Elemental Compositions at Stand-Off Distances From a Rover: Development and Testing of a Laser-Induced Breakdown Spectroscopy (LIBS) Field Prototype Instrument. R. C. Wiens[1], D. A. Cremers[2], M. Ferris[2], R. E. Arvidson[3], F. P. Seelos[3], J. D. Blacic[4], and J. E. Nordholt[5], [1]Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545; rwiens@lanl.gov), [2]Chemistry Division, LANL, [3]Dept. of Earth & Planetary Sciences, McDonnell Center for the Space Sciences, Washington University (St. Louis, MO 63130), [4]Physics Division, LANL, [5]Earth & Environmental Sciences, LANL.

Introduction: LIBS is a technique for obtaining rapid comprehensive elemental compositions at distances of up to 20 meters from the instrument. The method has many advantages compared to current elemental analysis methods. Under the Mars Instrument Development Program an initial field prototype was built and mechanically integrated into the Ames K9 rover for joint JPL-Ames rover field tests in Nevada in May, 2000. The field testing was augmented by further testing using rocks taken from the field site. Results of both are reported here.

The LIBS Technique: In the LIBS method [1], powerful laser pulses are focused on the target sample to form a laser spark or plasma. Material within the spark is the result of vaporization/atomization of a small amount of target material. The spark contains the emission spectra of the elements within the plasma. Collection of the plasma light, followed by spectral dispersion and detection, permits identification of the elements via their unique spectral signatures. When calibrated, concentrations can be determined. Advantages of the method compared to more conventional elemental analysis methods include: (1) rapid analysis (one measurement/pulse); (2) simultaneous multi-element detection; (3) ability to detect all elements (high and low z); (4) ability to remove dust or weathering layers off of sample surfaces; and (5) stand-off analysis capability [2]. Stand-off analysis is possible because the laser pulses can be focused at a distance to generate the laser sparks on a solid.

We have shown [3,4] using a laboratory instrument that 1) semi-quantitative results (e.g., 10-20% accuracy) can be obtained for nearly all elements at distances of up to 20 m. using a compact laser and a 100 mm diam. objective lens for light collection, 2) detection limits for nearly all elements at these distances are in the range of 10 to several hundred ppm, 3) LIBS works well at all atmospheric pressures from 1 bar to vacuum, and 4) Typical excavation rates in ~5 Torr CO_2 for the ~1 mm diam. laser-produced craters range from ~200 μm/shot in sand or dust [3] to ~1 μm/shot in basalt.. The capability to remove surface material from a sample is important, as all Mars rock observations to date appear to be contaminated with dust [5].

Prototype Design and Testing: A relatively simple prototype instrument was built consisting of two sections: 1) the sensor head, including the laser, variable focus beam expander with a 50 mm diam. objective lens, beam splitter, and a fiber optic cable for receiving the return signal; 2) the body-mounted portion consists of the spectrograph, detector, and laser controller. Commercial off-the-shelf (COTS) components were used throughout, so weight, volume, power consumption, and some of the optical parameters were not optimized. The working range is 2-6 m, the near distance limited primarily by the height of the rover masthead. The spectral range is from 240 to ~800 nm, with a resolution of ~2 nm. The Nd:YAG laser output is ~100 mJ per ~10 ns pulse, with a repetition rate of 0.1 Hz, limited by thermal considerations.

The prototype was mechanically integrated with the Ames K9 rover and tested during the combined rover tests at Lunar Lake, NV in May, 2000. Due to the fire at Los Alamos, the field tests could not be properly supported, and only a small amount of data were taken in the field. However, a number of rocks were taken for a joint study between visible and infrared (VISIR) spectroscopy and LIBS, which also included whole-rock x-ray fluorescence (XRF) analysis for comparison.

Initial Results [6] focused on a qualitative comparison of two dissimilar samples. Fig. 1 (top) shows a portion of the LIBS spectrum of sample A01, taken at 2 meters distance. For comparison, the same spectral region is shown for a basalt rock powder standard in Fig. 1 (bottom). The close correlation of these two small portions of the spectra confirms a basalt-like elemental composition. Independent compositional analysis in Table 1 bears this out. A portion of the spectrum from a second sample, A02, is shown in Fig. 2 (top), with a dolomite standard (Table 1) shown in Fig. 2 (bottom).

VISIR spectra of the same region of A01 showed evidence for olivine along with evidence for montmorillonite. The initial LIBS shot confirmed higher surfical Al and H, consistent with a thin weathering coat. For sample A02, the VISIR spectrum displayed features consistent with dolomite, kaolinite, and ferric oxide. Further investigation with LIBS showed patches of low Ca, high Al consistent with kaolinite. The overall interpretation is that A02 is primarily dolomite, but includes representative materials exposed in many areas in and around the rover test site.

Work to date shows that LIBS and passive emission spectroscopy are very complementary because the combination yields both mineralogical and elemental composition information. A more quantitative study of a broader range of rocks from the field is currently underway, calibrating LIBS with a number of known standards and then comparing the field sample compositions with XRF results.

Near-term Plans: Current development work is proceeding on several fronts. 1) The sensor head is being redesigned for better optical throughput. 2) A new spectrograph and detector are being outfitted to provide broad spectral coverage. 3) Characterization of Raman spectroscopy signals obtainable with the prototype LIBS instrument [7] continues. 4) Additional field work is planned for this year. We plan to again intercompare LIBS and VISIR, this time making all of the measurements in the field and including tests of remote Raman spectroscopy capabilities. A flight instrument would be <2 kg, require <3 W power, have a ~200-850 nm spectral range, and stand-off analysis range to ≥10 m.

