DEVELOPMENT AND TESTING OF LASER-INDUCED BREAKDOWN SPECTROSCOPY FOR THE MARS ROVER PROGRAM: ELEMENTAL ANALYSES AT STAND-OFF DISTANCES.

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Introduction: One of the most fundamental pieces of information about any planetary body is the elemental composition of its surface materials.

The Viking Martian landers employed XRF (x-ray fluorescence) and the MER rovers are carrying APXS (alpha-proton x-ray spectrometer) instruments upgraded from that used on the Pathfinder rover to supply elemental composition information for soils and rocks to which direct contact is possible. These in-situ analyses require that the lander or rover be in contact with the sample.

In addition to in-situ instrumentation, the present generation of rovers carry instruments that operate at stand-off distances. The Mini-TES is an example of a stand-off instrument on the MER rovers. Other examples for future missions include infrared point spectrometers and microscopic-imagers that can operate at a distance. The main advantage of such types of analyses is obvious: the sensing element does not need to be in contact or even adjacent to the target sample. This opens up new sensing capabilities. For example, targets that cannot be reached by a rover due to impassable terrain or targets positioned on a cliff face can now be accessed using stand-off analysis. In addition, the duty cycle of stand-off analysis can be much greater than that provided by in-situ measurements because the stand-off analysis probe can be aimed rapidly at different features of interest eliminating the need for the rover to actually move to the target.

Over the past five years we have been developing a stand-off method of elemental analysis based on atomic emission spectroscopy called laser-induced breakdown spectroscopy (LIBS). A laser-produced spark vaporizes and excites the target material, the elements of which emit at characteristic wavelengths. Using this method, material can be analyzed from within a radius of several tens of meters from the instrument platform. A relatively large area can therefore be sampled from a simple lander without requiring a rover or sampling arms. The placement of such an instrument on a rover would allow the sampling of locations distant from the landing site. Here we give a description of the LIBS method and its advantages. We discuss recent work on determining its characteristics for Mars exploration, including accuracy, detection limits, and suitability for determining the presence of water ice and hydrated minerals. We also give a description of prototype instruments we have tested in field settings.

LIBS Method: The LIBS method has been studied for many years and has recently seen a huge growth in applications [1-6]. The method is diagrammed in

Fig. 1 for measurements at stand-off distances and a photo of a laser plasma formed on a cliff face at 18 meters distance is shown in Fig. 2.

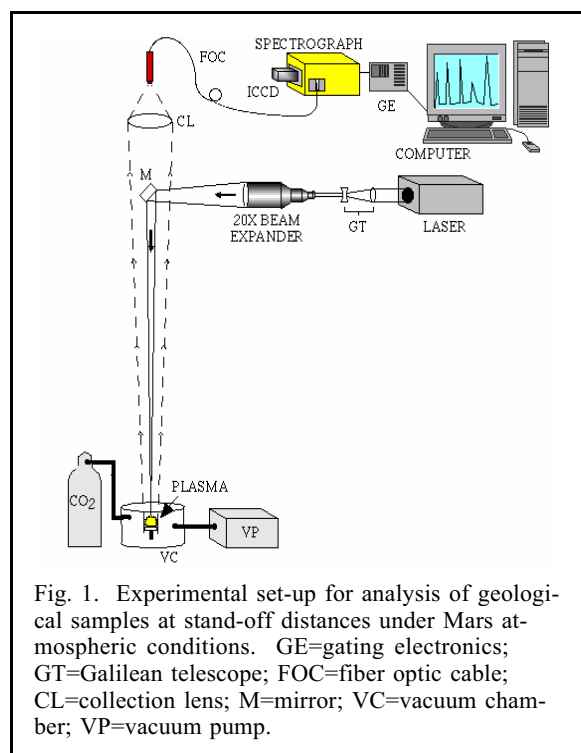In the LIBS method, powerful laser pulses are fo-

