Instruments of Cosmochemistry posted October 26, 2006

# LIBS : Remote Chemical Analysis

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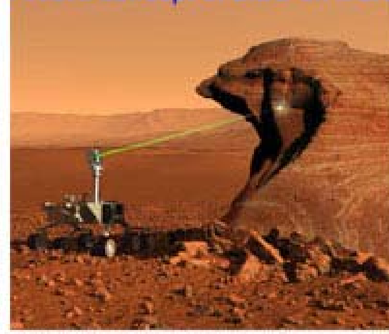
Artist's concept of LIBS on Mars



NASA/JPL-Caltech/LANL/ J.-L. Lacour, CEA

In this series of articles, "Instruments of Cosmochemistry," PSRD highlights the essential tools and amazing technology used by talented scientists seeking to unravel how the solar system formed. You will find information on how the instruments work as well as how they are helping new discoveries come to light.

## Laboratory Caliber Instrument on a Rover

Laser-induced breakdown spectroscopy (LIBS) is an active remote sensing technique used for the rapid characterization of elemental compositions of materials. Used for years in laboratory and industry applications, it will make its debut performance on rocks and soils on another planetary surface in 2012 as part of the ChemCam instrument package onboard NASA's Mars Science Laboratory (MSL) rover scheduled for a 2011 launch to Mars. A combined Raman-LIBS is also planned to be part of the Pasteur instrument payload on the ExoMars rover mission planned by the European Space Agency for a 2016 launch.

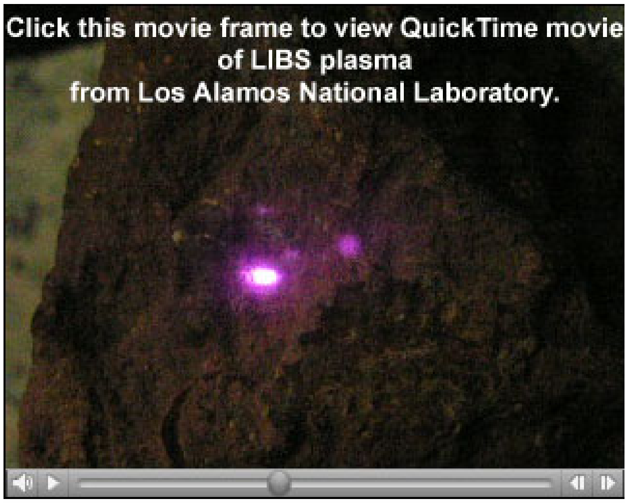
In preparation for use on Mars, a team of scientists at Los Alamos National Laboratory, Roger Wiens, Justin Thompson, James Barefield, David Vaniman, Sam Clegg, and colleague Horton Newsom (Institute of Meteoritics at the University of New Mexico) have tested the LIBS technique on two Martian meteorites and a terrestrial analog rock. Their work confirms that LIBS is capable of determining even subtle differences in rock types from a stand-off distance of 5.4 meters. This high-quality remote sensing on the surface of Mars is exactly what's needed to push the state-of-the-art of cosmochemical investigations as we prepare for follow-up Mars sample return missions.

Reference:

- Thompson, J. R., R. C. Wiens, J. E. Barefield, D. T. Vaniman, H. E. Newsom, and S. M. Clegg (2006) Remote Laser-Induced Breakdown Spectroscopy Analyses of Dar al Gani 476 and Zagami Martian Meteorites. *Journal of Geophysical Research,* v. 111, doi: 1029/2005JE002578,2006.

## How LIBS Works

Laser-induced breakdown spectroscopy (LIBS) uses a high power pulsed laser, focused on the target, to provide more than a megawatt of power on a small spot less than a millimeter diameter for a few billionths of a second. The target rock can be up to 13 meters away from the instrument (otherwise known as the stand-off distance). Each laser pulse vaporizes thin layers of the target rock--a process known as laser ablation--producing a hot spark or plasma. This supersonically expanding plasma glows with electronically excited ions, atoms, and small molecules from the target rock (see image below.)




Click on the movie frame to view a QuickTime movie in a new window.

This picture shows the glowing LIBS plasma produced in air during a laboratory test where the laser was five meters away from the rock. The high-temperature ablated material breaks down into electronically excited atoms and ions, giving off light when they decay back to lower energy levels. The light emitted by the plasma can be collected and analyzed through spectrometers to resolve the characteristic emission lines of the elements that are present in the target rock.

