

ANALYSIS OF WATER ICE AND ICE/DUST MIXTURES USING LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS). D.A. Cremers¹, K. Brown¹, L. Gibson¹, M.J. Ferris¹, R.C. Wiens², S. Maurice³ and B. Sallé⁴; ¹Chemical and Advanced Diagnostics and Instrumentation, Los Alamos National Laboratory (MS J565, Los Alamos, NM 87545 USA; cremers_david@lanl.gov), ²Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545 USA; rwiens@lanl.gov), ³Observatoire Midi Pyrennees, Laboratoire d'astrophysique de Toulouse (Observatoire midi pyrennees, 14 avenue Edouard Belin, 31400 Toulouse, France; maurice@obs-mip.fr), ⁴Laboratoire d'Analyse par Laser et d'Etude des Surfaces (CEA, 91191 Gif sur Yvette, France, rivoallan@carnac.cea.fr).

Introduction: In 1992, LIBS was proposed as a new method for stand-off detection of geological samples for use on landers and rovers to Mars [1]. Recently, there has been increased interest in the technique for this and other space applications and studies have determined some of the characteristics and capabilities of the method under the conditions that these measurements will have to be made [2-4]. In addition to rocks and soils, there is interest in using LIBS to analyze ices and dusts entrained in ice. This is especially true for missions to the Mars polar regions. Of particular interest is determining the nature of polar layered deposits, the geochemistry of polar surface materials, detection of water ice and the distribution of ice, and the presence of possible organics in these materials (via C/N ratios)

Background: Briefly, LIBS is a method of elemental analysis that uses a powerful laser pulse focused on the target sample to generate a hot plasma. Material in the plasma is vaporized/atomized and the resulting atoms are excited to emit light. The plasma light is collected, spectrally resolved and detected to determine elements in the target. At stand-off distances of interest, 2-20 meters, the laser pulse can be used to interrogate solid materials. The generation of a useful laser plasma on liquids has not been demonstrated at stand-off distances. In addition, because of the reduced pressure on Mars (5-7 Torr), the generation of a free-standing plasma in the Mars atmosphere is unlikely.

Experimental: The experimental step-up used here is shown in Fig. 1. The samples were maintained in a chamber with 7 Torr CO₂ to simulate the Martian atmosphere. Ice samples were prepared by freezing water or water/soil mixtures in a small aluminum container (30 mm wide x 7 mm deep). This was accomplished by fixing the container to a copper rod that protruded into the Mars chamber. The rod external to the chamber was immersed in a dewar of liquid nitrogen to freeze the aqueous samples. The ice samples produced in this way appeared opaque and frosty rather than clear and so probably simulate the appearance of ice to be found on Mars. After freezing, the samples were rotated 90 degrees and positioned to intercept the laser pulses that were directed into the chamber horizontally. During the measurements, a constant flow of CO₂ gas was maintained through the chamber.

Laser pulses were from a Q-switched Nd:YAG laser (1-10 Hz, 1064 nm). The plasma light was collected by a 50

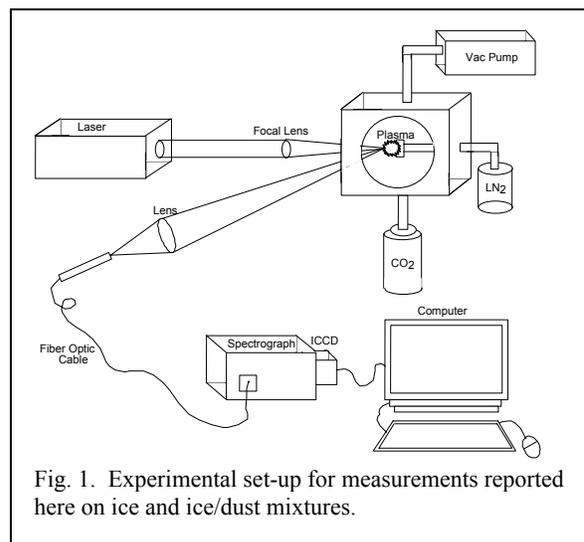


Fig. 1. Experimental set-up for measurements reported here on ice and ice/dust mixtures.

mm-diameter quartz lens and focused on the end of a fiber optic cable. The distal end of the fiber was connected to an echelle spectrograph ($\lambda/\Delta\lambda=2500$) and detected using an intensified CCD camera. The wide spectral coverage provided by the echelle spectrograph permitted recording the entire spectral region of interest for LIBS on each laser shot.

Results: Previous work has shown that a useful laser plasma can be formed on soil at 19 m using only 35 mJ of energy [2]. In the case of water ice, which is much more transparent at 1064 nm, greater energies are required and stand-off distances must be reduced for LIBS. In these experiments, using 100 mJ, it was possible to generate a laser plasma at a distance of 2 meters on the ice. At greater distances, useful spectra were not obtained with the echelle spectrograph, which requires greater incident light intensity.

Main spectral features. The LIBS spectrum of pure water ice is relatively simple compared to the spectrum from a complex sample such as soil. The main features observed were: OH (306.4 nm); H (656.2, 486.1, 432.1 nm); C (247.8 nm); O (725.4, 777.4 nm). The carbon signal was due to the 7 Torr pressure of CO₂ in the chamber. The OH feature at 306.4 nm was found to be specific for the presence of water. This feature, shown in Fig. 2, was not observed from plastics and other organic materials interrogated that contained H, C, and O.