References: [1] Cremers D.A. and Radziemski L.J. (1986) In *Laser Spectroscopy and Its Applications* (L.J. Radziemski, et al., eds.), Chapter 5, Marcel Dekker, New York. [2]Cremers D.A. (1987) *Appl. Spectrosc. 41*, 1042. [3] Knight A.K. et al. (2000) *Appl. Spectrosc. 54,* 331. [4] Knight A.K. et al. (1999) *Lunar Planet. Sci.XXX,* 1018-1019. [5] McSween H.Y. Jr., et al. (1999) *JGR 104*, 8679-8715. [6] Wiens R.C., et al. (2001) Combined remote mineralogical and elemental measurements from rovers: Field and laboratory tests using reflectance and laser induced breakdown spectroscopy. Subm. To JGR-Planets. [7] Wiens R.C. et al. (2000) *Lunar Planet. Sci. XXXI*, 1468-1469. [8] Govindaraju K. (1994) *Geostandards Newsletter 18*, 1-158.

Table 1. XRFS analyses of samples A01 and A02 and major element composition of standard samples [8] used for comparison of LIBS spectra.

Element	A02	Dolomite NBS-88b	A01	Basalt std. JB-2
SiO_2	3.93%	1.13%	44.33%	53.2%
Al_2O_3	0.85	0.36	15.36	14.67
Fe_2O_3T	0.44	0.28	14.65	14.34
MnO	0.02	0.016	0.20	0.2
MgO	15.86	21.03	8.55	4.66
CaO	33.96	30.12	9.12	9.89
Na_2O	0.01	0.03	3.37	2.03
K_2O	0.03	0.1	1.14	0.42
TiO_2	0.05	0.016	2.88	1.19
P_2O_5	0.04	0.004	0.50	0.1
H_2O	-------	0.24	-------	0.38
CO_2	-------	46.67	-------	
LOI*	44.51	N/A	-0.32	N/A
Total	99.70	100.00	99.77	101.08

*LOI = loss on ignition

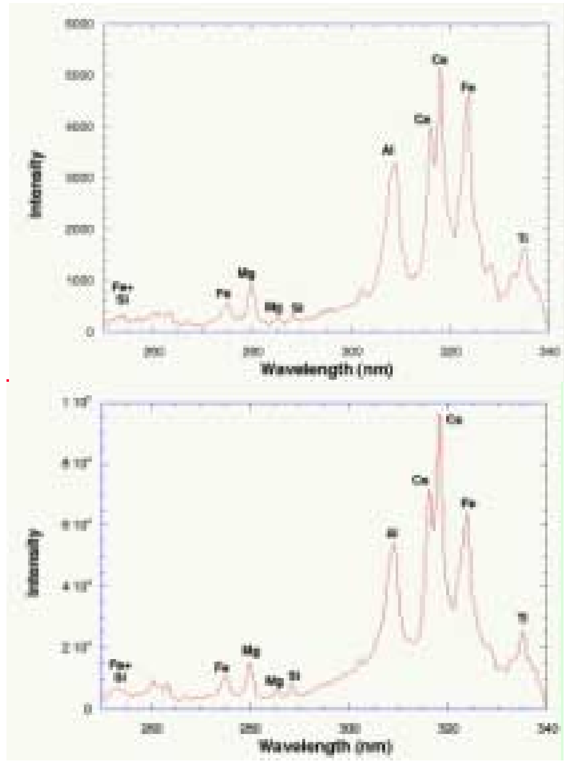

Fig. 1. A small portion of the LIBS spectrum of sample A01 (top) and basalt standard JB-2 (bottom). Spectra are 10-20 shot averages taken after several cleaning shots.

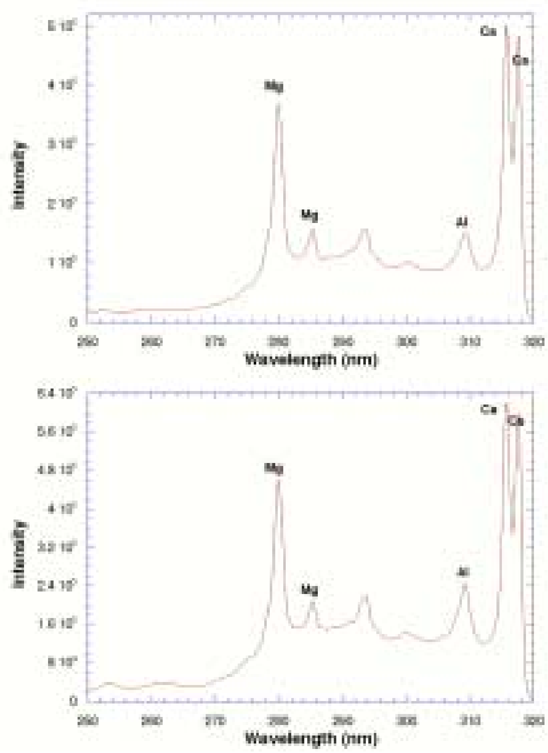

Fig. 2. Sample A02 (top) & dolomite std. NBS88b (bottom).