

Laser-induced breakdown spectroscopy measurement under low pressure simulating vacuum conditions

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Abstract

Laser-induced breakdown spectroscopy (LIBS) is a very useful elemental analysis tool in planetary exploration. In this study we conduct LIBS measurements under low pressure (1×10^{-3} mbar) to investigate the feasibility of LIBS measurement under vacuum conditions. Although the optical emission intensity decreases remarkably under low ambient pressure, our preliminary experimental results indicate that the precision of elemental abundance measurements does not decrease drastically even under 1×10^{-3} mbar. This suggests that LIBS can be used at the surface of airless bodies, such as the Moon and asteroids.

1. Introduction

LIBS for planetary exploration has been mainly developed for Mars exploration so far [e.g., 5]. It is known that the intensity of emission lines depends on the ambient pressure and is drastically reduced under vacuum conditions [e.g., 2, 4]. This might be disadvantage for LIBS measurement on airless bodies. Therefore we examine the prediction precision for several elements under low-pressure conditions that simulates vacuum conditions.

2. Methods

First, we acquired LIBS spectra of rock samples. Samples were set in the vacuum chamber. The distance from LIBS to the sample is 3 m. Laser pulse energy and laser intensity are ~ 50 mJ and $\sim 1 \times 10^9$ W/cm² respectively at the surface of samples. The measured wavelength range is from 300 to 900 nm, and the wavelength resolution is ~ 1 nm. We used 15 igneous rock samples, the elemental abundances of which had been measured with XRF. Air is filled in the chamber with pressures of 1 bar or $\sim 1 \times 10^{-3}$ mbar. It is known that 1×10^{-3} mbar is enough to simulate

laser ablation in high vacuum conditions less than 1×10^{-3} mbar [2]. This is because mean free path is larger than the scale of laser plumes. The light collecting mirror of 50-, 75-, or 150-mm diameter was used to control the amount of the light introduced in the spectrometer, changing the S/N ratio of the spectra. In each experimental run 100 spectra were accumulated. Then, the spectra were analyzed using partial least squares regression (PLS-2), which is one of the multivariate statistical analysis methods [e.g., 1, 3] to predict the elemental abundances of samples. We evaluate the prediction precision using root mean squared error (RMSE) for each element: $RMSE = \left\{ \sum_i (y_i - \hat{y}_i)^2 / z \right\}^{1/2}$, where z is the number of the samples, and XRF-measured and predicted elemental abundance for sample i are denoted by y_i and \hat{y}_i , respectively.

3. Results and discussions

3.1 Comparison of Spectra

Examples of the acquired spectra are shown in Figure

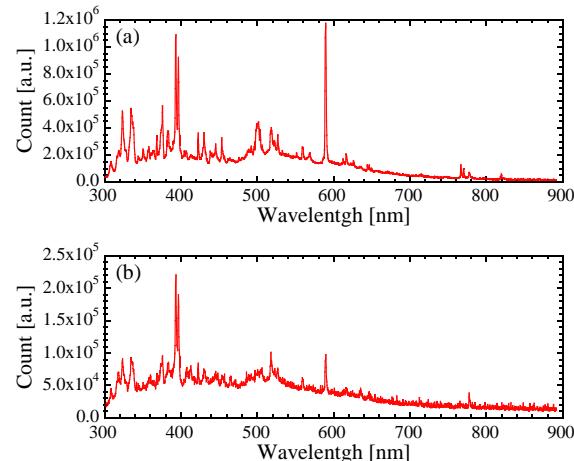


Figure 1. Example LIBS spectra of basalt: (a) 1 bar and (b) 1×10^{-3} mbar.

1. The intensity of the emission lines in the 1×10^{-3} -mbar case is about one order of magnitude lower than the 1-bar case, and S/N ratio decreases with decreasing ambient pressure. Furthermore, the relative intensities of emission lines vary when the ambient pressure changes. For example, low pressure reverses the ratio of the Na emission line at ~ 590 nm to the Ca and Al emission lines at ~ 390 -400 nm.