Original source: http://libs.lanl.gov/LIBS_movies.html. Note that the apparent wandering of the plasma position on the rock is due to motion of the rock during the test. There is no positional instability of the laser relative to the spark size.

The plasma light is collected by a reflecting telescope and directed through a fiber-optic cable to spectrometers, which resolve and measure the elemental emission lines in the plasma spectrum. In a typical analysis, the spectra from multiple pulses (for example 75 to 100 pulses) are averaged for greater statistical accuracy into one final spectrum for the analysis spot.

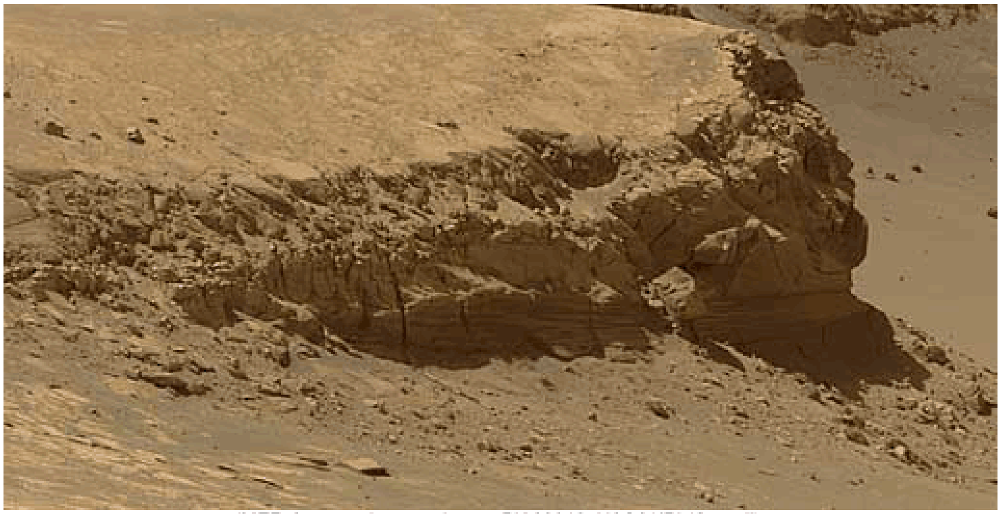
The LIBS technique yields detailed, quantitative information on compositions of the elements (high and low atomic numbers), including some minor and trace elements, that are present in the target rock. This information is obtained very quickly, within minutes, and will allow scientists to identify rocks on the surface of Mars that are of greatest interest and may be chosen for further investigation by instruments that require physical contact or for collection.

Why LIBS is an outstanding tool for planetary surface analyses:

- no sample preparation is required
- operates at a stand-off distance (typically 2-13 meters), which permits remote analysis of inaccessible rocks (perhaps up on cliff)
- the laser removes dust from target surfaces, again without the need to drive to and touch the surface
- repetitive laser pulses on the same analysis spot permits ablation down through weathering rinds to measure composition through depth profiling and examine the pristine rock chemistry
- simultaneous multi-element detection (major, minor, trace elements)
- rapid analysis (a typical analysis sequence is six minutes)
- good detection sensitivity; 10 ppm detection limits for some elements
- laser requires only an average of 3 Watts of power during the several minutes of instrument operation time

(For more details see the ChemCam Fact Sheet produced by Los Alamos National Laboratory. Link opens in a new window.)

Tall Cliff of Layered Rock at Victoria Crater, Mars



(MER Opportunity rover image PIA08810. NASA/JPL/Cornell)

This view of a cliff of layered rocks at Victoria crater was made by the panoramic camera on NASA's Mars Exploration Rover Opportunity in September, 2006. The cliff is about six meters (20 feet) tall. In the future, scientists will be able to use LIBS to analyze the rocks up on the cliff that are out of reach of the rover. Theoretically, LIBS could produce elemental profiles of the entire wall of the outcrop. [Click the image for higher resolution versions.]