Fig. 1. Experimental set-up for analysis of geological samples at stand-off distances under Mars atmospheric conditions. GE=gating electronics; GT=Galilean telescope; FOC=fiber optic cable; CL=collection lens; M=mirror; VC=vacuum chamber; VP=vacuum pump.

cused 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
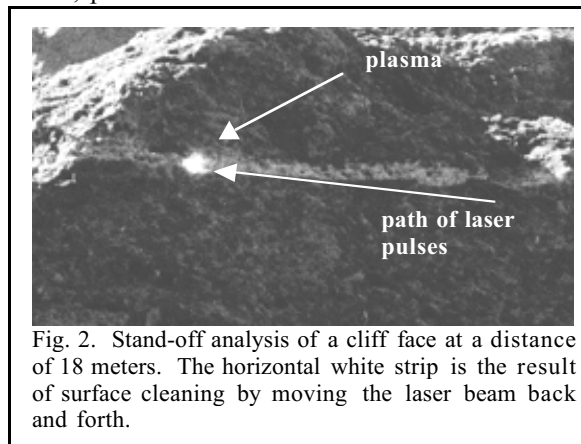

Fig. 2. Stand-off analysis of a cliff face at a distance of 18 meters. The horizontal white strip is the result of surface cleaning by moving the laser beam back and forth.

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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) stand-off analysis capability [7]; (5) ability to remove surface dusts and weathered layers to permit analysis of underlying bulk materials. 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. The use of LIBS for space applications has been discussed previously [8] but detailed studies for this application have only recently been carried out [9-11].

Experimental Apparatus: Using a laboratory "breadboard" LIBS system, a number of experiments have been carried out demonstrating the capabilities of LIBS for remote analysis. The breadboard system consists of an Nd:YAG laser (10 ns pulsewidth, 35-100 mJ/pulse, 1064 nm wavelength), a beam expander (x10 or x20) to expand and focus the pulses on the sample, a target chamber that can be adjusted to simulate the composition of the Martian atmosphere (5-8 Torr CO_2), a lens to collect the spark light and a spectrograph and optical array detector to process the spectra. Simulation of the Mars atmosphere is useful, as the plasma characteristics are affected by the partial pressure of the surrounding gas. Earlier results [9] showed that elemental emissions are significantly stronger at Mars atmospheric pressures than at Earth pressures due to increased ablation of surface material. Stand-off distances up to 19 meters between the target and the optics have been achieved [9].

Results:

Analytical Figures of Merit. Analytical figures of merit for LIBS soil analysis include detection limits, accuracy, and precision. A calibration curve for the detection of K (in 6 Torr CO_2) in a series of basalt
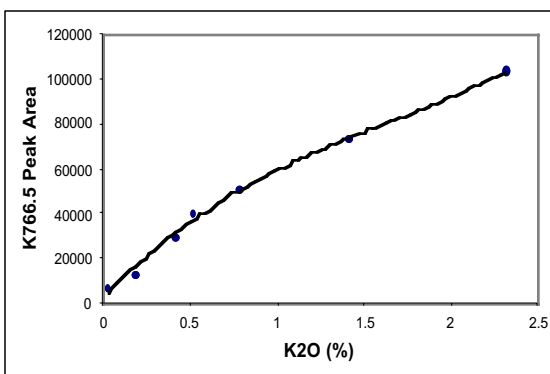

Fig. 3. Calibration curve for K (as K_2O) in basalt samples. Determination of K is being developed for use in K-Ar dating of Martian rocks.

samples is shown in Fig. 3.   Each measurement involved averaging the spectra from 20 laser plasmas. The average accuracy for the samples with the five highest K concentrations (>0.42% K_2O) was 8.1%.

