RAPID ELEMENTAL ANALYSIS AT STAND-OFF DISTANCES USING THE LIBS CONCEPT FROM THE MARS INSTRUMENT DEVELOPMENT PROGRAM. R. C. Wiens, D. A. Cremers, M. Ferris, and J. D. Blacic, Los Alamos National Laboratory (MS D-466, Los Alamos, NM, 87545, rwiens@lanl.gov).

Introduction: The elemental composition of rocks and soils is one of the most fundamental types of information needed to understand geologic contexts and to search for likely locations of biological activity. Nearly all methods for determining elemental composition involve in-situ analysis, requiring time-consuming maneuvering of a rover to acquire the desired sample. By contrast, analyses at stand-off distances allow nearly a ten-fold increase in the number of samples obtainable over in-situ techniques [1]. Additionally, methods such as APXS have difficulty distinguishing between the pristine sample and rock coatings of either dust or weathering products [2].

Under the auspices of the Mars Instrument Development Program, we have built and are testing a prototype LIBS (Laser-Induced Breakdown Spectroscopy) instrument which can rapidly determine elemental compositions at a distance. Additionally, by depth profiling µm to mm into the sample, LIBS can distinguish between dust or weathering products and the pristine sample. Here we summarize the LIBS concept, describe the initial performance of our prototype, including work at the combined rover tests in Nevada, and summarize potential LIBS contributions to the Mars exploration program.

The LIBS Concept: In the LIBS method [3], 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 light contains the emission spectra of the elements within the plasma. Collection of the plasma light, followed by spectral dispersion and detection, permit 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 clean dust or weathering layers off of sample surfaces; and (5) stand-off analysis capability [4]. Stand-off analysis is possible because the laser pulses can be focused at a distance to generate the laser sparks on a solid. The distance that can be achieved depends on characteristics of the laser and the optics used to focus the pulses on the target.

Recent LIBS Results: We have recently shown [5,6] using a laboratory instrument that a) semi-quantitative results (e.g., 10-20% accuracy) can be obtained for nearly all elements at stand-off distances of up to 20 m. using a compact laser and a 4" objective lens and detector, b) detection limits for nearly all elements at these distances are in the range of 10 to several hundred ppm, c) LIBS works well at all atmospheric pressures from 1 bar to vacuum, with a maximum efficiency between 10 and 100 Torr, and d) the target mass ablated per laser pulse increases with decreasing atmospheric pressure.

The capability to remove surface material from a sample is important, as all Mars rock observations to date appear to be contaminated with dust [2]. In one recent test, layers of sea sand 1, 2, and 3 mm thick overlying a rock sample were removed in 4, 14, and 28 laser pulses, respectively, under Martian conditions (5 Torr CO_2 atmosphere) [5]. Typical excavation rates for the ~1 mm dia laser-produced craters in basalt are much lower, at ~1 µm/shot, but still sufficient to remove weathering layers with repeated pulses.

Prototype Design and Testing: A relatively simple prototype instrument was produced over the last year. As shown in Fig 1, it consists of two sections: 1) the sensor head, including the laser, variable focus beam expander with a 2" diameter objective lens, beam splitter, and a fiber optic couple for receiving the return signal. 2) The body-mounted portion consists of the spectrograph and detector, and the laser controller. Commercial off-the-shelf (COTS) components were used throughout, so weight, instrument volume, power consumption, and some of the optical parameters were not optimized. The prototype was built to fit the K9 rover testbed fielded by NASA Ames. Its working range is 2-6 m, the near distance limited primarily by the height of the rover masthead. The working spectral range is from 240 to ~800 nm, with a resolution of ~2 nm. The YAG laser output is ~100 mJ in ~10 ns pulses, with a repetition rate of 0.1 Hz, limited by thermal considerations.

The prototype was integrated with the rover and tested during the combined rover tests at Lunar Lake, NV in May, 2000. Due to the fire at Los Alamos, which resulted in lab closure and evacuation of the entire county, we were not able to support the testing as planned, and obtained only limited data at the test site. A portion of a spectrum obtained using a single laser shot during the field test is shown in Fig. 2. Joint Wash. U./LANL comparison of reflectance spectroscopy, XRF, and LIBS results are planned as follow-up work on a dozen rocks taken from the site.

Calibration data were taken at several stand-off distances prior to the rover exercises. Samples consisted of standard rock powders. Fig. 3 compares a portion of the spectrum containing Mg and Si peaks for rock powders of pyroxenitic, basaltic, and granitic compositions. Spectra from 10 laser shots were averaged, with a stand-off distance of two meters.

Envisioned Applications: The results show that semi-quantitative elemental compositions are rapidly obtainable at stand-off distances using an instrument of this format. "Quick-look" compositions of rocks and soils some distance from the rover provide a rapid way to determine a) which direction a rover should travel and b) where to use more time-consuming in-situ analysis techniques.

