

PRELIMINARY RESULTS ON THE CAPABILITIES OF THE CHEMCAM LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) INSTRUMENT TO DETECT CARBON ON MARS. A. M. Ollila^{1,2}, J. G. Blank³, R. C. Wiens⁴, J. Lasue^{4,5}, H. E. Newsom², S. M. Clegg⁶, A. Cousin⁷, S. Maurice⁷. ¹Department of Earth and Planetary Sciences, University of New Mexico, MSC03 2050, 1 University of New Mexico, Albuquerque, New Mexico USA 87131, aollila@unm.edu, ²Institute of Meteoritics, MSC03 2050, 1 University of New Mexico, Albuquerque, NM USA 87131, ³Carl Sagan Center, SETI Institute, 189 Bernardo Avenue, Suite 100, Mountain View, CA USA 94043, ⁴ISR-1, MS D466, Los Alamos National Laboratory, Los Alamos, NM USA 87545, ⁵Lunar and Planetary Institute, Houston, TX USA 77058, ⁶C-PCS, MS J565, Los Alamos National Laboratory, Los Alamos, NM USA 87545, ⁷Centre d'Etude Spatiale des Rayonnements, Université de Toulouse, CNRS, Toulouse, France

Introduction: The Mars Science Laboratory (MSL) rover, Curiosity, will explore the surface of Mars beginning in 2012, seeking evidence of past or present habitable environments. One of the instrument packages onboard, ChemCam, is comprised of a laser-induced breakdown spectroscopy (LIBS) instrument to provide chemical data on geologic targets and a remote micro-imager (RMI) for morphological context. ChemCam will be the primary geochemical survey instrument on MSL. Accurate detection of C, and thus differentiation of atmospheric C ($P_{CO_2} = 95.5\%$) from sample C, is important because it may indicate whether organic compounds or carbonates are present. The identification of either of these materials would provide clues into the history of water and the potential for life on Mars. In this work, we used the ChemCam flight instrument to (1) inventory C peaks and C_2 Swan bands present in spectra taken with samples held under Mars-like conditions and (2) document peaks that interfere with the detection of C in geologic materials, in preparation for future work on distinguishing atmospheric and sample C.

ChemCam: ChemCam is an active remote sensing instrument that can directly detect carbon as well as small, carbon-bearing molecular species such as C_2 . ChemCam uses LIBS, a spectrochemical atomic emission technique in which a pulsed laser is focused on a surface, ablating the surface and locally ionizing the atmosphere to form a plasma of excited species that emit at characteristic wavelengths as the plasma cools [1]. ChemCam is able to detect all elements simultaneously and can operate remotely up to 7 m from the rover [2]. It is time and energy efficient, able to conduct an analysis in < 6 minutes using < 2 W-hr of energy. ChemCam is also capable of removing dust layers and probing up to 1 mm into the rock's surface [2].

Samples: Selected samples encompass a range of geologic materials that may be present on the surface of Mars. The majority of samples were obtained from the Brammer Standard Company, Inc. (www.brammerstandard.com) as certified reference powders that were then pressed into pellets. Additional samples were acquired as powders from the United States Geologic Survey, the Canadian Natural Re-

sources department, and from the private collections of M. D. Dyar at Mt. Holyoke University and M. Rhodes at the University of Massachusetts. Samples are predominantly igneous but some sedimentary rocks are represented, including sulfates, clays and carbonates. Several marine and stream sediments were analyzed, as well as replicates of the rover calibration targets, including graphite. Igneous rocks typically have a very small C content (< 500 ppm) while the sedimentary rocks and sediments have a wide range of C concentrations. Absolute C concentrations were obtained from the source certificate or from [3].

Instrument Description: ChemCam uses a Nd:KGW 1067 nm laser operating at 3 Hz with 5 ns pulses at ~ 15 mJ/pulse to interrogate targets. The laser is Q-switched and, once triggered, passes through a 110 mm diameter telescope to focus on the target material, ablating the surface. Light emitted from the plasma is collected via the telescope and directed to either the RMI or to a 300 μ m diameter optical fiber. The optical fiber transmits the light to a demultiplexer, which splits the light into three wavelength ranges (UV: 240.0 - 342.2 nm; VIS: 382.1 - 469.3 nm; VNIR: 473.7-906.5) and transmits it to one of the three spectrographs.

Experimental Configuration: The results we report here are a part of a larger test effort to gauge the response and efficacy of the ChemCam flight model (FM) in simulated Mars conditions. The data used in this study were collected in 2010 at the Los Alamos National Laboratory in Los Alamos, NM, USA, with the samples in a 7 Torr CO_2 environmental chamber placed 3 m from the instrument, while the FM was housed in a thermal vacuum chamber (TVAC, $-45^\circ C$, 7 Torr). The laser energy was ~ 14 mJ/pulse and 50 spectra were collected at four locations on each sample.

Results: In total, 18 C peaks and 21 C_2 Swan bandheads were identified in graphite. All 18 C peaks and 4 C_2 Swan bandheads were also identified in the spectra of one or more of the geologic materials (Swans were seen only in SGR-1, a petroleum-rich shale with 28% C). Identified C peaks and interfering peaks are listed in Table 1. Selected C peaks are shown in Fig 1 and selected C_2 Swan bandheads are shown in Fig 2. We have found the identification of a

particular C peak is dependent on the interfering peaks as well as the laser-to-sample coupling efficiency (poor coupling = lower emission intensity).

