LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) OF PHYLLOSILICATES: PREPARING FOR CHEMCAM ON MARS. R.C.F. Lentz1, S.K. Sharma1, A.K. Misra1, S.M. Clegg2, R.C. Wiens2, R. Clark3, 1HIGP, University of Hawaii, Honolulu, HI 96822; rclentz@higp.hawaii.edu, 2Advanced Diagnostics and Instrumentation Group, Los Alamos National Laboratory, Los Alamos, NM 87545, 3Space Sciences and Applications Group, Los Alamos National Laboratory, Los Alamos, NM 87545, 4USGS, MS 964, Denver, CO 80222.

Introduction: One of the most promising of the chemical instruments selected for the upcoming Mars Science Laboratory (MSL) mission, is the Laser-Induced Breakdown Spectrometer (LIBS) on the ChemCam instrument package. The LIBS technique involves firing a focused laser pulse at a target with sufficiently high energy that plasma is made, reducing a small spot on the target into electronically excited ions and atoms. Upon relaxing from their excited states, the atoms emit characteristic spectra, which can be used to determine the elemental composition of the target. An additional useful aspect of this technique, particularly for Mars, is that the ablation of the target spot can be used to drill through outer rinds or dust coverings as are commonly seen on Martian rocks [1]. A difficulty with LIBS is the prevalence of matrix effects, which affect the relative intensities of emission lines depending on the target material, making quantification of elemental abundances complex.

In an effort to help with the calibration of the instrument to account for these matrix effects, and the development of a quantitative analytical technique for the data to be returned, several studies have been conducted gathering LIBS spectra of major rock types [e.g. 2-4]. In addition, there have been some preliminary investigations into LIBS of sulfur and sulfate minerals [5,6].

However, another group of alteration minerals that has proved important on Mars is phyllosilicates. Originally, phyllosilicates such as illite, montmorillonite, and smectite were recognized in the Martian meteorites [e.g. 7]. More recently, areas of ancient terrain with phyllosilicate signatures have been identified by orbiting high-resolution instruments like OMEGA on Mars Express [e.g. 8, 9], and most of the six candidate MSL landing sites also have phyllosilicate-rich signatures.

As the first stage in a program to investigate the effects of alteration minerals on primary rock LIBS signatures, we have begun measuring LIBS spectra of several common phyllosilicates detected (or likely to be) on Mars: montmorillonite, illite, nontronite (an Fe-bearing smectite), and sepiolite (a hydrous Mg-silicate) (Table 1). The rest of the suite of samples to be measured include 21 other Na, Ca, Al, and Fe-rich phyllosilicates from the USGS collection. Here we present the preliminary observations of the LIBS spectra, with the aim of more quantitative comparative analyses (using the multivariate analysis techniques of [4]) to follow, once more of the samples have been measured.

Experimental Technique: The measurements presented here cover two wavelength ranges at high resolution: the UV from 244-321 nm, at 0.02 nm/pixel, and the visual from 533-700 nm, at 0.09 nm/pixel. These ranges include prominent peaks for Si, Al, Mg, Ca, Fe, Na, K, Ti, and H (indicating water). Spectra in both ranges were induced from targets at 9 m by a 1064-nm Nd:YAG Continuum Powerlite laser powered at ~74mJ/pulse. The emissions were collected by a 10.8-cm Newtonian reflecting telescope and directed along a 1-m, 200-µm fused silica fiber to a spectrometer, and thence to an I-CCD detector. The UV wavelengths were collected by a SPEX 270M spectrometer with a 3600-line diffraction grating, and the visible wavelengths were measured using a Kaiser HoloSpec equipped with a dual HoloPlex grating (after passing through a 532-nm holographic super-notch filter) [10].

The four phyllosilicates shown here were each small rock chips, but multiple measurements at different spots showed very good agreement, suggesting fairly homogenous samples. In addition, we analysed a NIST standard basalt sample (BHVO-2) for interlab comparison to the Los Alamos ChemCam measurements.

Preliminary Spectral Data: Figure 1 shows the LIBS spectra of the phyllosilicate and basalt samples in the UV wavelengths. The labelled peaks illustrate most of the major elements detectable over this wavelength range, and also demonstrate the possible detec-
tion of K and Ti. The identification of peaks can yield general information about the abundance of some of the major elements (i.e., whether the peaks are even detectable), particularly the minor elements. When calibrated, the LIBS relative peak heights can be used to quantify the abundances as well.

However, the overall patterns of the traces may be more useful for full mineral identification. For example, nontronite, with its higher Fe abundance (Table 1) is distinct from the other phyllosilicates, and clearly mimics the Fe-rich nature of the basalt standard, BHVO-2. However, the other phyllosilicates, while very similar, do have distinguishing peaks that would separate them in a quantitative characterization of the spectra. For example, sepiolite has stronger Si and Mg peaks with no Ca peaks, while illite has a small K peak (substantiated by two K peaks in the VIS spectra in Fig. 2) and more Fe peaks, indicative of its slightly more Fe-rich nature.

Figure 2 shows the LIBS results in the visible wavelengths, and illustrates similar relationships, but with a different assortment of peaks. Again, nontronite is most similar to the basalt, this time due to its higher Ca content. But it distinguishes itself as a hydrous mineral with a strong H peak, as do all these phyllosilicates. Once we have measured more samples, with some multiple mineral analyses, we will apply multivariate analysis, like that used by [4], to illustrate these relationships more quantitatively.

Further work: For the near future, we plan to measure the rest of the 21 USGS phyllosilicate samples for comparison of the same minerals with different elemental enrichments (e.g., Na-rich and Ca-rich montmorillonite). The next step will then be to construct a vacuum chamber to allow measurements at 7 Torr CO₂, to simulate the Martian atmosphere. Repeat LIBS measurements should then help to determine the effects of reduced oxygen on the interaction of the elements in the hydrous species.