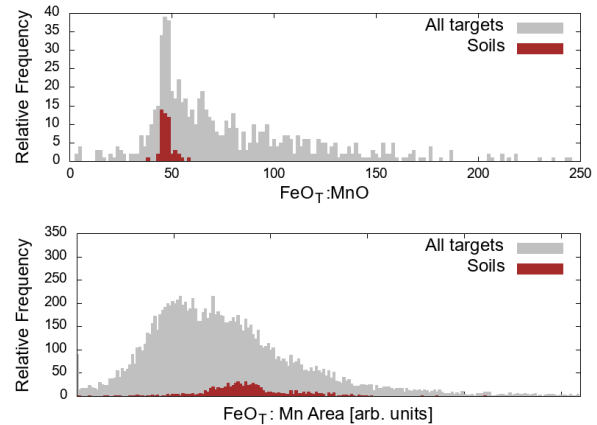
**Figure 2:** Top: Channel summation method of the Mn doublet for the calibration target: GBW07313 (MnO 0.43 wt%). The uncertainties plotted correspond to the standard deviation in each channel over 50 localized shots. Bottom: Comparison of the channel summation method with all peak areas reported in the PDS.

**Fe:Mn ratio:** As a start for a cross comparison of ChemCam and APXS Mn values, we applied the derived peak areas to the Fe:Mn ratio, which is often used by the APXS team to indicate alteration.  $\text{Fe}^{2+}$  and  $\text{Mn}^{2+}$  have similar ionic radii and therefore distribute with a constant Fe:Mn in primary igneous materials of similar composition [6]. Redox alteration often results in a change in Fe:Mn, thus making it an effective indicator of alteration when used appropriately. On Mars, the APXS measured a very consistent Fe:Mn ratio of ~50 in usual soils (red) and a large range for rock targets as captured in Figure 3 (top).

Using the reported  $\text{FeO}_T$  values for all ChemCam targets and the peak area derived for the Mn doublet, we get the values shown in Figure 3 (bottom) with the same color code for rocks and soils. Unsurprisingly, the ChemCam distribution is broader for soil, as it captures a much larger variety of grains, especially for soil where it's known that the shock wave of the laser can disturb soil and sample new grains after each shot.

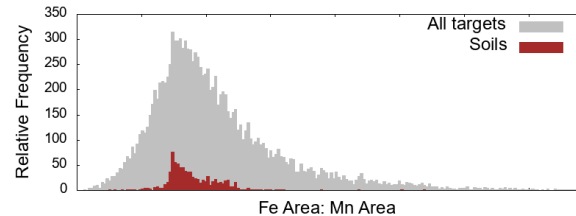
Going one step further, we then used peak area ratios for three isolated Fe peaks at 404.6, 414.5, and 432.7 nm wavelengths, analyzed similar to the Mn area

described above. The distribution of these Fe:Mn values is outlined in Figure 4. The resulting distribution for soils appears to be much narrower than using  $\text{FeO}_T$ , which could indicate dominant mineral(s) that have a constant emission ratio of Fe and Mn lines.



**Figure 3:** Top: Histogram of APXS  $\text{FeO}_T:\text{MnO}$  values. Bottom: Distribution of the ChemCam's reported  $\text{FeO}_T$  values to the normalized Mn peak areas.

The same approach was employed on the first shot of all targets analyzed by the ChemCam instrument and documented on the PDS. The resulting Fe:Mn is even narrower distributed at the value corresponding to soils, possibly sampling a specific Fe and Mn containing mineral in the dust.



**Figure 4:** Distribution of the ratio of peak areas of all isolated Fe and Mn peaks in ChemCam's visible spectrometer.

**Summary:** The Fe:Mn ratio of Martian samples can be a useful value to constrain the extent of chemical alteration [7,8]. We developed a simple method to derive the Mn peak area for ChemCam spectra and found good agreement with published data. We applied this to compare Fe to Mn ratios between data sets and found some interesting trends that seem worthwhile to follow up on.

**References:** [1] Gellert et al., (2015), *Elements*, 11., [2] Wiens R.C. et al., (2013) *Spa. Sci. Rev.* 175, 93, [3] Lanza et al. (2014), *GRL*, 41(16), 5755-5763. 124., [4] Clegg S.M. et al., (2017) *SCAB*, 129, 64. [5] Lanza, N.L. et al. (2016) *GRL* 43, 7398- 7407. [6] Laul J. C. et al. (1972) *LPS III*, Abstract #1176. [7] Yen A. S. et al. (2010) *LPS XLII*, Abstract #2546. [8] Hurowitz et al. (2017) *Science*, 356.

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