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Calibrating the ChemCam LIBS for carbonate minerals on Mars

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Abstract

The ChemCam instrument suite on board the NASA Mars Science Laboratory (MSL) rover includes the first LIBS instrument for extraterrestrial applications. Here we examine carbonate minerals in a simulated martian environment using the LIBS technique in order to better understand the in situ signature of these materials on Mars. Both chemical composition and rock type are determined using multivariate analysis (MVA) techniques. Composition is confirmed using scanning electron microscopy (SEM) techniques. Our initial results suggest that ChemCam can recognize and differentiate between carbonate materials on Mars.

OCIS Codes

300.6365	Spectroscopy, laser induced breakdown
350.6090	Space optics
120.0280	Remote sensing and sensors

The ChemCam instrument suite

The first laser-induced breakdown spectroscopy (LIBS) instrument for extraterrestrial applications has been selected as part of the ChemCam instrument package onboard the NASA Mars Science Laboratory (MSL) rover, scheduled for launch in 2011. The ChemCam consists of two instruments: a LIBS instrument and a Remote Micro Imager (RMI). LIBS will provide microbeam (60-200 μm radius) chemical analyses for target materials using 5 ns pulses of 1067 nm photons [1]. The RMI has a field of view of 20 mRad and is capable of resolving <0.5 mm features at a distance of 5 m, and will provide a telescopic context image of small-scale textures for the LIBS data [2]. The primary objective of MSL is to determine past and present habitability on Mars in a variety of environments [3]; this is not a search for life per se, but rather for materials and environments that would support life as it is currently understood on Earth. As such, the detection of H_2O, water-formed minerals, and organic molecules are key aspects to the mission.

The LIBS technique is particularly well suited for an extraterrestrial rover application. Firstly, the ChemCam LIBS can provide information about targets that are at a distance from the rover. The LIBS will be installed on the rover mast ~2 m from the ground and has a standoff distance of 1-7 m [1], allowing the rover to remotely obtain information about targets without the need for direct contact with them. In addition, the LIBS technique is sensitive to the majority of elements, and will allow for direct observation of light elements such as H, C, N, O, Li, Be, and B on the martian surface for the first time. Multiple LIBS analysis spots on a single rock will provide information on individual mineral grains as well as providing a bulk rock composition.

Additionally, repeated laser pulses on the same spot can be used to remove dust and to create a depth profile of chemical composition within weathering rinds. Analysis times for both the ChemCam LIBS and RMI are relatively short, and total power requirements remain relatively low, allowing ChemCam to efficiently gather large amounts of information about the martian surface.

Detecting carbonate minerals on Mars

Carbonate minerals are based on the $(CO_3)^{2-}$ anion. The carbonate mineral calcite in particular is very common in sedimentary environments on Earth; it is the main constituent of limestone, and its presence indicates the past presence of liquid water. On Mars, carbonates are predicted to have formed early in the planet's history when water may have been more abundant [4, 5], but have not been detected in large quantities on the planet [6].

Carbonates will begin to form when CO_2 in the atmosphere dissolves in H_2O to form carbonic acid, H_2CO_3. This acid will interact with silicate rocks to place cations such as Ca and Mg into solution [5]. As the concentrations of Ca and Mg increase, carbonate minerals will form as the solution becomes saturated. Carbonates require a relatively neutral pH to form. While carbonates have been observed in ancient martian meteorites [7-9], observations of sulfate minerals in situ on the martian suggest a more acidic environment [10], which is not conducive to carbonate formation. This poses a conundrum that has yet to be resolved. Complicating the problem is the fact that detecting CO_3 through the ~6mbar CO_2 atmosphere on Mars poses difficulties for many orbital remote sensing instruments, such as reflectance IR spectrometers, currently orbiting the planet.

