Strategies for Mars remote Laser-Induced Breakdown Spectroscopy analysis of sulfur in geological samples

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ABSTRACT

The key to understanding the sulfur history on Mars is to identify and determine sulfate and sulfide compositions and then to draw from them geologic clues about their environments of formation. To lay a foundation for use of remote LIBS to sulfur analysis in planetary exploration, we have undertaken a focused study of sulfur LIBS in geological samples in a simulated Mars atmosphere, with experimental parameters replicating the ChemCam LIBS instrument. A suite of twelve samples was selected, including rocks rich in minerals representative of sulfates and sulfides that might be encountered on Mars. Univariate analysis of sulfur emission lines did not provide quantitative information. Partial least squares (PLS) analysis was successful at modeling sulfur concentrations for a subset of samples with similar matrices. Sulfide minerals were identified on the basis of other siderophile or chalcophile peaks, such as those arising from Zn and Cu. Because the S lines are very weak compared to those of other elements, optimal PLS results were obtained by restricting the wavelength range to channels close to the most intense sulfur lines ~540–570 nm. Principal components analysis was attempted on the dataset, but did not differentiate the samples into meaningful groups because the sulfur lines are not strong enough. However, areas of the relatively weak S, H, and O peaks may be used to correctly classify all samples. Based on these outcomes, a flowchart that outlines a possible decision tree for identification and quantification of sulfur in remote LIBS analysis was constructed. Results suggest that LIBS data acquired under Mars conditions can meet the science requirements for the ChemCam instrument.

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1. Introduction

From a geological perspective, sulfur is a common and significant element occurring throughout the solar system and beyond. Both direct measurements and compositions inferred from meteorites and remote spectroscopy suggest that the terrestrial planets all contain ~1–4% S by weight, with varying mineralogical and geological hosts. Light elements like S are important constituents of both surface rocks and minerals and of planetary cores, where S lowers the melting temperature of pure Fe metal in solid solutions. In our solar system, the terrestrial planets formed from accretion of planetesimals originating from a zone extending from the current position of Mercury to the current asteroid belt, and because temperatures were appropriate for S condensation at those distances from the Sun, S is widely distributed there.

For example, Mercury's core has 1–5% sulfur by weight [1]. Geochemical modeling implies that interactions between the S-rich Venusian atmosphere and surface basalts would result in the formation of many different sulfate and sulfide minerals [2]. Venus likely has a sulfur-rich core, though its concentration of sulfur is still unknown [3]. In the Earth's crust, sulfur occurs most commonly as S^{2-} in sulfides like pyrite, or as S^{6+} in sulfate (SO_4^{2-}). In Earth's interior, the observed density difference between Fe metal and the inner core is used as evidence for the presence of at least several atomic percent sulfur [4]. Finally, many direct chemical analyses of S on Mars are available: 3.1 ± 0.5 wt.% in dust and soil as measured by the Viking landers; 0.3–2.7% S reported by Mars Pathfinder [5], and 4.9–6.6% SO_3 (2.65% S) measured by the Mars Exploration Rovers [6,7]. A Mars global average surface sulfur abundance of 1.76 wt.% (4.40 wt.% SO_3) was reported based on Odyssey gamma-ray spectrometer (GRS) integrated observations [8], reflecting a mixture of soils with higher sulfur abundances and bedrock with lower average sulfur abundances. King and McLennan [9] further note that the sulfur cycle is arguably the most important geochemical cycle on Mars. Given the ubiquitous occurrence of sulfur on terrestrial planets, it is clear that

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analytical techniques for measuring sulfur with high precision and accuracy are important for planetary exploration.

In this paper, we discuss the remote analysis of sulfur in geological samples using Laser-Induced Breakdown Spectroscopy (LIBS). This technique was first proposed as an analytical technique in the mid-1960s [10] and gained popularity in the 1980s with the development of sophisticated CCD detectors and spectrographs [11]. The LIBS technique involves a laser pulse focused onto a sample to create a small plasma from which the optical emissions are recorded spectroscopically. The major emitting species of the plasma are neutral atoms and ions in the first few ionization states of the elements comprising the samples. LIBS spectra of geological samples from the near-UV to near-IR typically consist of dozens to hundreds of atomic emission lines. The basis for qualitative and quantitative chemical analysis is the dependence of the peak height on the abundance of that element in the sample.

The simplicity and versatility of the LIBS technique has allowed it to be applied to a wide variety of materials and substances in terrestrial laboratories. However, because other robust microanalytical methods for elemental analysis are available to geologists, there has been only limited interest in geological applications of the LIBS technique [e.g., reviews by 12,13]. This situation is now changing as a result of upcoming NASA missions that will use LIBS for remote exploration of planetary surfaces. ChemCam, a stand-off sensing instrument package including a laser-induced breakdown spectrometer (LIBS) and remote micro-imager (RMI), will provide geochemical analyses and context imaging as part of the Mars Science Laboratory (MSL) *Curiosity* rover payload scheduled to launch in 2011 [14,15]. The *Curiosity* LIBS instrument is designed for reconnaissance and quantitative elemental abundance determinations to a distance of 7 m from the rover. It uses a Nd:KGW laser to provide up to 17 mJ of 1067 nm light pulses to the target. The returned plasma light is collected in a 110 mm diameter telescope which, with the aid of fiber optic cables, feeds the light to three spectrometers covering the range of 240–850 nm [16]. The spectral range was selected to cover emission peaks from major and minor elements of geological importance.