3.2 Comparison of prediction precision

Figure 2 shows the comparison of RMSE in various experimental conditions for each element. They show that the prediction precision does not change drastically between 1-bar and 1×10^{-3} -mbar cases although for some elements, such as Fe, K, and Si, it becomes systematically slightly worse in the 1×10^{-3} -mbar cases. The elements that have no pressure dependence on prediction precision tend to have relatively strong emission lines within the wavelength range of our measurement (i.e., 300-900 nm) while Fe, K, and Si do not. The reason why the prediction precision becomes worse in the 1×10^{-3} -mbar case may be because plasma temperature is lower than in the 1-bar case, leading to disappearance of emission lines that need high temperatures to appear. The prediction precision of these elements may be improved by increasing the laser intensity that causes high plasma temperature and/or including the wavelength range where strong emission lines of those elements exist (e.g., UV range). It should be

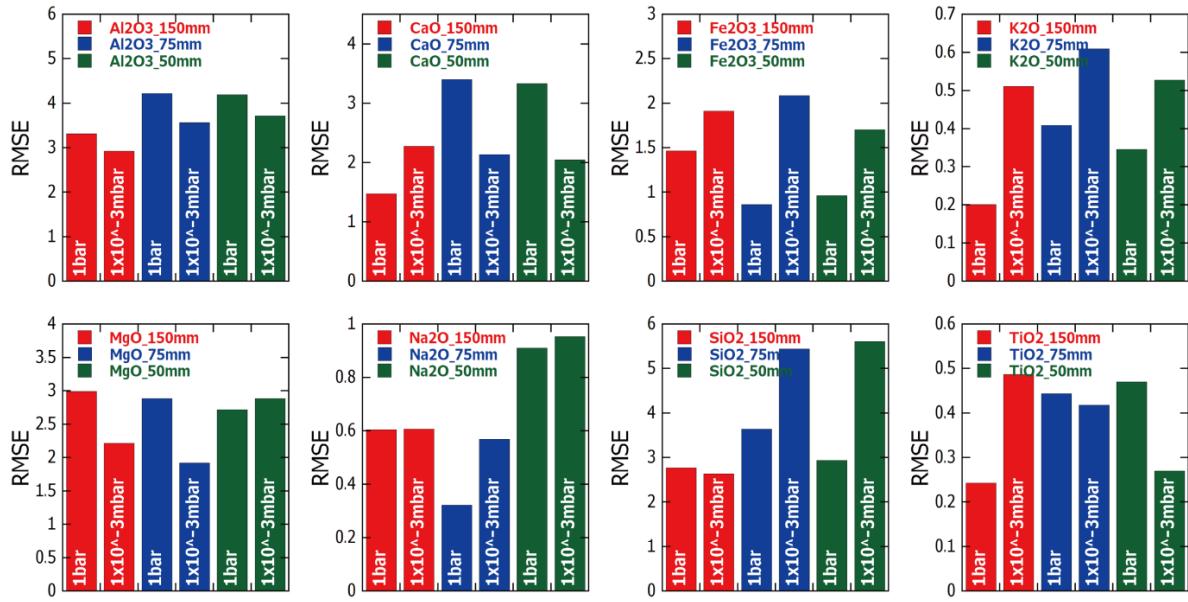


Figure 2. Comparison of RMSE under the ambient pressure of 1 bar and 1×10^{-3} mbar. The diameter of light collecting mirror is 150 mm (red), 75 mm (blue), and 50 mm (green).

noted that decrease in prediction precision does not occur when the amount of plasma light introduced in the spectrometer is reduced. This suggests that S/N ratio does not affect the prediction precision under our experimental conditions. Our preliminary results suggest that LIBS has a potential for being a useful elemental analysis tool even for high vacuum conditions, such as the surface of the Moon, satellites and asteroids.

References

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