PREDICTION OF THE ELEMENTAL COMPOSITION OF OLIVINE BY LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS).

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Introduction: Laser-induced breakdown spectroscopy (LIBS) is one of the elemental analysis methods [e.g., 1]. Pulsed laser beams are irradiated on targets to produce plasmas, and the emitted lights from plasmas are measured with a spectrometer. Qualitative and quantitative analysis can be carried out by analyzing the acquired spectra. LIBS has a potential for being a powerful elemental analysis method for satellite and planetary explorations, such as the Moon, Mars, Venus, and other planetary bodies [e.g., 2-4].

LIBS has a high spatial resolution because typically the laser beam spot of LIBS is much less than 1 mm. Therefore, LIBS has a potential for measuring minerals that are the components of rocks. In this study we investigated the possibility of predicting the elemental abundance of olivine, which is one of the important minerals, as a first step. We also investigated the effect of sample surface conditions and laser irradiation conditions on the prediction accuracy.

Reference samples are required for quantitative analysis of unknown samples. We have been using reference samples that have the bulk composition of rocks for quantitative analysis of homogeneous rock samples [2]. We have tested the elemental-abundance prediction of olivine with those reference samples. However, the prediction accuracy was extremely low; the relative error is more than several tens of percent. This might be because the compositions of reference samples are different from olivine or because the surface conditions of the unknown samples are different from those of the reference samples. Thus, we prepared the reference samples specialized for olivine analysis and the unknown olivine samples in different surface conditions.

Experiments: First, we prepared olivine samples and reference samples. Then, we acquired the LIBS spectra of them. The acquired spectra were analyzed using partial least squares regression method.

Sample preparation. Two types of olivine samples are prepared as "unknown" samples, which simulate different surface conditions. One is a single crystal olivine and the other is a pressed aggregate of olivine small grains; we call them "chip" and "pellet", respectively. The grain size is several tens of μm. The composition of the olivine we prepared was measured with EDX. The Mg number of the olivine is ~90.

We also prepared reference samples specialized for olivine analysis. The composition of them should have near-olivine compositions with wide ranged Mg number. We made reference samples with SiO_2, MgO, and Fe_2O_3 reagents. Those reagents were mixed well in appropriate ratios, and pressed. The size of reagent powder particles is sub-μm. Note that the elementally compositions of the reference samples are slightly different from olivine compositions. This is because we use a Fe_2O_3 reagent (trivalent Fe) though Fe exists as FeO (bivalent Fe) in olivine. Only the Fe and Mg mol abundances are matched with olivine compositions, resulting in different Si and O abundances from olivine.

LIBS measurement. We acquired the LIBS spectra of the olivine samples and the reference samples. LIBS system is composed of a Nd: YAG laser (Surelite I-20, continuum), a spectrometer (USB2000+, OceanOptics), and optical systems for laser beam focusing and plasma light collection.

The samples were set on a stage in a vacuum chamber. The chamber was evacuated until the pressure of 1×10^{-1} Pa was achieved. Then pulsed laser beams were irradiated on the samples. The spectra of olivine samples were acquired with laser pulse energy of 20 mJ, which corresponds to 2.7×10^9 W/cm^2 intensity, and those of reference samples were acquired with laser pulse energy of both 10 and 20 mJ, which correspond to 1.3×10^9 and 2.7×10^9 W/cm^2 intensity, respectively. All the other experimental conditions were the same for all samples: The beam spot size at the sample is ~400μm, the measured wavelength range is 300-800 nm, the wavelength resolution is ~1 nm, the exposure time is 500 msec, the ambient atmosphere is the air with 1×10^{-1} Pa, and the distance from LIBS system to the samples is 3 m. In each experimental run 100 spectra were accumulated.

PLS analysis. We analyzed the acquired spectra using partial least squares regression (PLS), which is one of the multivariate analysis methods [e.g., 5]. PLS carries out regression using the extracted components from raw spectra that correlate well with the elemental abundances. Since the information irrelevant to elemental abundances, which cause the prediction error, should be eliminated, the prediction accuracy by PLS is expected to be better than that by the typical calibration curve method.