Rapid, stand-off analysis is only one possible application of LIBS, which could be done either using a compact rover-mounted instrument of ≤1.5 kg with capabilities similar to the prototype, or using a slightly more robust lander-mounted instrument capable of 20+ m stand-off distances, though this is perhaps more applicable to, e.g., a Europa lander. The detector portion of such an instrument could double for Raman spectroscopy analyses [7] to yield mineralogical information at stand-off distances [8] as well. If more quantitative elemental analyses are desired from LIBS, such as to aid in radiometric dating, in-situ analyses using a fiber optic cable mounted adjacent to the sample can be done.

References: [1] Arvidson R.E. et al. (1998) A mission model for the 2001 Mars Rover/Athena payload, presented at the Mars Surveyor 2001 Landing Site Workshop Program, NASA Ames. [2] McSween H.Y. Jr., et al. (1999) *JGR 104*, 8679-8715. [3] 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. [4]Cremers D.A. (1987) *Appl. Spectrosc. 41*, 1042. [5] Knight A.K. et al. (2000) *Appl. Spectrosc. 54,* 331. [6] Knight A.K. et al. (1999) *Lunar Planet. Sci.XXX,* 1018-1019. [7] Wiens R.C. et al., (2000) *Lunar Planet. Sci. XXXI*, 1468-1469. [8] Lucey P.G. et al. (1998) *Lunar Planet. Sci. XXIX*, 1354-1355.

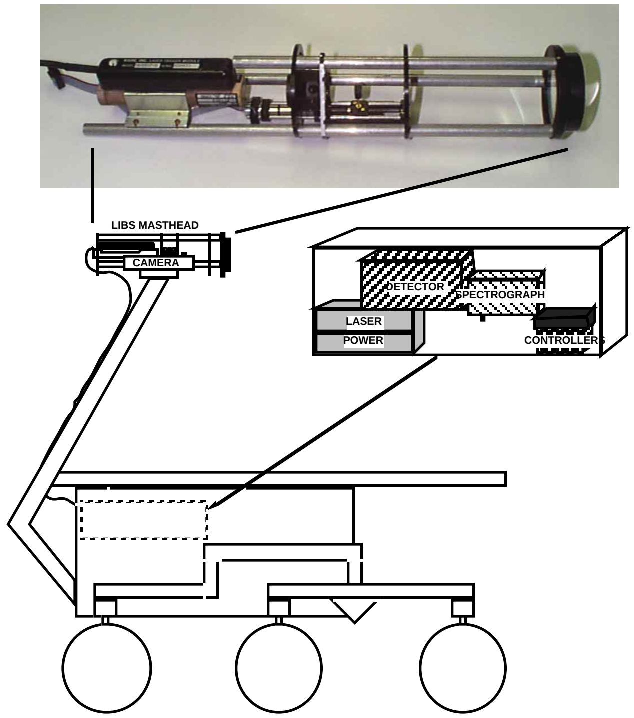

Fig. 1. Schematic view of the LIBS prototype components as mounted in the K9 rover testbed. The photo shows the sensor head with the cover removed. The prototype used only COTS parts, so weight and volume have not yet been optimized.

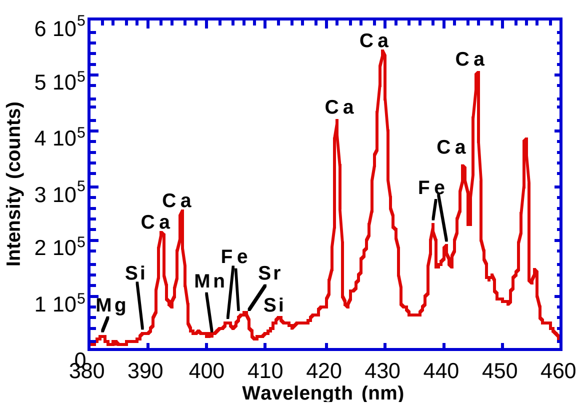

Fig. 2. Spectrum of a basalt rock recorded by the LIBS prototype on the K9 rover during field tests. This spectrum was obtained using a single laser pulse.

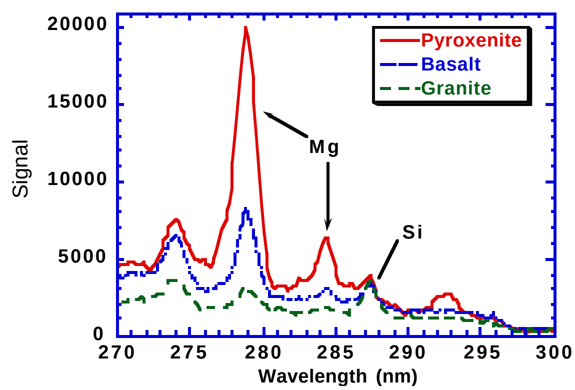

Fig 3. A portion of the spectrum showing two Mg peaks and a Si peak. The three rock types are very easily distinguished from the Mg/Si ratio. Ten-spectra averages were taken on standard rock powders at 2 m. The MgO abundance ranges from 25% to 4% to 0.04%.