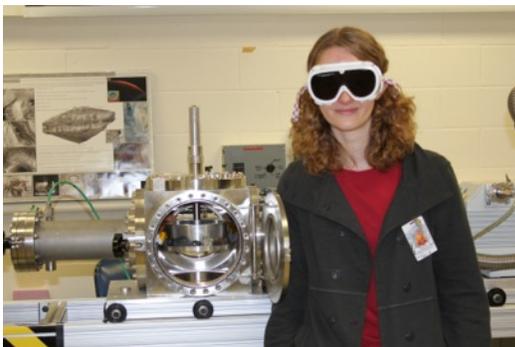


**LASER-INDUCED BREAKDOWN SPECTROSCOPY AS A TOOL TO DIFFERENTIATE COMPOSITIONS OF IRON-BEARING MINERALS.** A. L. Rosen-Gooding<sup>1,3</sup>, A. M. Ollila<sup>2</sup>, S. R. Gordon<sup>3</sup>, H. E. Newsom<sup>3</sup>, A. J. Williams<sup>4</sup>, R. K. Martinez<sup>5</sup>, R. C. Wiens<sup>5</sup>, S. M. Clegg<sup>5</sup>, <sup>1</sup>Albuquerque Academy, Albuquerque, NM ([anayalynn.rg@gmail.com](mailto:anayalynn.rg@gmail.com)), <sup>2</sup>Chevron Energy Technology Company, Houston TX, <sup>3</sup>Inst. of Meteoritics, Univ. of New Mexico, Albuquerque, NM, <sup>4</sup>UC Davis, Davis, CA, <sup>5</sup>Los Alamos National Laboratory, Los Alamos, NM.

**Introduction:** Laser-induced breakdown spectroscopy (LIBS) has been used by the ChemCam instrument to analyze elemental composition of rocks and soils on the martian surface since the landing of the Mars Science Laboratory (MSL) *Curiosity* rover in August 2012 [1,2]. The ChemCam instrument suite's LIBS instrument provides rapid quantitative analysis by ablating the surface of materials from a distance of 1.6-7 m away from the instrument.

The replica of the ChemCam instrument suite located at Los Alamos National Laboratory (LANL), which is identical to the one on MSL, along with a Mars simulation chamber, can be used to analyze and calibrate for situations MSL might encounter throughout its mission [3]. Terrestrial LIBS experimentation has proven beneficial to improving the quality of analyzed ChemCam data as MSL targets a broader compositional range of rocks than expected in pre-mission development of a calibration dataset [4,5]. LIBS analyses return intensities from 6,144 wavelengths in the range of 240.8-905.6 nm, allowing for consideration of all major, minor, and trace elements [4]; however, the proximity of emission lines can create complications in the interpretation of a sample's true elemental composition [6]. Elemental abundances can be more clearly shown by applying one of various methods, such as Principle Component Analysis (PCA) [7]. PCA uses linear combinations of the variables, called principal components (PCs), to explain the variation in a dataset. The importance of a variable in explaining variance displayed by the PC is calculated as its loading. This study gives an overview of PCA applied to a suite of terrestrial iron-bearing oxides, sulfates, sulfides, and carbonates.



**Figure 1:** The Mars simulation chamber at Los Alamos National Laboratory.

**Sample Selection and Experimentation:** Nine iron-rich samples were chosen: two goethite samples, one from Colorado, the other of unspecified origin; two hematite samples, one from Brazil and one from Arizona; one specular hematite sample; one limonite sam-

ple; one magnetite sample; one pyrite sample; and one siderite sample. Samples were selected with intention of covering a range of iron-rich minerals. None of the samples except limonite are known to be heterogeneous. Microprobe, X-Ray Diffraction, and other analyses are planned to confirm homogeneity of samples.