LIBS is also on the payload of the Surface and Atmosphere Geochemical Explorer (SAGE) mission to Venus that was selected as one of the three candidates for the next mission in the New Frontiers Program of space ventures to celestial bodies in our solar system. Several other countries are also considering or planning to use LIBS on upcoming missions.

As noted by numerous previous workers [e.g., 17–20], LIBS is capable of sulfur analyses, both in the laboratory and as part of remote instruments. To lay a foundation for use of remote LIBS to sulfur analysis in planetary exploration, we have undertaken a focused study of sulfur LIBS in geological samples. Its first contribution is the work of Clegg et al. [21], which characterizes the sulfur emission lines seen under Mars conditions (~7 Torr CO_2) in a comprehensive fashion. LIBS spectra were acquired with 20 and 80 mJ/pulses to more clearly define the positions of sulfur emission lines and distinguish them from the overlapping Fe emission lines that are ubiquitous in the geological samples. These follow the first mention of sulfur analyses by LIBS in a Mars environment by Sallé et al. [22], who noted that while sulfur emission lines cannot be detected in air at laser energies characteristic of ChemCam, a number of emission lines are visible when under the ambient pressure at the Martian surface.

The goal of this paper is to lay out a strategy for quantitative analysis of LIBS in complex geological samples where remote analysis is used so that the samples are truly unknown in composition. We explore here the precision, accuracy, and application of sulfur LIBS analyses under Mars surface atmospheric conditions, using comparisons between univariate and multivariate techniques. Spectra of 12 sulfur-bearing rock powders were explored and analyzed by multivariate analysis using procedures developed for rock analysis by Clegg et al. [16] and Tucker et al. [23]. Results make clear the

usefulness of remote LIBS spectroscopy in quantifying elemental abundances of sulfur and in helping constrain mineralogical identification of geological materials under Mars conditions.

2. Sulfur on Mars

To constrain the types of rocks that might be encountered on Mars, a brief overview of S-bearing mineralogy reported to date is useful. Theoretical, chemical, and spectroscopic evidence suggest that abundant sulfate and sulfide minerals occur on Mars; however, only a few specific types (chemistries) of sulfate minerals have been identified on the surface. On Earth, sulfates and sulfides are found in various geologic settings including volcanic, hydrothermal, evaporitic, and low-temperature chemical-weathering environments. The key to understanding the sulfur history on Mars is to identify and determine the sulfate/sulfide compositions and then to draw from geologic clues about their environments of formation. LIBS data from ChemCam will be prepared to make these distinctions. But which of the wide variety of S-bearing mineral and rock types are likely to be encountered?

2.1. Sulfides in Martian meteorites

Sulfides have been identified in Martian meteorites, occurring as pyrite, troilite, marcasite, chalcopyrite, pentlandite, and pyrrhotite [24–30]. Polymorphic sulfides like pyrite and marcasite would probably be indistinguishable to LIBS because they are all basically combinations of the same elements. Other sulfides would be identifiable on the basis of other siderophile or chalcophile peaks, such as those arising from Zn and Cu.

2.2. Sulfates in Martian meteorites

Both hydrous and hydrated sulfates have been identified through direct observation of the Shergottite–Nakhlite–Chassignite (SNC) meteorite suite that is thought to be derived from Mars [31–43].

2.3. Sulfates on Mars via remote sensing

Telescopic observations of Mars tentatively identified weak sulfate bands in near infrared [44] and thermal infrared [45] data. From orbital Mars Global Surveyor (MGS) Thermal Emission Spectrometer (TES) data, Bandfield [46] identified a small concentration of sulfate in Acidalia Planitia (at ~10–11%) and mapped sulfate elsewhere, correlated with high-albedo regions on Mars. Using Phobos 2 ISM and TES data, sulfate was identified in the bright regions of Mars, correlated with a 3-μm water band, suggesting that the sulfates may be hydrated [47]. Data from TES show the high-albedo regions to have a spectral feature at ~6 μm suggestive of the presence of hydrated sulfates [48]. Orbital data from the European Mars Express OMEGA instrument and from the Mars Reconnaissance Orbiter CRISM instrument have indicated sulfate in Valles Marineris, Aram Chaos, Meridiani Planum, the northern polar dunes, and elsewhere [49–64] [49–64]. The OMEGA and CRISM results suggest kieserite (or szomolnokite) and gypsum; as well as unspecified "polyhydrated sulfates", possibly Mg- or Fe-bearing (possibly dehydrated ferricopiapite [65]). These observations suggest that hydrous, anhydrous, and hydrated sulfates all exist on Mars; it is likely that the LIBS protocols to be described in this paper could discriminate between them.

2.4. Sulfates on Mars detected by landers

In situ bulk element analyses at the Viking, Pathfinder (PF), and both Mars Exploration Rover (MER) landing sites indicate that sulfur is present in the Martian soil (~5–10% by weight SO_3) (e.g., [66–72]) and it dominantly resides in sulfates [73–79]. Because cohesive soils