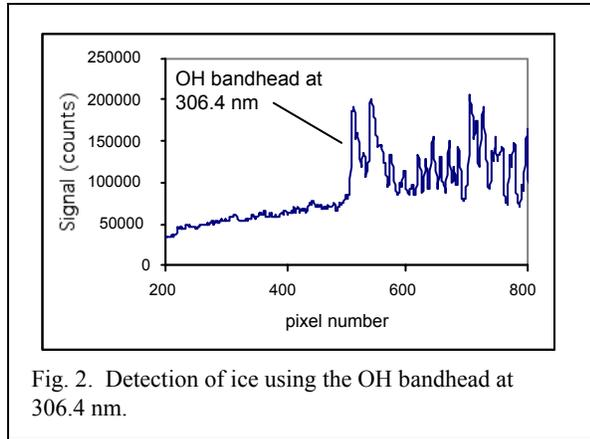


Fig. 2. Detection of ice using the OH bandhead at 306.4 nm.

Ice/soil mixtures. A LIBS spectrum of 10% soil in ice by wt. is shown in Fig. 3. The strong features due to H, O, and C are clearly evident in this complex spectrum along with features due to the elements in soil.

In addition to monitoring the presence of ice and the composition of soil, there is interest in determining the relative amounts of ice and soil in a mixture. This is possible for ice containing small amounts of soil as shown in Fig. 4.

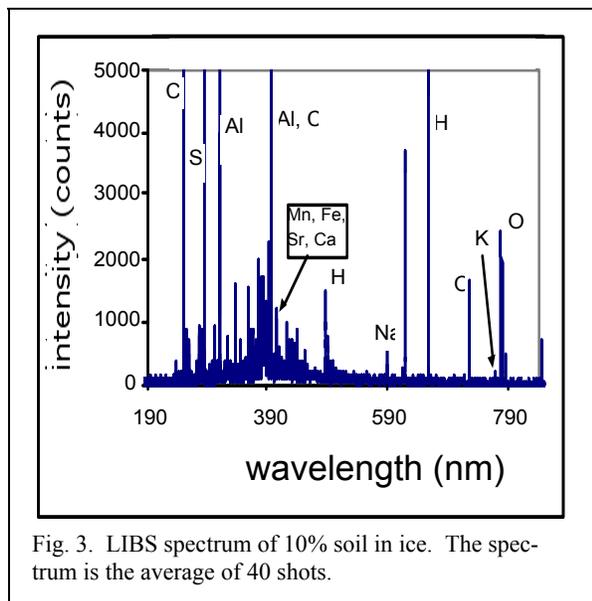


Fig. 3. LIBS spectrum of 10% soil in ice. The spectrum is the average of 40 shots.

Here, we have plotted the ratio OH/Si versus the percent soil in ice. Above 3% soil, the method becomes relatively insensitive to changes in the fraction of soil to ice.

Detection limits (DL) for various elements in soils at stand-off distances in a Mars simulated atmosphere were determined previously [2]. It is known from prior work on terrestrial soils that the presence of water can degrade detection limits. By depositing synthetic soil simulants having different (certified) concentrations of selected elements in water ice and recording LIBS spectra, detection limits in the presence of ice were determined. This was accomplished by constructing calibration curves for each element and then

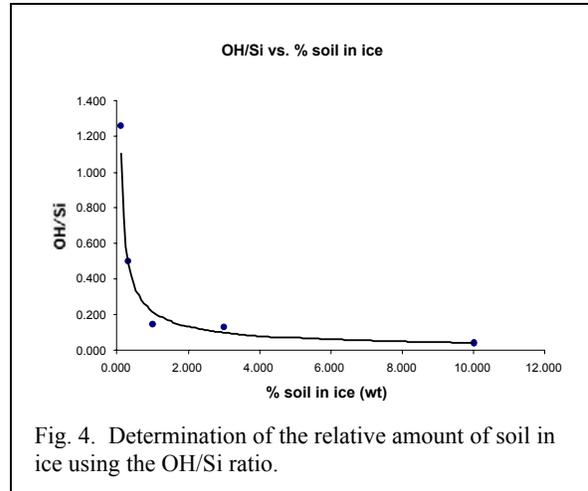


Fig. 4. Determination of the relative amount of soil in ice using the OH/Si ratio.

computing the detection limit using the formula $DL=3s/m$ (m = the slope of the linear calibration curve; s = the standard deviation of replicate measurements). The results are listed in Table 1. For comparison, DL values obtained at 19 m with dry soil in a Mars atmosphere are also listed [2]. The differences are element specific but in general somewhat greater DLs are obtained with the soil in ice.

Element	Ice/soil DL at 2 m	Dry soil DL at 19 m
Ba	192	21
Cu	24	43
Li	48	20
Mn	1023	---
Sr	88	1.9

References: [1] J.D. Blacic, D.R. Pettit, and D.A. Cremers, (1992) "Laser-Induced Breakdown Spectroscopy for Remote Elemental Analysis of Planetary Surfaces," Proceedings of the *International Symposium on Spectral Sensing Research*, Maui, HI, November 15-20, 1992. [2] Knight A.K. et al. (2000) *Appl. Spectrosc.* 54, 331. [3] 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." *JGR-Planets*, 107, E11. [4] C. Fabre, Brennetot, R., Fichet, P., Vors, E., Lacour, J.L., Dubessy, J., Boiron, M.-C., Rivoallan, A., Maurice, S., Cremers, D., and Wiens, R. (2002) "A LIBS spectral database obtained in Martian conditions with an echelle spectrometer for in situ analysis of Mars rocks and soils," Technical Digest *Laser Induced Plasma Spectroscopy and Applications*, Sept. 25-28, 2002, Orlando, FL, 96-98.