## LIBS Cosmochemical Applications to Mars

The ability to identify and quantify the elemental compositions of rocks and soils on Mars is of paramount importance to understanding important issues of the planet's formation and alteration. LIBS spectra will play a vital role in allowing scientists to address these key issues:

- igneous processes and what they tell us about planetary differentiation and evolution of magma compositions through time
- sedimentary processes and what they tell us about the interactions between rock and water or atmosphere
- hydrothermal and weathering processes that have modified (or are currently altering) the Martian crust and what they tell us about the history of water on Mars
- movement and deposition of materials
- climate and habitability of Mars

In preparation for use on the Martian surface, the research team at Los Alamos and University of New Mexico tested the LIBS technique in their laboratory on natural rock samples under simulated Martian conditions. The ability of LIBS to distinguish between rocks of widely differing compositions is well known. But what Thompson, Wiens, and colleagues wanted to test specifically was the ability to remotely distinguish a range of igneous compositions on Mars. So, they chose to study two basaltic Martian meteorites with slightly different compositions and textures and an andesite rock powder standard. The team analyzed Dar al Gani 476 and Zagami, two basaltic shergottite meteorites. Both samples were in the form of sawn slabs, shown below.

(From Wiens *et al.*, 2005, *LPSC XXXVI*, abstract 2209.)

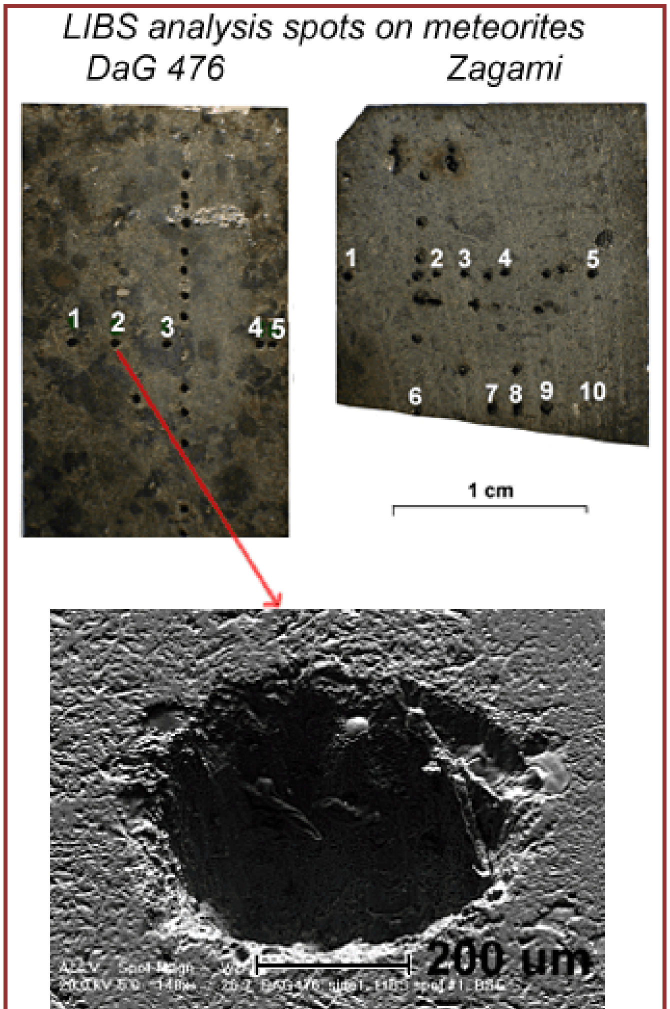
Dar al Gani 476 is a basaltic shergottite with olivine and pyroxene phenocrysts up to 5 millimeters in size set in a fine-grained groundmass of average grain size of 0.13 millimeters. This sample is roughly 1 centimeter across.

(From Wiens *et al.*, 2005, *LPSC XXXVI*, abstract 2209.)

Zagami is a basaltic shergottite described as a composite of up to three related lithologies and minor shock-melted glass. Overall this rock is finer grained than DaG 476. This sample is roughly 1.5 centimeters across.

The LIBS analyses were conducted under simulated Martian conditions, with the Martian meteorites and andesite sample each placed in a vacuum chamber maintained at a static pressure of ~7 Torr $CO_2$. Each analysis spot was shot 100 times with a pulsed Nd:YAG laser resulting in ablation pits that ranged in diameter from 0.4 to 0.5 millimeter.