Selected detection limits are presented in Table 1 for samples at a distance of 19 meters in an atmosphere of 5 Torr CO_2 and a laser energy of 100 mJ/pulse. These limits were determined by constructing a calibration curve for each element using synthetic silicate soil samples and then plotting the element signal versus concentration. Also listed in the Table is the average

Table 1. Detection limits (DL) for elements in synthetic soils at 19 meters.

element	DL(ppm)	%RSD
Ba	21	5.5
Cr	39	8.2
Cu	43	10
Hg	647	27
Li	20	8.8
Ni	224	14
Pb	95	13
Sn	84	14
Sr	1.9	6.3

precision of the measurements designated as the %RSD (% relative standard deviation). Figure 4 shows the dependence of measurement precision on the number of LIBS spectra averaged. Clearly, precision increases with the number of measurements averaged.
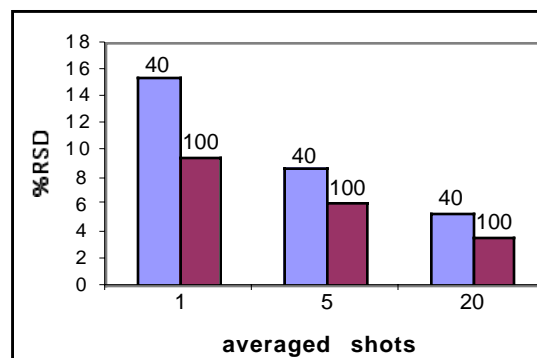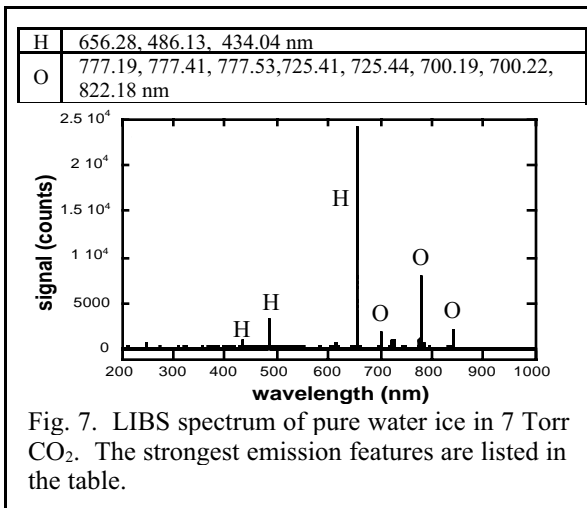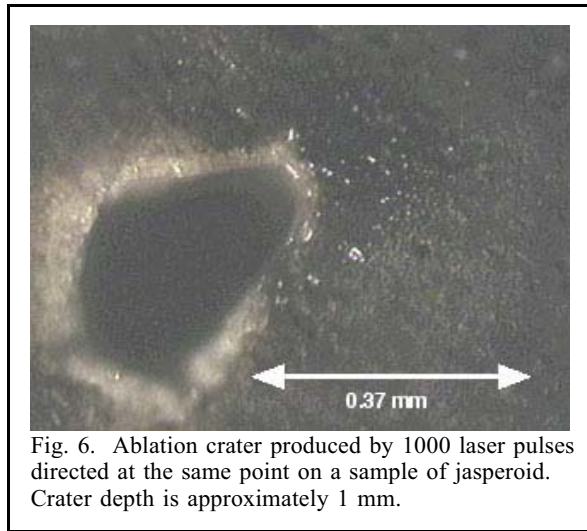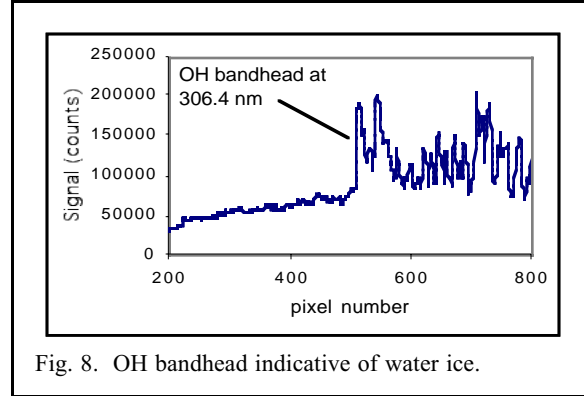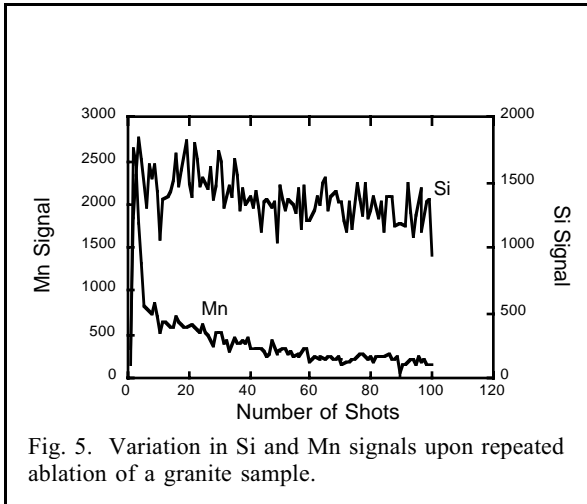

