ANALYSIS METHOD FOR MINERALS WITH LASER-INDUCED BREAKDOWN SPECTROSCOPY (LIBS) FOR IN-SITU LUNAR MINERAL MEASUREMENT.
K. Ishibashi[1], T. Arai[1], K. Wada[1], M. Kobayashi[1], S. Ohno[1], H. Senshu[1], N. Namiki[1], T. Matsui[1], S. Kameda[2], Y. Cho[3], and S. Sugita[4], [1]Planetary Exploration Research Center, Chiba Institute of Technology (2-17-1 Tsudanuma, Narashino, Chiba 275-0016, Japan; ko.ishibashi@perc.it-chiba.ac.jp), [2]Col. of Sci., Rikkyo Univ. (Tokyo, Japan), [3]Dept. of Earth and Planet. Sci., Univ. of Tokyo (Tokyo, Japan), [4]Dept. of Comp. Sci. & Eng., Univ. of Tokyo (Chiba, Japan).

Introduction: Laser-induced breakdown spectroscopy (LIBS) is the elemental analysis method that uses pulsed laser beams to generate plasmas of a small amount of a sample and a spectrometer to measure the light emitted by excited atomic and ionic species in the plasma. Both qualitative and quantitative analyses are carried out by analyzing the acquired spectra [e.g., 1, 2]. LIBS is expected to be a new analyzing method for future lunar and planetary landing missions. LIBS is going to be used in planetary exploration for the first time in Mars Science Laboratory Mission launched in 2011 [3].

LIBS has several advantages for in-situ planetary surface explorations such as ability of analyzing almost all elements including light elements, high spatial resolution (several tens to several hundred of micrometers), capability of remote analysis (up to ten meters or more depending on laser intensity), and rapid data acquisition (a few second to a few minutes) [e.g., 2]. LIBS also has a disadvantage. Physical properties and elemental compositions of samples affect the intensity of emission lines of elements, which are called physical matrix effects and chemical matrix effects, respectively [e.g., 1, 2]. Matrix effects alter the intensity of emission lines even though both the elemental abundance of samples and the laser irradiation condition remain constant, leading to decrease in analytical accuracy. However, recent studies show that the use of multivariate statistical analysis for analyzing LIBS spectra can overcome this problem [4, 5].

Since LIBS has high spatial resolution of several tens to hundreds micrometers, LIBS is capable of analyzing individual minerals in rocks. Although LIBS measurements of samples that have bulk rock composition have been studied [e.g., 4, 5], the measurement of elemental composition of minerals has not been investigated intensively so far. In this study, we examined mineral measurement with LIBS, excluding the influence of matrix effects. Measurement of two of the major lunar minerals, olivine and plagioclase, was tested.

Methods: The number of major elements included in minerals is limited and the ranges of elemental composition of minerals are also limited stoichiometrically. That is, unlike the rocks that are compounds of multiple minerals, each mineral has a specific and inherent elemental composition. This may cause strong chemical matrix effects. Thus, measurement of minerals should be conducted for each mineral separately to measure elemental compositions with high accuracy.

Several olivine and plagioclase samples included in rocks and meteorites were prepared. The pressed-powder samples that have the elemental composition of olivine and plagioclase were also prepared to simulate the samples of different physical properties. The elemental compositions of the samples are listed in Table 1 with Mg# (defined as Mg/(Mg+Fe)×100 in molar ratio) for olivine and An value (defined as Ca/(Ca+Na)×100 in molar ratio) for plagioclase. LIBS spectra of the samples were acquired with a LIBS system, which has a feasible specification for lunar explorations.

Then, the acquired LIBS spectra were analyzed with partial least squares (PLS) regression to predict the elemental abundances. PLS extracts the information that correlated well with elemental abundances from spectra data, and regression models are constructed with that. Thus, PLS is expected to eliminate the influence of physical matrix effects caused by the physical property of samples. PLS requires reference samples the elemental compositions of which are known. Here, we tested two types of analyses for both minerals separately. Type I analysis: One sample is regarded as an unknown sample and all the other samples are regarded as reference samples. Then, this process was conducted for all samples in rotation. Type II analysis: The mineral samples are regarded as unknown samples, and the pressed-powder samples are regarded as reference samples. The elemental abundances were predicted with PLS, and Mg# and An value were calculated with the predicted values.

Results and Discussions: We evaluated the prediction precision with root mean squared error of prediction (RMSEP $= \sqrt{\sum_{i=1}^{n}(y_i - \hat{y}_i)^2/n}$, where y_i is the measured value, $\hat{y}_i$ is the predicted value, i is the subscript for samples, n is the number of samples).

Table 1. Composition of the samples.

Olivine, Mg#	83.9, 87.8, 90.2, 90.2, 90.9, 91.2
Olivine-composition pressed powder, Mg#	75.0, 77.5, 80.0, 82.5, 85.0, 87.5, 90.0, 91.1
Plagioclase, An value	75.5, 82.4, 83.0, 92.5, 95.3, 96.1, 96.6, 97.4
Plagioclase-composition pressed powder, An value	72.5, 77.5, 82.5, 87.5, 92.5, 97.5

Table 2. RMSEP for olivine.