Understanding carbonate formation on Mars is important because it not only answers questions about the presence and abundance of water on the planet, but also addresses the type and evolution of aqueous alteration processes that have occurred there. As a result, it is important to be able to recognize carbonate materials in situ should MSL encounter them. The ChemCam LIBS is one of two instruments on MSL that is capable of detecting carbon. LIBS is sensitive to environmental conditions such as atmospheric composition and pressure [11, 12], and as a result requires calibration for materials in a specific environment in the laboratory.

Study objectives

Here we examine natural carbonate minerals within whole rocks in a simulated martian environment using the LIBS technique in order to better understand the in situ signature of these materials on Mars. Of particular importance in this initial study is to determine if LIBS can distinguish between carbonate target material and the CO_2 atmosphere, and whether different types of carbonate materials can be differentiated from one another in this environment.

In this study, four types of carbonate materials were examined: dolomite ($CaMg(CO_3)_2$), siderite ($FeCO_3$), calcite ($CaCO_3$), and hydromagnesite ($Mg_5(CO_3)_4(OH)_2 \cdot H_2O$). A single rock containing each mineral was studied except calcite, for which several samples with varying trace elements (indicated by mineral color) were used. The carbonates 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 addition to the carbonate samples, several geological reference materials were also examined as standards in order to determine whether carbonates could be distinguished from other geologic materials containing similar elements. These reference materials include basalt and andesite, both igneous rocks, as well as several reference dolomites. All standards were prepared as pressed powder pellets in order to ensure homogeneity.

Methods

LIBS. 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 to sample target material. The laser beam was focused on the sample surface, which was positioned ~9 m standoff distance. The samples were placed within a vacuum chamber filled with 7 Torr CO_2 to simulate martian surface conditions. Some of the plasma emission was 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.

MVA. The LIBS data were analyzed using two multivariate analysis (MVA) methods: 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. Recent work suggests that PLS compensates for most of the chemical matrix effects, assuming an appropriate set of standards are used [13]. 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 the geologic reference materials of basalt, andesite, and dolomite. Models were built using the software Unscrambler after the methods of Clegg et al. [13].

SEM. Samples were also examined using a JEOL 5800LV Scanning Electron Microscope (SEM) 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 in order to ensure that the samples were in the same condition as during the LIBS experiment. A qualitative analysis of composition was done on several locations for each sample with the energy dispersive spectrometer (EDS). These results were then compared with the LIBS PLS results for sample and reference material compositions.

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 calcite 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. However, this is consistent with the EDS results, which suggest a high clay content. This points to significant aqueous alteration within the hydromagnesite sample, resulting in a significantly different composition than expected.

Discussion

Our initial results suggest that LIBS can detect carbonates and distinguish between different carbon-bearing minerals and rocks within a martian environment. In our model, the igneous standards of basalt and andesite were distinct from the sedimentary carbonate materials, including the reference dolomite and the sample carbonates. LIBS was also able to correctly identify that the hydromagnesite sample was highly altered, and thus more similar in composition to the igneous reference materials than to the dolomites. The MVA data analysis tools that have been used to analyze LIBS data appear to compensate for some of the chemical matrix effects to produce compositions that match SEM results. 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. The chosen carbonate samples appear to make good training samples to include in future MVA models and laboratory validation experiments should ChemCam detect carbonates on Mars. Future work will involve a more systematic examination of mixtures of carbonate minerals to determine how the major cation and anion affects the LIBS signature, and whether the individual mixture components may be identified and differentiated. Given the importance of detecting carbonates on Mars, it is extremely important that the

ChemCam LIBS instrument is calibrated in the laboratory on Earth for these materials so that they may be recognized in situ on Mars.

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Figure captions

Figure 1.

Principal component analysis (PCA) plot of carbonate samples and geological reference material standards. In the legend, standards (open symbols) are listed to left and carbonate samples (closed symbols) to right. Rock types generally plot together, as seen in labeled circles. The rock type of the standards are as follows: Basalt = GBW07015, BIR1, BHVO2, GUWBM; Andesite = JA1; Dolomite = JDO1, NBS88b.

Figures

Figure 1.