Fig. 4. Dependence of the percent relative standard deviation (%RSD) on the number of laser pulses averaged. Energies were 40 and 100 mJ.

Repetitive ablation for surface cleaning. Repetitive ablation at the same spot on the sample can be used to remove dusts and weathered surface layers. This is demonstrated in Fig. 5 illustrating the change in Mn and Si signals as a weathered granite surface is ablated. The ablation crater (depth ≈ 1mm) produced on jasperoid by repeated sampling (1000 shots) at the same spot is shown in Fig. 6.
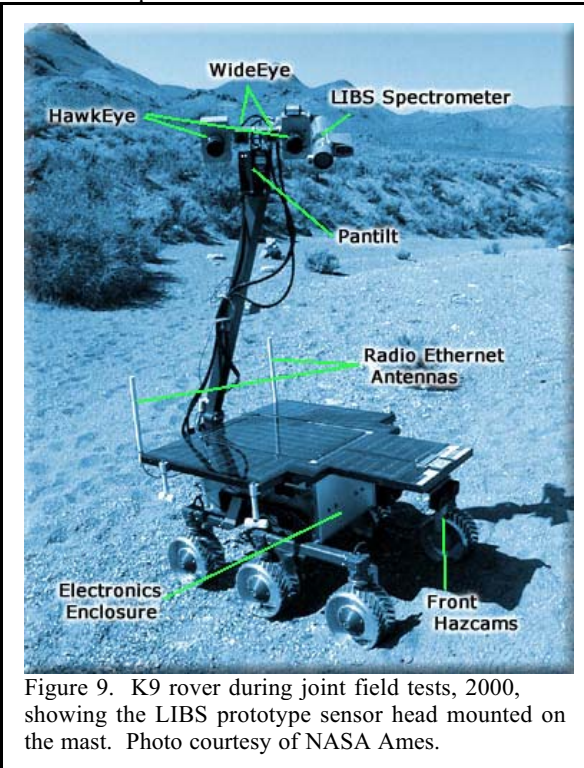
Detection of water ice. For these experiments, water ice samples and water ice/soil mixtures were positioned on a cold finger chilled by liquid N_2 or by a eutectic mixture of ethanol/dry ice. The samples were

Fig. 5. Variation in Si and Mn signals upon repeated ablation of a granite sample.

Fig. 6. Ablation crater produced by 1000 laser pulses directed at the same point on a sample of jasperoid. Crater depth is approximately 1 mm.

H	656.28, 486.13, 434.04 nm
O	777.19, 777.41, 777.53,725.41, 725.44, 700.19, 700.22, 822.18 nm

Fig. 7. LIBS spectrum of pure water ice in 7 Torr CO_2. The strongest emission features are listed in the table.

Fig. 8. OH bandhead indicative of water ice.

with a list of the stronger emission lines observed. Figure 8 shows the strong emission at 306.4 nm due to OH emission indicative of water.