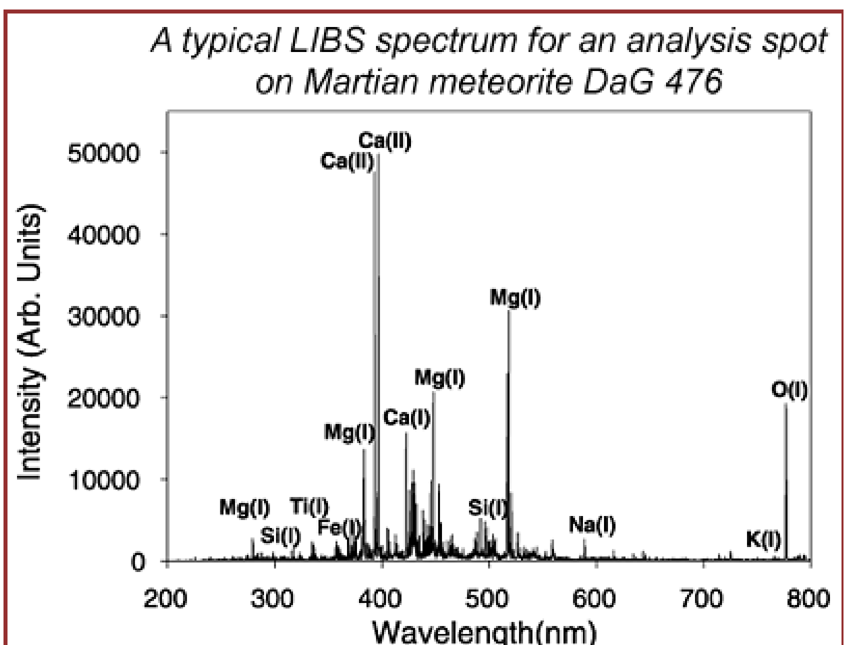
Fourteen analysis spots were recorded on DaG 476 (five are shown in the figure below) and nine spots were used on Zagami (also shown below). Thompson and his coauthors chose a larger number of analyses on DaG 476 to try to compensate for the rock's larger grain sizes.




(FromThompson *et al.*, 2006, *JGR*, v. 111, Figs. 2 and 3.)

These pictures show some of the LIBS analysis spots or pits (~400 micrometers diameter) on slabs of DaG 476 (top left) and Zagami (top right). Each pit was produced by 100 pulses of the laser beam. The red arrow from spot 2 on DaG 476 points to a magnified back-scattered electron image of the pit. Each LIBS spectrum used by the research team was produced by averaging 100 laser pulses.

A typical LIBS spectrum for an analysis spot on DaG 476 collected by the research team is shown below.