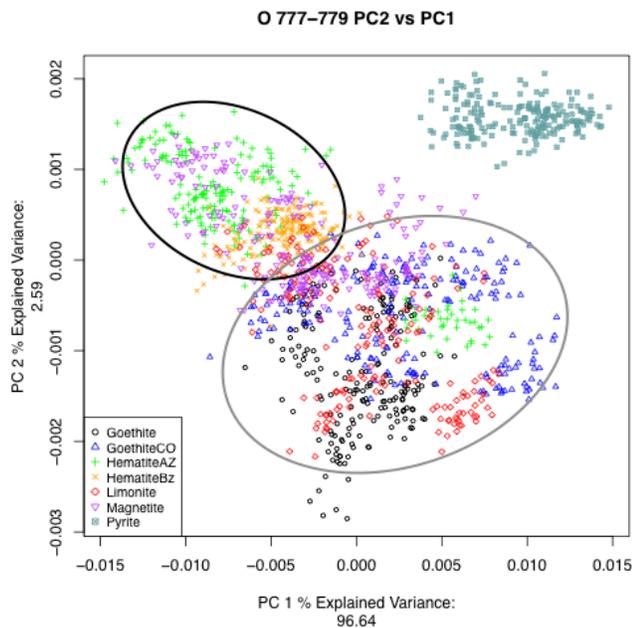
Samples were placed into the LANL mars simulation chamber, which is filled with 7 Torr of CO<sub>2</sub> to mimic the martian atmosphere, for analysis. The samples were aligned such that a relatively flat surface faced toward the LIBS instrument's laser, which fired sets of 50 shots with electrical current of 100 A at 13.5 mJ per pulse with repetition rate of 3 Hz from 1.6 m away. The simulation chamber was rotated by hand after each set of 50 shots until each sample had five spots of laser ablation.



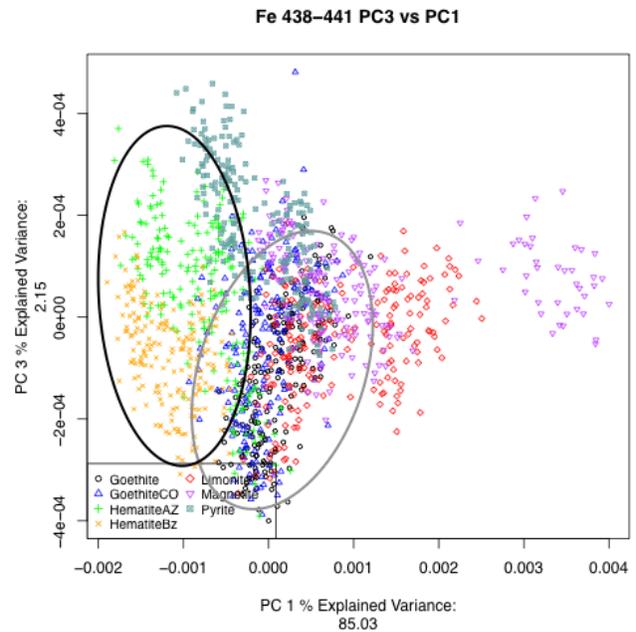
**Figure 2:** Visible spots of laser ablation on three samples. From left to right: goethite, Brazilian hematite, and pyrite. Dimes shown for scale.

**Results:** After normalization to total emission by spectrometer, PCA revealed primary differences due to sample heterogeneity and remnant surface contamination. Siderite and specular hematite samples were removed from the PCA analysis and remaining samples were reanalyzed. PCA was run on the total spectra, groups of oxygen peaks, groups of iron peaks, and individual iron peaks.

Loadings of PC1 for the total spectra showed most variation in oxygen peaks, especially those located at 777.4 nm, 777.6 nm, and 777.8 nm. PCA of this region showed little clustering of data in the plots of PC2 against PC1 (Figure 3) or PC3 against PC1, which explain most relevant variation in the dataset. Pyrite, which is the only non-oxide/non-oxide-hydroxide of the remaining samples, did show clustering away from the rest of the samples. Loose correlation can be seen between limonite/goethite samples and hematite samples, with one hematite spot falling within the limonite and goethite cluster. Magnetite does not appear to be contained within either of these groupings.