Results and discussion: Figure 1(a) shows the LIBS spectra of olivine samples for different experimental conditions, and Figure 1(b) shows the spectra moralized by the spectrum of the chip sample irra-
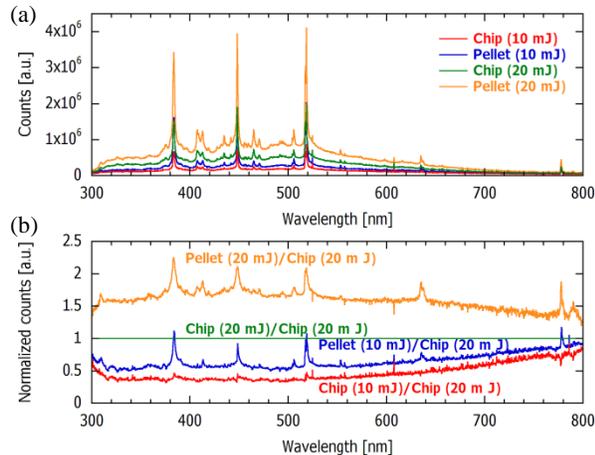
Figure 1. (a) The acquired row spectra of olivine samples in different experimental conditions: the chip olivine and the pellet olivine, both of which are irradiated with 10 and 20 mJ laser pulses. (b) The spectra normalized by the spectrum of the pellet olivine irradiated with 20 mJ laser pulses.
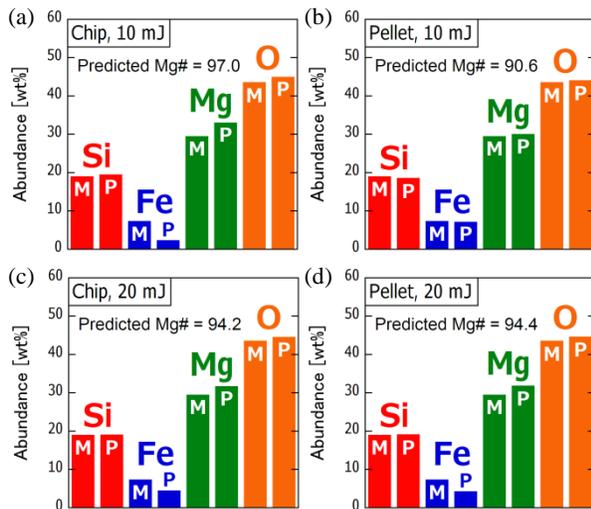
Figure 2. The results of elemental abundance prediction for (a) the chip irradiated with 10 mJ laser pulses, (b) the pellet irradiated with 10 mJ laser pulses (c) the chip irradiated with 20 mJ laser pulses, and (d) the pellet irradiated with 20 mJ laser pulses. "M" and "P" denote the measured value and the predicted value, respectively. The predicted Mg numbers are also indicated for each case.

diated by 20 mJ laser pulses. They indicate that both the absolute intensity of spectra and the relative intensities of emission lines are different for all spectra.

Figure 2 shows the comparison of measured (i.e., true) and predicted elemental abundance for each experimental condition. In every case relative prediction error is less than 10% except for Fe, and the prediction accuracy is almost the same.

The reference samples and the olivine samples are in different surface conditions: the reference samples are made of fine reagent powders, one of the olivine

samples is a single crystal, and the other olivine sample is a pressed aggregate of olivine small grains. However, regardless of such different sample conditions, the elemental abundance prediction could be carried out for the chip and the pellet olivine with almost the same accuracy.

Although the LIBS spectra of reference samples were acquired with 20 mJ laser pulses (i.e., 1.3×10^9 W/cm^2), the prediction accuracy were almost the same for both olivine-sample spectra acquired with 10 mJ (i.e., 1.3×10^9 W/cm^2) and 20 mJ (i.e., 2.7×10^9 W/cm^2). This indicates that the laser energy or laser intensity does not affect the prediction accuracy.

Note that there exists a systematic error: In every case the prediction value for Fe is smaller and the prediction values for Mg and O are larger than the true values, which leads to the higher predicted Mg number than true value of 90. Although such a small systematic error exists, the experimental results indicate that the prediction accuracy does not significantly differ regardless of the sample conditions and the laser irradiation conditions.

Effect of elemental composition of reference samples. The systematic error appeared in elemental abundance prediction might be due to the systematic deviation of the elemental composition of reference samples from true olivine compositions. The results indicate that even PLS cannot overcome completely such kind of systematic deviation in reference samples. The reference samples that have precise olivine compositions should be prepared for more accurate prediction.

Effect of surface condition of samples and laser intensity. The experimental results indicate that the surface conditions of the olivine samples and the reference samples do not affect the prediction accuracy. This suggests that materials in various conditions can be used as reference samples as long as the elemental compositions are appropriate and that unknown samples in various surface conditions can be measured. The experimental results also show that the laser energy and intensity do not affect the prediction accuracy. This suggests that the elemental abundance prediction is possible even if the laser output were slightly changed from that for reference data acquisition or even if the laser intensity were changed by poor focusing of laser beam. These features are of advantage when we use LIBS in planetary exploration.

References: [1] Cremers, D. A. and Radziemski, L. J. (2006) *Handbook of Laser-Induced Breakdown Spectroscopy.* [2] Ishibashi, K. et al. (2010) EPSC Abstracts Vol. 5, EPSC2010-453, [3] Wiens, R. et al. (2005) *LPS XXXVI,* Abstract #1580. [4] Sharma, S. K. et al. (2009) *LPS XL,* Abstract #2548. [5] Clegg S. M. et al. (2009) *Spectrochim. Acta Part B 64,* 79–88.