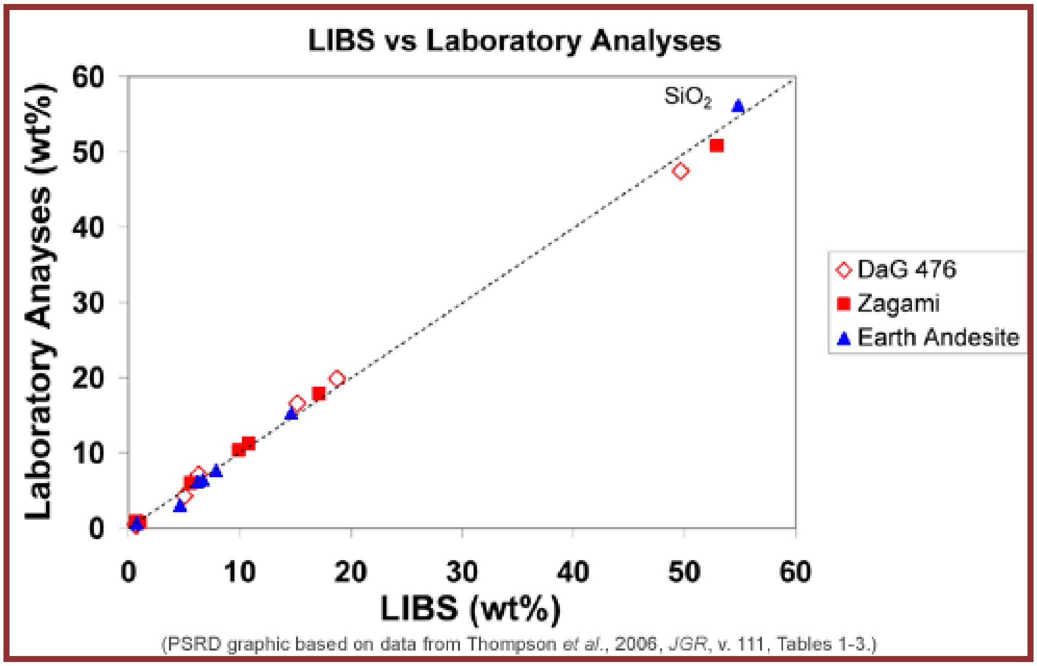


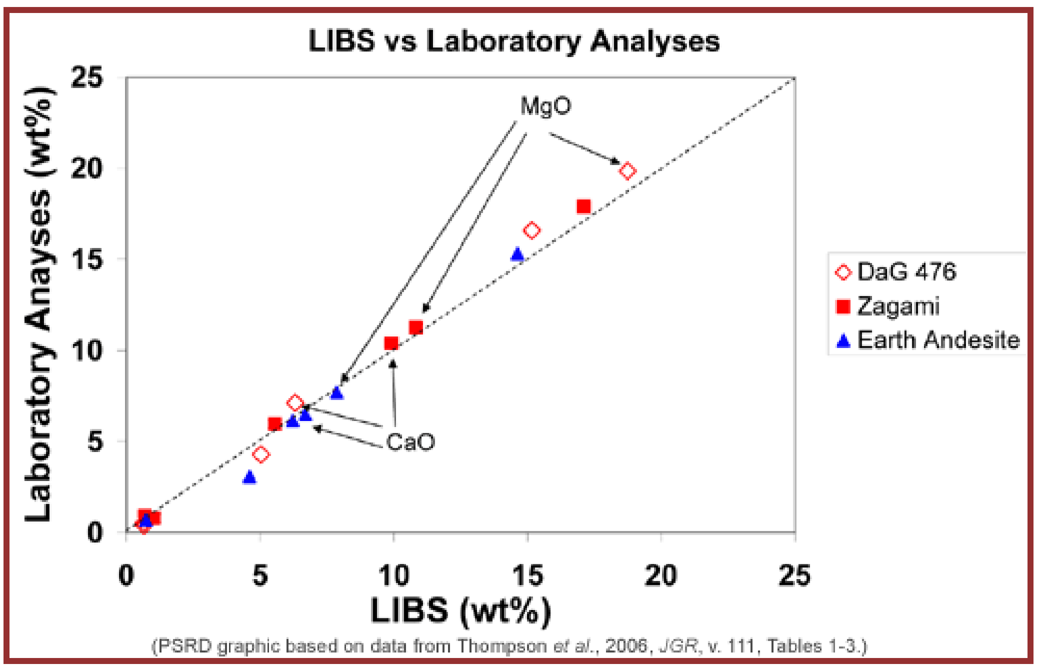

(From Thompson *et al*, 2006, *JGR*, v. 111, Fig. 4.)

Major elemental emission lines in the LIBS spectrum for DaG 476 are labeled in this plot. The Roman numeral in parentheses refers to the ionization state of the atom. (I) is an excited neutral atom, (II) is a singly-ionized atom. LIBS spectra obtained for Martian meteorite Zagami and the andesite rock powder standard

(JA-2) are similar at the level of detail shown. The spectrum was collected from a stand-off distance of 5.4 meters.

The diagrams below show how well the LIBS results compare with the average of published chemical analyses (averages of several analyses) of the two Martian meteorites and the andesite. In general, the LIBS results are within 10% of the oxide compositions reported in the literature.




Elemental compositions obtained by the research team using LIBS (shown as weight percent on the x-axis) are compared to literature whole-rock compositions (y-axis) of DaG 476, Zagami, and andesite JA-2. An exact match in oxide composition between the LIBS tests and published laboratory results would plot on the straight line. The oxides plotted here are $SiO_2$, FeO, CaO, MgO, $TiO_2$, $Al_2O_3$, and $Na_2O$. The lower plot is an enlargement of the left half of the top plot. For clarity, we have labeled the CaO and MgO data points, which are discussed below. Click here to see a table of values that were used to create these plots (table will open in a new window.)

In their study, Wiens, Thompson, and colleagues demonstrated that the LIBS technique is capable of determining subtle differences in rock types from a remote distance of 5.4 meters. The differences between LIBS and values determined by traditional laboratory techniques differed by less than 12% (relative) for most of the major elements (most were better than 6%). The agreement for titanium and sodium were not as good, but their concentrations are low (less than 1 wt%), hence the emission signals are low. The comparison with the andesite was particularly good with all elements agreeing to within 5% (relative), except for titanium. Even for titanium the difference between the LIBS and accepted concentration for the andesite was only about 8%. The andesite was a powdered sample, hence homogeneous on the scale of the LIBS laser pit. In contrast, the Martian meteorites were slabs of rock. Getting a good average analysis in this case requires numerous analytical points because sometimes the laser zaps only one mineral, other times a mixture, and so on.

