

IDENTIFYING CARBONATE ROCKS IN A MARTIAN ENVIRONMENT USING LIBS. N.L. Lanza¹, A.M. Ollila¹, S.M. Clegg², J.E. Barefield², H.E. Newsom¹, and R.C. Wiens², ¹Earth and Planetary Sciences Department, Institute of Meteoritics, MSC03 2050, 1 University of New Mexico, Albuquerque, NM 87131-0001 (nlanza@unm.edu), ²Los Alamos National Laboratory, Los Alamos, NM.

Introduction: Laser-Induced Breakdown Spectroscopy (LIBS) is an emission spectroscopy technique used to determine the elemental composition of a target material. The ChemCam instrument selected for the Mars Science Laboratory (MSL) rover includes a remote LIBS instrument capable of probing samples up to 9 m from the rover mast. LIBS is sensitive to environmental conditions such as atmospheric composition and pressure [1, 2], and as a result requires calibration for materials in a specific environment in the laboratory. Here we examine carbonate samples in a simulated martian environment using the LIBS technique in order to better understand the signature of these materials should MSL encounter them on Mars. Both chemical composition and rock type are determined using multivariate analysis (MVA) techniques, which exploit matrix effects due complex interactions between specific sample characteristics. Composition is confirmed using scanning electron microscopy (SEM) techniques.

Background: Carbonate mineral are expected to have formed on Mars given the CO₂ atmosphere and a large quantity of water [3, 4] but have not been observed on the surface [5], although small quantities have been observed in martian meteorites [6, 7, 8]. Two scenarios are possible: 1) No carbonates have precipitated on Mars, or 2) the carbonate signature has been altered or masked. The acidic environment needed to form sulfate minerals, which have been observed in situ [9], would dissolve carbonates [10], making it unlikely that the two minerals will coexist. New work by [11] suggests that early carbonate formation was inhibited by the presence of SO₂ in the atmosphere, leading to a lack of carbonates and a wealth of sulfates. This model suggests a narrow range of fluid pH, in which carbonate formation is inhibited (low pH) while clay formation is allowed (higher pH). However, minerals such as jarosite suggest an extremely low pH environment not conducive to clay formation. Given both the surface presence of jarosite as well as carbonates in martian meteorites, the question of carbonate formation on Mars has yet to be fully resolved. As a result, it is important to be able to recognize carbonate materials in situ should future surface missions such as MSL encounter them.

Study objectives: The ChemCam LIBS and Sample Analysis at Mars (SAM) are the only instruments on MSL that is capable of detecting carbon. Given the importance of martian carbonates, it is important that

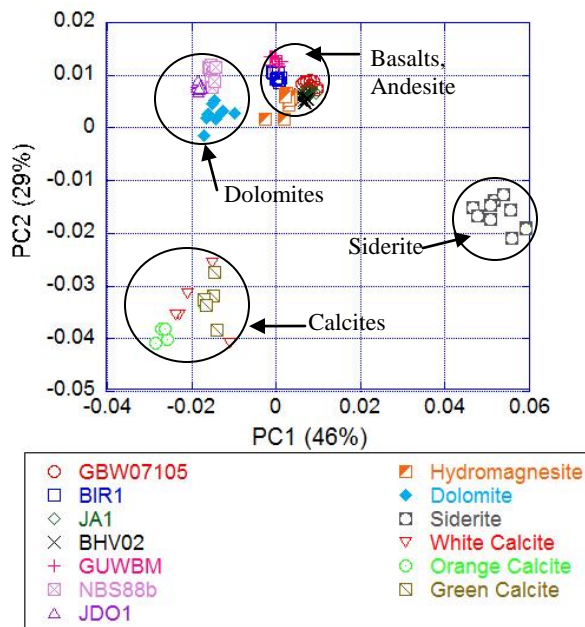


Figure 1. PCA plot with standards listed to left and samples to right. Rock types plot together, as seen in labeled circles. The rock type of the standards are as follows: Basalt = GBW07015, BIR1, BHV02, GUWBM; Andesite = JA1; Dolomite = JDO1, NBS88b.