Sample		Mg [mol%]	Fe [mol%]	Si [mol%]	O [mol%]	Mg#
Type I	Olivine	0.35	0.31	0.011	0.017	1.11
	Pressed powder	0.33	0.29	0.046	0.034	1.03
	All	0.32	0.28	0.031	0.025	0.99
Type II	Olivine	1.47	1.39	0.076	0.046	4.94

Table 3. RMSEP for plagioclase.

Sample		Ca [mol%]	Na [mol%]	Al [mol%]	Si [mol%]	O [mol%]	An value
Type I	Plagioclase	0.31	0.20	0.29	0.22	0.044	2.59
	Pressed powder	0.11	0.12	0.12	0.12	0.002	1.50
	All	0.23	0.16	0.22	0.17	0.031	2.05
Type II	Plagioclase	0.36	0.38	0.46	0.30	0.102	4.55

RMSEP represents the magnitude of absolute error. Tables 2 and 3 show RMSEP for olivine and plagioclase, respectively. RMSEP for major elements, Mg# (for olivine), and An value (for plagioclase) are listed. For the type I analysis, RMSPE for mineral samples and pressed-powder samples as well as for all samples are shown. The prediction error for the type I analysis is smaller than that for the type II analysis for both olivine and plagioclase. Note that prediction errors for mineral samples and pressed-powder samples are almost the same in type I analysis. The results of type I analysis indicates that Mg # of olivine and An value of plagioclase are predicted within the error of about 1 and 2.5, respectively. These are sufficient accuracy for lunar exploration. Figures 2 and 3 plot the predicted values against the true values for Mg# and An values for olivine and plagioclase, respectively. These indicate that the type II analysis is not just worse in prediction precision but also having systematic error; predicted values tend to be smaller than true values.

The results of the type II analysis indicate that even the use of PLS cannot overcome matrix effects completely when physical properties of reference samples is specific and different from those of unknown samples. In this case regression model may include the information that is not essentially related to elemental abundances and should be eliminated from the regression model.

However, the results of the type I analysis indicate that elemental abundances are predicted with high precision and accuracy for all samples when reference samples include the samples that have different physical properties. In this case PLS extracted the information correlated to elemental abundances from spectra appropriately. The use of reference samples that have different physical properties makes it easy to identify and eliminate the information that is not correlated to elemental abundances and is affected by physical properties of samples.

Conclusions: We confirmed that the elemental abundances of olivine and plagioclase are predicted with LIBS by using PLS regression. It is important to prepare reference samples for PLS regression with various physical properties for constructing robust regression model, which leads to a high degree of precision and accuracy of prediction.

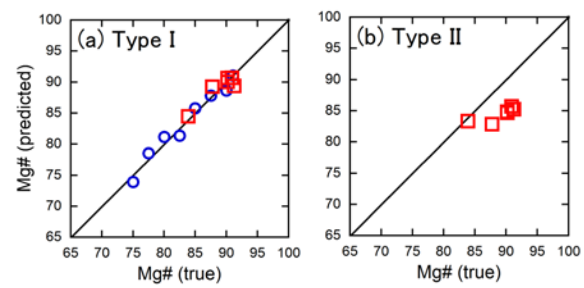

Figure 2. Predicted Mg# against true Mg# value for olivine; (a) Type I analysis and (b) Type II analysis. The red squares and the blue circles represent olivine and pressed-powder samples, respectively.

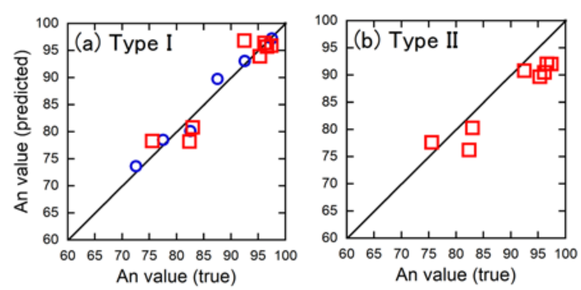

Figure 3. Predicted An value against true An value for plagioclase; (a) Type I analysis and (b) Type II analysis. The red squares and the blue circles represent olivine and pressed-powder samples, respectively.

References: [1] Cremers, D. A. and Radziemski, L. J. (2006) *Handbook of Laser-Induced Breakdown Spectroscopy*. [2] Miziolek, A. W., Palleschi, V., Schechter, I., Eds. (2006) *Laser-Induced Breakdown Spectroscopy (LIBS): Fundamentals and Applications*. [3] Maurice et al. (2005) *LPS XXXVI*, Abstract #1735. [4] Clegg, S. M. et al. (2009) *Spectrochimica Acta Part B* 64, 79-88. [5] Anderson, R. B. et al. (2011) *Icarus* 215, 608-627.