The most important result of this test of LIBS analytical capability is that it is possible to distinguish between the two Martian meteorites. This is particularly noteworthy for MgO and CaO, as shown in the diagram above. DaG 476 and Zagami are clearly different in composition. This shows that LIBS will be capable of distinguishing rock types as the rover journeys across the Martian surface.

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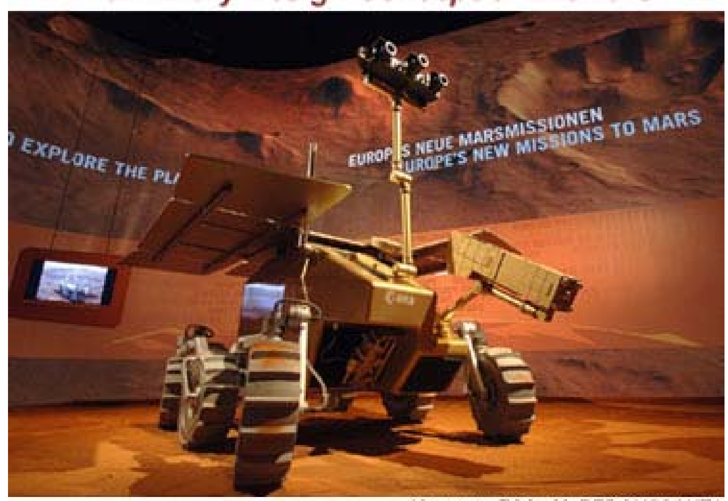
## What's Planned for LIBS on Mars

LIBS instruments are planned for NASA's Mars Science Laboratory rover (scheduled to launch in the fall of 2011) and ESA's ExoMars rover (slated for launch in 2016).

Design of Mars Science Laboratory

(Courtesy NASA/JPL-Caltech)

Preliminary Design Concept of ExoMars




(Courtesy ESA - M. PEDOUSSAUT)

Click on the images for more information about these future missions.

Mars Science Laboratory rover is designed to operate for a full Martian year, which is almost two Earth years. LIBS, as part of the ChemCam instrument package, is expected to make thousands of measurements to help scientists characterize the geology of the landing region, help analyze surface ices or salts or evaporite minerals or rocks and soils that have been altered by water, help identify possible organic materials if they exist or ever existed, and help check for toxic materials. A typical analysis sequence for LIBS will begin when the science team identifies a target rock and commands ChemCam to fire a burst of up to 75 laser pulses at a $\leq 1$ millimeter spot on the target. The rover's onboard spectrometers will determine the elemental compositions of the ablated plasma. Acquiring a LIBS spectrum for an analysis spot is expected to take six minutes. This is very rapid compared with previous techniques that have taken up to three Martian sols for analogous dust-free analyses that required contact with the target rock.

Like all scientific instruments, LIBS has to be calibrated using standards of known composition. A challenge on Mars faced by the ChemCam science team is that they will not have a suite of calibration standards that they can expose at the same conditions (distance, etc.) Roger Wiens and team are currently working on determining how the calibration curves vary with instrument-to-sample distance. They will have some calibration standards on the rover, which will be at a close range of 1.4 meters. Over time, the team will also be able to cross-calibrate between LIBS and the other ChemCam instruments APXS and CheMin. [See this ChemCam web page for additional information on the science instruments.] These aspects should allow LIBS to be an extremely useful quantitative geochemical and geological mapping tool.

The research team at Los Alamos and University of New Mexico who tested LIBS on the Martian meteorites and terrestrial analog rock, as well as other teams of cosmochemists who are working to better calibrate LIBS for the entire variety of rocks it will encounter on Mars, are eagerly anticipating what they'll see in the glowing LIBS light.

## Additional Resources

**LINKS OPEN IN A NEW WINDOW.**

- ChemCam LIBS instrument description from Jet Propulsion Laboratory.
- ExoMars mission homepage from the European Space Agency.
- LIBS planetary science applications website from Los Alamos National Laboratory.
- Mars Science Laboratory rover homepage from Jet Propulsion Laboratory.
- Thompson, J. R., R. C. Wiens, J. E. Barefield, D. T. Vaniman, H. E. Newsom, and S. M. Clegg (2006) Remote Laser-Induced Breakdown Spectroscopy Analyses of Dar al Gani 476 and Zagami Martian Meteorites. *Journal of Geophysical Research,* v. 111, doi: 1029/2005JE002578,2006.

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