Prototype Development and Testing. A relatively simple prototype LIBS instrument was built and incorporated into the NASA Ames K9 rover testbed. The instrument and testing are described in [10]. Figure 9 shows the LIBS sensor head on the right side of the K9 mast head. The spectrograph, detector, and laser power supply were contained inside the rover body. The results were compared with VISIR spectra of the same rocks. The LIBS results demonstrated the importance of obtaining elemental compositions to complement passive spectroscopy, even if the results are somewhat qualitative in nature. The results also

Figure 9. K9 rover during joint field tests, 2000, showing the LIBS prototype sensor head mounted on the mast. Photo courtesy of NASA Ames.

located in a sealed chamber containing CO_2 at 7 Torr. A spectrum of pure water ice is shown in Fig. 7 along

pointed to the importance of the depth profiling and surface cleaning capabilities of LIBS. Samples that showed IR signatures of alteration products were in

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some cases shown by LIBS to carry thin layers of alteration covering the pristine rock composition. This surface cleaning capability is expected to be all the more useful on Mars, where dust coatings are ubiquitous and the nature of surface alteration is unknown.

Our present development work is focused on improving the spectrograph and detector system in anticipation of eventually building a flight instrument. The spectrograph used for the work described in [10] was not ideal in that it had a low spectral resolution of λ/Δλ~500 and a moveable grating with a range of ~80 nm at any given time. A resolution of at least λ/Δλ~2000 is desirable, and ideally the spectral range should cover all useful emission lines from 180 to 800 nm. In reality, alternate lines can be used on a number of elements, reducing the range actually needed. We are investigating both fixed-grating spectrographs and echelle spectrographs. Echelle spectrographs have the advantage of easily accommodating the full spectral range with sufficient resolution, but they are not optimized for size and optical throughput. A relatively compact echelle spectrograph (~11x14x29 cm) was used in field work at the FIDO rover site in 2001. A LIBS spectrum from this instrument is shown in Fig. 10. We are hoping to optimize the echelle design to the point where size, optical throughput, spectral resolution, and range are all suitable for a flight LIBS instrument.

References: [1] Cremers D.A. and Radziemski L.J. (1986) Laser Spectroscopy and Its Applications; Marcel Dekker: New York; Chapter 5. [2] Radziemski L.J. and Cremers D.A. (1989) Laser-Induced Plasmas and Application; Marcel Dekker: New York; Chapter 7. [3] Moenke-Blankenburg, L. (1989) Laser micro analysis; John Wiley: New York. [4] Rusak D.A., Castle B.C., Smith B.W., Winefordner J.D. (1997) *CRC Crit. Rev. Anal. Chem., 27*, 257-290. [5] Song K.; Lee, Y-I.; Sneddon J. (2002) *J. Appl. Spectrosc. Rev., 37*, 89-117. [6] Tognoni E., Palleschi V., Corsi M., Cristoforetti G. (2002) *Spectrochim. Acta, B57*, 1115-1130. [7] Cremers D.A. (1987) *Appl. Spectrosc 41*, 1042. [8] Blacic J.D., Petit D.R., Cremers D.A., and Roessler N. (1992) *Proc. Intl. Symp. on Spectral Sensing Res.*, 302-312, Maui, HI. [9] Knight A.K., N.L. Scherbarth, N.L., Cremers, D.A., Ferris M.J. (2000) *Appl. Spectrosc., 54*, 331-340. [10] Wiens R.C., et al. (2001) *JGR-Planets, 107*, E11. [11] Fabre C., Brennetot R., Fichet P., Vors, E., Lacour J.L., Dubessy J., Boiron M.-C., Rivoallan A., Maurice S., Cremers D., and Wiens, R. (2002) Technical Digest *Laser Induced Plasma Spectroscopy and Applications*, Sept. 25-28, 2002, Orlando, Fl, 96-98.

Figure 10. LIBS spectrum of a basalt rock powder standard taken at 3 m distance during a field test, using a compact echelle spectrograph.