ChemCam be calibrated to recognize C-bearing minerals such as carbonates in a CO₂ atmosphere. Here we examine four types of materials: dolomite (CaMg(CO₃)₂), siderite (FeCO₃), calcite (CaCO₃), and hydromagnesite (Mg₅(CO₃)₄(OH)₂·H₂O). A single rock containing each mineral was studied except calcite, for which several samples with varying colors were used. These materials were chosen on the basis of their potential to be found on the martian surface. Siderite in particular has been predicted as the first carbonate to precipitate from an early martian ocean [12]. The samples examined in this project are not standards or pure samples, but rather rocks with multiple minerals from various field locations. This was done in order to provide a realistic context for the minerals of interest that would mimic how they might be found on Mars by MSL. In this experiment, we seek 1) to confirm the accuracy of LIBS measurements of sample composition with SEM measurements, and 2) to use MVA techniques to identify rock type using LIBS data.

Methods: *LIBS.* The LIBS experiment uses a pulsed laser to create a plasma on the surface of the target, which in turn emits light of wavelengths characteristic of the constituent species [13]. Here a Spectra-Physics Indi Nd:YAG laser operating at 1064 nm, a repetition rate of 10 Hz, and an energy of 17 ± 1 mJ/pulse was used. The laser beam is focused onto the sample surface, which is positioned at a distance of 9 m from the laser and telescope. The samples are placed within a vacuum chamber filled with 7 Torr CO₂ to simulate martian surface conditions. Some of the plasma emission is collected with a telescope and then directed to one of three Ocean Optics HR2000 spectrometers, each covering a different spectral region ranging from ~220-800 nm (UV, VIS, and VNIR). The integration time was set to 1 s and five spectra were averaged for each LIBS spectrum, so that each recorded spectrum is the combination of 50 laser shots. Each sample was probed along a profile on 5-10 locations on the surface.

SEM. Samples were also examined using a JEOL 5800LV Scanning Electron Microscope (SEM) at the University of New Mexico operating at a low vacuum of 30 Pa, an accelerating voltage of 20 kV, and a beam current of 0.66 nA. Samples were placed directly in the chamber with no additional preparation. A qualitative analysis of composition was done on several locations for each sample with the energy dispersive spectrometer (EDS).

MVA. Multivariate Analysis (MVA) involves several techniques that involve the development of statistical models in order to analyze complex data sets. Two such methods are employed here: Partial Least Squares regression (PLS) and Principal Components Analysis (PCA). In PLS, a model is developed that describes a statistical correlation between each pixel in the LIBS spectrum and the variations in the elemental compositions. PLS also identifies correlations between elements and the rest of the sample matrix. [14] found that PLS tends to compensate for most of the chemical matrix effects, assuming an appropriate set of standards are used. PCA is also employed to identify the spectral variations generated from each sample. With the correct training set, PCA can predict the rock type of the sample. Here, the training set used consists of several standards of basalt, andesite, and dolomite. Models were built using the software Unscrambler.

Results: The LIBS model correctly identified the presence and general amount of the major constituent elements of each mineral of interest. Significant quantities of other elements were detected by both LIBS and EDS in the hydromagnesite sample, most notably Si, Al, and Fe. The difference between EDS and LIBS measurements was most pronounced for the three cal-

cite samples, with EDS values for Ca, C, and O consistently lower than those measured by LIBS. At a 9 m standoff distance, the LIBS laser did not couple as well to these three samples, and the emission intensity was relatively low. Figure 1 shows a PCA plot for the sample carbonate minerals as well as the standards used to calibrate the LIBS spectra. In PCA space, spectrally similar materials are grouped together. Figure 1 shows that our PCA model has properly distinguished between basalts/andesites and dolomites. The three calcite samples were also well clustered and distinguished from the remaining samples. The siderite sample was well clustered, and its spectra appear unique among the materials measured. The hydromagnesite sample plots closer to the basalts than the dolomites where it is expected to be. EDS results for the hydromagnesite suggest a high clay content, pointing to significant aqueous alteration, which may result in a significantly different composition than expected.

Discussion: Our results suggest that LIBS can distinguish C-bearing minerals and rocks in a martian environment. The MVA data analysis tools that have been used to analyze LIBS data appear to compensate for some of the chemical matrix effects. It also appears that PCA can be used to exploit these chemical matrix effects to differentiate between various rock types and minerals, as seen in Figure 1. It appears that the chosen carbonate samples may make good training samples to include in MVA models and laboratory validation experiments should ChemCam detect carbonates on Mars.

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