DECIPHERING SAMPLE AND ATMOSPHERIC OXYGEN CONTENTS WITH CHEMCAM ON MARS.

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Introduction: ChemCam is a Laser-Induced Breakdown Spectroscopy (LIBS) experiment onboard *Curiosity*, the rover of Mars Science Laboratory [1; 2]. Spectra obtained through LIBS are very rich in information, with several lines per chemical element [3]. Multivariate analyses of LIBS spectra has proved effective in removing systematic bias and extracting results such as the composition of the target [4; 5; 6].

In some cases, it is still useful to work with only one or a few lines, which must be corrected first for physical and chemical matrix effects (e.g. [7]). Such corrections can be based on internal normalization, i.e. by using a signal in the spectrum strongly sensitive to these effects. For example, in lunar gamma-ray processing, the oxygen line intensity at the poles was used to evaluate non-compositional fluctuations in the time-series [8], especially since the oxygen content in the regolith varies much less than the abundances of the other major elements.

Here, we evaluate whether one of the LIBS oxygen lines can be used to quantify the oxygen content in target samples, in the atmosphere, or to normalize other element lines of interest. The measurements presented were obtained with the Engineering Qualification Model of the Mast Unit (i.e., laser and telescope) but using commercial spectrometers.

LIBS Oxygen Lines: Sixteen oxygen lines were identified in ChemCam spectra during calibrations [9], all in the visible-near-infrared spectrometer range ($500 < \lambda < 900$ nm). The most intense line, at 777.6 nm, is actually a triplet, but only two lines can be seen with the resolution of the laboratory spectrometer, and we will report here the maximum intensity of this line complex.

Laboratory Measurements: ChemCam focuses a powerful laser on a target, which ablates and vaporizes a few nanograms of material, creating a plasma of ionized atoms. The plasma is so hot (typically 10,000 K) that it also heats and ionizes the surrounding atmosphere. Excited atoms return to equilibrium and recombine while emitting photons.

Like all the LIBS lines, the oxygen line intensity varies with the pressure of the gas surrounding the sample (Fig. 1), with a maximum around a few mbar, a typical pressure at the surface of Mars [10; 11].

Although the intensities in different gases are not directly comparable (due to different conductivities and ionization energies), Fig. 1 and Fig. 2 suggest a significant contribution from the oxygen present in the atmosphere: The line intensity in air (as 23 wt% O_2) and in the martian atmosphere (as 97 wt% CO_2), which both have significant amounts of oxygen, is much stronger than in nitrogen when the contribution comes exclusively from the sample (here a picritic basalt similar to one of the flight calibration targets mounted on the rover, with a total of about 51 wt% O in various oxides [12]).

Because the trend defined by the three gases is the same as a function of pressure (Fig. 1), we believe that the oxygen line is a good candidate to monitor systematic effects associated with LIBS emissions, such as the coupling between the laser and the target.

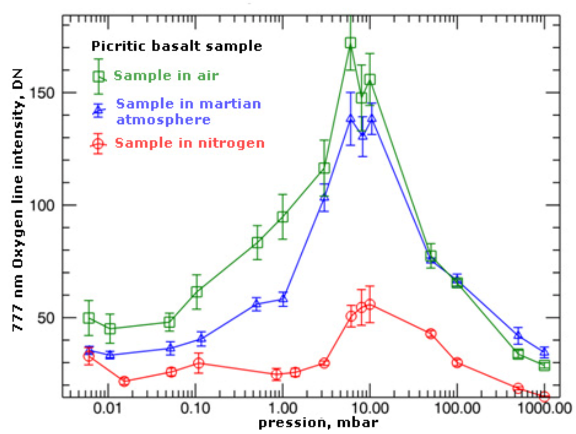

Figure 1: Intensity of the oxygen line as a function of atmospheric pressure, using a picritic basalt target and 3 different atmosphere compositions: two with oxygen (Earth and Mars) and one with no oxygen (nitrogen).

Under both terrestrial and martian atmospheres, the oxygen line intensity is slightly stronger with an AlSi plate than with the picritic basalt (Fig. 2), though the former (an alloy made of 88 wt% Al and 12 wt% Si) contains almost no oxygen. This observation supports the idea that free oxygen atoms are excited easily when present, although the quantity of excited atoms may also depend on the other properties of the target. There are only two cases where the relative line intensity reflects primarily the oxygen content in the target: (1) when the oxygen content in the atmosphere is negligible (e.g. the nitrogen case in Fig. 2); and (2) when the samples are comparable in terms of physical and chemical matrix effects involved in LIBS.

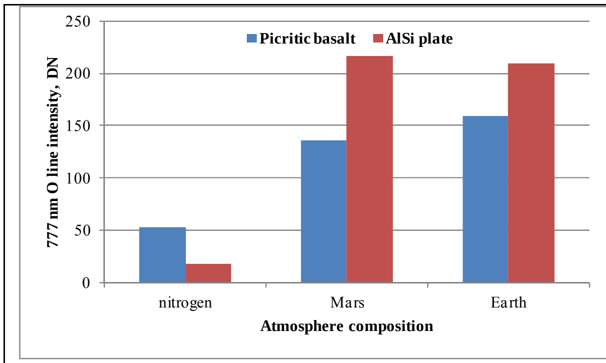

Figure 2: Intensity of the oxygen line around 8 mbar for 3 atmospheric and 2 target compositions.

Discussion: The LIBS signal from the atmosphere is less subject to inverse Bremsstrahlung absorption than the signal coming from the plasma center, i.e. from the target. It is therefore not surprising that the experiment is sensitive to the presence of oxygen in the atmosphere.

The results presented here illustrate how difficult it may be to distinguish an atmospheric contribution from the sample contribution in the LIBS oxygen lines. Although it has been shown that ChemCam is sensitive to variations of the oxygen content in the target, the atmospheric oxygen signal dominates. Variations in the atmospheric properties (like in this experiment) or in the plasma properties would induce variations in the atmospheric oxygen signal. However variations in the atmospheric conditions at the landing site should be negligible for LIBS physics. Therefore on Mars, only the plama properties, such as its temperature, will vary from one measurement to another, which may be monitored through the oxygen line.

The plasma temperature is a function of many parameters, including the quality of the coupling between the laser and the target, the strength and the composition of the target, and the properties (particularly composition and pressure) of the surrounding atmosphere.

Conclusion: To first order, the oxygen line intensity at 777.6 nm seems to be a good proxy for internal normalization of the LIBS signal. An alternative approach would be to normalize to the total intensity of the spectrum; such normalizations are necessary when comparing lines from several measurements. The use of single emission lines normalized to oxygen or total emission is complementary to the techniques that perform statistical analyses of the full spectrum.

On targets fairly comparable, such as surficial materials on Mars, one may to first order assume that the LIBS conditions are similar enough to use these types of normalization. Preliminary work on iron oxides shows that in these cases the relative oxygen line intensities are correlated to the oxygen content in the samples [13]. This result suggests that ChemCam measurements on Mars will also be indicative of the oxygen present in the samples in some conditions. More calibration studies are in progress to demonstrate these capabilities.

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www.msl-chemcam.com

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