

**THE APPLICABILITY OF LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) TO MARS EXPLORATION.** R. C. Wiens<sup>1</sup>, S. Maurice<sup>2</sup>, D. A. Cremers<sup>3</sup>, and S. Chevrel<sup>2</sup> <sup>1</sup>Space and Atmospheric Sciences, Los Alamos National Laboratory (MS D466, Los Alamos, NM 87545 USA; rwiens@lanl.gov); <sup>2</sup>Observatoire Midi-Pyrénées (31500 Toulouse, France); <sup>3</sup>Chemistry and Advanced Diagnostic Instruments, LANL.

**Introduction:** Measurements of elemental composition of Mars' rocks and soils have been limited to a very few missions, most notably Viking and Mars Pathfinder [e.g., 1,2], and to the martian meteorites. While the Mars Exploration Rover (MER) missions to be launched later this year represent a significant step forward, many of the key questions of today will remain for future missions to be answered. A new technique for remote elemental composition measurements from rovers or landers is being developed in the US and France: Laser-induced breakdown spectroscopy (LIBS). Here we lay out some of the key science questions yet to be answered and explore the potential for LIBS to answer these questions.

**LIBS Overview:** The application of LIBS for planetary geochemistry has been discussed in numerous places over the past several years [3-12]. Very briefly, LIBS uses a pulsed laser beam to remotely analyze sample spots up to ~1 mm dia at distances up to ~20 m from the instrument by observing the characteristic spectral lines in the induced plasma "spark" to obtain elemental abundances. Advantages include the following:

- The technique offers nearly complete elemental coverage with low detection limits in the range of 1-500 ppm. Nearly all elements except the noble gases have useable emission lines in the range 200-800 nm. Elements typically observed above detection limits in terrestrial soils include H, Be, Li, C, O, Na, Mg, Al, Si, K, Ca, Ti, Cr, Mn, Fe, Ni, Cu, Zn, Sr, and Ba. Other elements such as B, N, S, Ag, As, Sn, Rb, Cs, Pb, and U have been seen in terrestrial soils when above normal concentrations, and still other elements can be observed if they exist at higher concentrations on Mars.
- LIBS yields very rapid, remote analysis. Each spot analysis takes approximately 2 minutes. The fact that it can analyze samples remotely increases the time advantage, as contact or in-situ techniques require hours longer to position the rover. As a result, far more LIBS analyses will be possible than in-situ or contact measurements, placing

LIBS in the same league as other remote techniques such as visible, IR, or thermal spectroscopy. With LIBS, new investigation methods become available: millimeter-sized spots on rocks up to several meters away, statistics within a field of view for different spots on a given rock, measurements well above the ground, such as on an exposed outcrop or cliff face.

- Depth profiling and removal of dust from surfaces is a significant advantage. Depths of 1-2 mm are projected to be achievable in solid rock in approximately 1 hour of analysis time, and this at distances of several meters.
- LIBS gives direct detection of water ice via both the H atomic and OH molecular lines, as discussed in a companion abstract [13].
- The technique can be tailored to different mission profiles, by adapting the spectral window and resolution to the most relevant elements for the scientific objectives of the mission.

**Key Issues in Mars Geochemistry:** Elemental composition data are fundamental to determining petrographic types and the processes that form rocks and soils (volcanism, alteration, etc.). Elemental composition can also aid in mineralogical identification. Altogether, when sufficient data are returned, the genesis of the surface and its evolution can be determined. Here are a few such issues of specific interest for Mars.

*Identification of sedimentary rocks:* The search for sedimentary rocks on Mars is crucial because of the importance of water for biological habitats. Because Pathfinder landed in flow channels, and because surface textures were suggestive of layering, a sedimentary origin of the rocks at the Pathfinder site was considered. The major element compositions were consistent with a volcanic origin [e.g., 14]; however, the ability to analyze minor and trace elements would give definitive proof of origins.

*Coatings on rocks:* Much speculation has centered on the possibility of alteration and/or weathering coatings on Mars rocks. This is true not only of ground data, but of the orbital data as

well [e.g., 15,16,17]. Use of the Rock Abrasion Tool (RAT) on MER may settle the issue of whether rock coatings exist, however, detailed analyses of the coatings themselves, if they exist, may await future missions. The relatively large footprint of the APXS does not lend itself to the use of depth profiling with the RAT.

If most rocks on Mars are found to have chemical or glassy coatings (in addition to dust coatings), LIBS may turn out to be the most useful of the remote sensing instruments because of its ability to analyze and remove such coatings. Various kinds of terrestrial chemical or glassy rock coatings make identification of the underlying mineralogy difficult to passive systems if the coatings are sufficiently thick [18].

*Determining the source of the global dust component using minor and trace elements:* Suggested origins of the sulfur-rich salt component of the Mars global dust have included "acid-fog", or volcanic aerosol [19,20], hydrothermal fluids, or weathering of pre-existing ocean deposits [e.g. 21]. The roles of hydrothermal fluids and possible oceans or standing water is of great interest, again because of its biological potential. It has been suggested that certain trace element ratios [22] will easily distinguish between the various possible origins of this salt component. Measurement of these element ratios by LIBS appears quite feasible, as discussed previously [11].

*Polar layered deposit composition variations:* The nature of the albedo variations in the polar layered deposits is currently a subject of significant speculation, but it is generally thought that understanding them will enable a much greater understanding of the recent climate history of Mars, as well as dust transport processes. If the differences between layers are due to differences in source regions of the dust, dust and water transport processes, or dust and water depositional processes, LIBS should prove highly useful, with its ability to make some determinations

of ice/dust ratios [13] measure minor and trace as well as major elements, and with its spatial resolution down to 1 mm side-to-side and on the order of microns depth-wise.

*Abundances of biogenic marker elements:* If a site with exobiological potential is found, such as a paleo-hydrothermal springs area, elemental ratios of H, C, N, O, P by LIBS may prove important in determining where in-situ analyses should be made. It is also possible that rock coatings will be informative with respect to biological activity, as in the case on Earth of Mn coatings even in the absence of sunlight [23].

**Conclusions:** LIBS is ideally suited to the types of problems in Mars geochemistry mentioned here. Based on its advantages, LIBS was selected by the MSL Science Definition Team to be part of the strawman payload for MSL.

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