Conclusions: C peaks and C₂ Swan bandheads were identified in graphite and a variety of geological materials using the ChemCam flight model under Mars atmosphere conditions. This work is preliminary to determining if there is a way to distinguish C from the CO₂-rich Mars atmosphere from C in the sample. We have observed that many C peaks are present in samples with C content below the detection limit of 2400 ppm observed in a different study [4], thus are showing atmospheric influence. Future work will explore ways to accurately detect and quantify C using univariate and multivariate regression modeling.

| State | λ (nm) | Interfering Peaks |
|-------|----------------------|----------------------|
| C I | 247.931 | Fe I 248.023 |
| C II | 250.988 | Si I 250.766 |
| C II | 251.282 | Si I 251.508/251.687 |
| C II | 283.754 | Cr II 283.646 |
| C II | 283.843 | Fe I 284.481 |
| C II | 299.349 | Fe I 299.250 |
| C II | 387.729 | Fe I 387.36 |
| C II | 387.751 | Fe I 387.912/387.928 |
| C II | 387.775 | Fe I 387.912/387.928 |
| C II | 392.009 | Ca I 393.477 |
| C II | 392.180 | Sr II 407.886 |
| C II | 407.567 | Sr II 407.886 |
| C II | 407.700 | Sr II 407.886 |
| C II | 426.820 | Fe I 426.167 |
| C II | 426.846 | Fe I 426.903 |
| C II | 514.492 | Fe I 514.068/514.089 |
| C II | 514.659 | Ti I 514.690 |
| C II | 514.659 | Fe I 516.371/516.772 |
| C II | 514.659 | Mg I 516.876 |
| C II | 564.807 | Ti I 654.414 |
| C II | 566.247 | Fe I 566.08/566.135 |
| C II | 566.247 | Ti I 566.216 |
| C II | 569.430 ^a | Si II 569.039 |
| C II | 657.987 | |
| C II | 658.470 | H I 656.460 |
| C I | 658.943 | |
| C II | 678.577 | 1 unidentified peak |
| C I | 711.514 | |
| C I | 711.715 | |
| C II | 711.759 | Ti I 714.088 |
| C I | 711.895 | Ca I 715.012 |
| C II | 712.186 | |
| C II | 723.331 | |
| C II | 723.841 | Ti I 724.686 |
| C I | 833.744 | Fe I 833.421 |

^a In air

Table 1 C peaks (I = neutral, II = singly ionized) identified and peaks that may interfere with the identification in geological materials. Wavelengths are from NIST in vacuum except as noted. FWHM spectral resolutions are ~0.15, 0.20, and 0.60 nm for UV, VIS, and VNIR ranges, respectively. Lines contained in a contiguous region are indistinguishable.

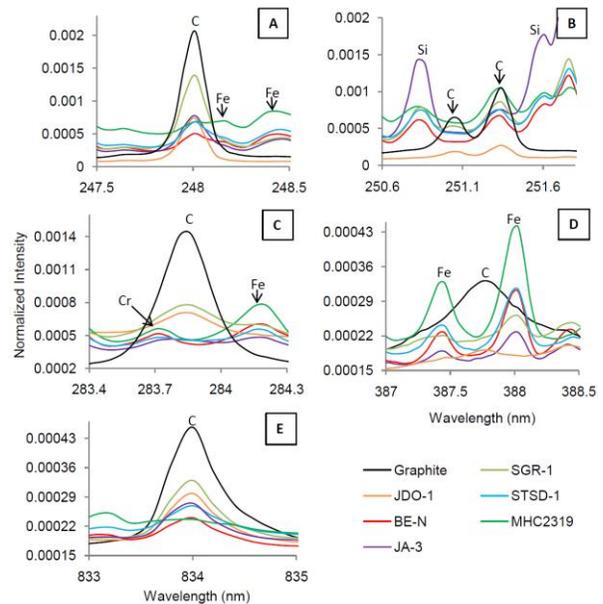


Figure 1 Selected C peaks. Spectra have been normalized to the total emission. Wavelengths are approximate (see Table 1). SGR-1 = petroleum-rich Green River shale (28% C), JDO-1 = dolomite (12.8% C), STSD-1 = stream sediment (12.3% C), BE-N = basalt (2000 ppm C), MHC2319 = melanterite (90 ppm C), JA-3 = andesite (61 ppm C). The graphite spectra in (A), (B) and (C) has been divided by 3 to fit on the graph.

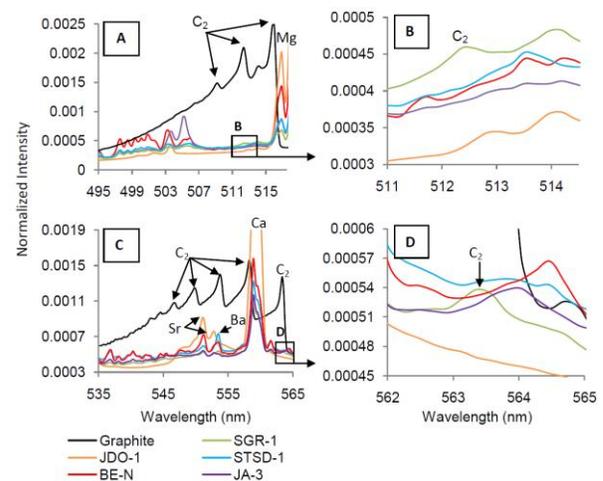


Figure 2 Selected C₂ Swan bands. See the caption for Figure 1 for a description of samples.

References: [1] Cremers DA, Radziemski LJ (2006) *Handbook of laser-induced breakdown spectroscopy*. John Wiley & Sons, New York. [2] Wiens et al. (2010) *LPS XXXXI* Abstract # 2205. [3] Govindaraju, K. (1994) *Geostand. Newslett.*, 18, 1-158. [4] Radziemski, L. et al. (2005) *Spectrochim. Acta*, 60, 237-248.