**Figure 3:** PCA of oxygen peaks around 777-779 nm, showing differentiation of pyrite and clustering of hematite (black oval) and goethite/limonite (gray oval).



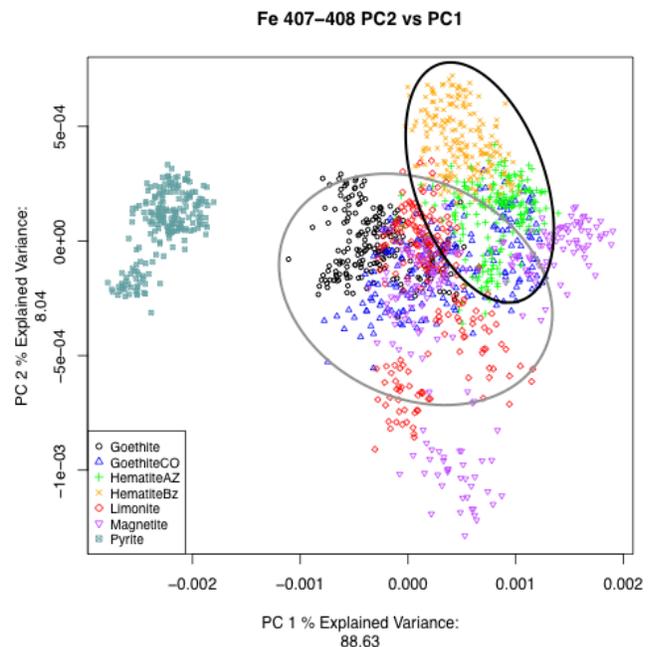
**Figure 4:** PCA of iron peaks around 438-441 nm, showing lack of differentiation of pyrite and clustering of hematite (black oval) and goethite/limonite (gray oval).

Analysis of individual iron peaks and groupings of iron peaks (e.g. 406.7-407.3 nm) generally provided more distinct clustering than oxygen peaks, especially between hematite samples and goethite/limonite samples, though clustering remained ambiguous in many cases. PCA on all iron peaks and groupings not including the middle iron peak, located at 407.3 nm, showed no clustering of pyrite apart from other samples (Figure 4). Analyses including the middle iron peak showed clustering of pyrite separate from the rest of the data (Figure 5).

**Conclusion:** Overall, analyses suggest a correlation between goethite and limonite samples, both of which are iron(III) oxyhydroxides (Figures 3,4,5). Hematite samples, which are iron(III) oxides, also showed clustering with each other. Pyrite, which is an iron sulfide, stood out from other samples in various regions of the spectra, such as oxygen peaks and the middle iron peak. Magnetite, an iron(II,III) oxide, was not conclusively distinguishable from the other samples when focusing specifically on iron and oxygen peaks.

This work demonstrates that LIBS onboard the MSL *Curiosity* rover can be used to differentiate various classes of iron-rich minerals on Mars using PCA of specific elemental peaks, though further work must be done; analysis of this data by Partial Least Squares (PLS) using ChemCam's new calibration dataset [8] is planned for the near future and may yield more conclusive results.

**References:** [1] Grotzinger J. P. et al. (2012) *Space Sci Rev*, 170, 5-56. [2] Maurice S. (2012) *Space Sci Rev*, 170, 95-166. [3] LANL LIBS papers, [4] Wiens R. C. et al. (2012) *Space Sci Rev*, 170, 167-227. [5] [6] Ollila A. M. et al. (2014) *JGR*, 119, 255-285 [7] Lanza N. L. et al. (2010) *Applied Optics*, 49, C211-C217. [8] Clegg S. et al. (2014) 45th LPSC, Abstract 2378.



**Figure 5:** PCA of iron peak at 407.3 nm, showing clear differentiation of pyrite and clustering of hematite (black oval) and goethite/limonite (gray oval).