ELEMENTAL ANALYSIS OF LUNAR METEORITES USING LASER-INDUCED BREAKDOWN SPECTROSCOPY. A. J. Ogura[1] (ogura@eps.s.u-tokyo.ac.jp), K. Yumoto[1], Y. Cho[1], T. Niihara[2], S. Kameda[3], and S. Sugita[1], [1]Department of Earth and Planetary Science, The University of Tokyo, Tokyo, Japan, [2]School of Engineering, The University of Tokyo, [3]College of science, Rikkyo University.

Introduction: Laser-induced breakdown spectroscopy (LIBS) is an elemental analysis method based on the spectra from plasma generated by focused laser pulses. In-situ measurements with LIBS have already been conducted on planetary missions taking advantages of multiple capabilities of LIBS, such as high-spatial resolution (hundreds of microns), rapid, and remote analysis without sample pretreatment (>3 m distance in minutes) [1]. Such examples include ChemCam on NASA's Curiosity rover [1], SuperCam on the Perseverance rover [2], and China's Tianwen-1 rover [3].

LIBS would be a powerful tool for lunar explorations as well. In particular, the capability of rapid analysis with LIBS would be important to maximize the number of measurements in a limited mission period if a rover is not designed to survive lunar nights. In fact, India's Chandrayaan2 lunar rover was equipped with a compact LIBS instrument [4]. However, the emission from the laser-induced plasma becomes weak under a high vacuum condition ($<10^{-1}$ Pa), making LIBS signal detection on the Moon more difficult than on Mars [5]. Although a previous study assessed the capability of elemental analysis with LIBS under the high vacuum condition [6], the capability of LIBS for a concentration range that covers typical lunar samples (e.g., with Al_2O_3 > 20 wt% for highland rocks [7]) has not been investigated yet. Expanding the sample set is crucial for investigating the LIBS application to lunar materials because the capability of LIBS analysis highly depends on the range of the sample set [8].

Thus, in this study, the performance of elemental and mineralogical analysis with LIBS was tested using a calibration sample set compositionally broader than that of the previous study [6]. The elemental composition of actual lunar meteorites was predicted to investigate the feasibility of LIBS analysis on the moon.

Experimental: *Samples.* For calibration we measured 25 pressed-powder samples, including geological standards from USGS and AIST, as well as their mixtures with chemical reagents (pure Al_2O_3- or Fe_2O_3 powders). The range of elemental composition of our calibration samples was determined to contain the elemental abundances characteristic to known lunar samples [7] (Table 1). We also measured two lunar meteorites of different types: Northwest Africa 479 (NWA 479, mare basalt) and Northwest Africa 11474 (NWA 11474, feldspathic breccia). NWA 479 contains chromite-spinel, olivine, and pyroxene as phenocrysts in the dark groundmass [9]. NWA11474 is characterized with gray groundmass and white feldspathic clasts (Fig. 1). All samples were measured in a vacuum chamber maintained at $< 3 \times 10^{-2}$ Pa.

Data acquisition. We used an Nd:YAG laser (1064 nm, 2 Hz repetition rate, 30 mJ pulse energy). The laser spot diameter was 800 μm. The spectra were obtained at a distance of 1 m with an exposure time of 50 ms. 5-9 spots were measured per sample and 100 spectra were obtained per laser spot. The lunar meteorite NWA 479 was measured at light-toned phenocrysts and darker groundmass. NWA 11474 was measured at the region in the middle of the sample in Fig. 1, which consists of black groundmass and white clasts.

Table 1: Compositional range of calibration samples.

	SiO_2	TiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	Fe_2O_3
Max. (wt%)	54.10	3.32	34.65	22.52	14.10	3.16	1.79	2.72
Min. (wt%)	35.54	0.49	13.40	3.59	7.12	0.52	0.03	21.18

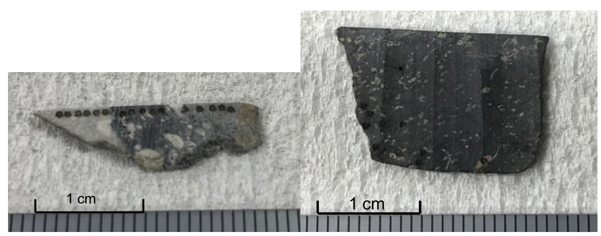

Fig. 1: Image of NWA 11474 (left) and NWA 479 (right).

Data processing. Dark subtraction, noise removal based on wavelet transform, continuum subtraction, and normalization were applied to the raw spectra following the protocol described by [10]. The elemental compositions were predicted with a partial least squares-2 regression (PLS2) algorithm. The PLS2 model was constructed from the spectra of the calibration samples of known compositions. This model was then applied to the LIBS spectra of the lunar meteorites. The composition of NWA 11474 feldspathic breccia was predicted for 5 spots and the average composition for the 5 spots were derived. For the mare basalt NWA 479, the elemental composition of two phenocrysts was predicted separately from groundmass.

Prediction Accuracy. The accuracy of the elemental analysis for the 8 major elements (Si, Ti, Al, Mg, Ca, Na, K, Fe) was estimated by a leave-one-out cross validation. The root mean square error prediction (RMSEP) and median relative error prediction (Med REP) were calculated for each element as indicators of the measurement accuracy:

$$RMSEP = \sqrt{\frac{1}{N}\Sigma_{i=1}^{N}\left(y_{ref}^{i} - y_{pred}^{i}\right)^{2}},$$

$$\text{Med REP} = 100 \times \text{median}\left(\frac{|y_{pred}^{i} - y_{ref}^{i}|}{y_{ref}^{i}}\right),$$

where y_{ref}^{i} is the known concentration of the sample, y_{pred}^{i} is the predicted value, and N is the number of measured spots.

Results and discussion: *Prediction Accuracy*. The RMSEP and Med REP values of all major elements are summarized in Table 2. Table 2 indicates that the composition of every element can be predicted with accuracies better than 3 wt% and Med REP better than 17% except for potassium, which exhibits a low abundance (< 1 wt%). These results imply, for instance, highland (typically ~20 wt% Al_2O_3) and mare (typically ~10 wt% Al_2O_3) rocks can be distinguished by the predicted Al_2O_3 concentrations. This capability will be used to study the spatial distribution and heterogeneity of rocks/regolith around the lander/rover based on their compositions. It also helps select the samples for further in situ measurements or even Earth sample return.

Table 2: Accuracy of prediction achieved in this study.

	SiO_2	TiO_2	Al_2O_3	MgO	CaO	Na_2O	K_2O	Fe_2O_3
RMSEP (wt%)	2.70	0.33	3.05	2.32	1.36	0.28	0.37	2.14
Med REP (%)	3.70	16.72	7.10	14.60	7.45	8.68	45.7	17.34

Analysis of Lunar Meteorites. The predicted elemental compositions of the feldspathic breccia NWA 11474 and mare basalt NWA 479 are illustrated in Figs. 2 and 3. First, the predicted elemental abundances of NWA 11474 (SiO_2, Al_2O_3, MgO, CaO, and Fe_2O_3) matched those measured with SEM-EDS within the margin of the errors. In particular, our LIBS analysis yielded Al_2O_3 of 24.7 ± 3.0 wt% for the sample with 28.2 ± 0.9 wt% Al_2O_3, a high concentration characteristic to highland samples. This value is 10 wt% higher than the highest abundance in the calibration set investigated by [6]. This result indicates the capability of LIBS analysis for lunar highland materials containing high (> 18 wt%) Al_2O_3.

Second, our LIBS prediction suggests that the light-toned phenocrysts measured with NWA 479 were pyroxene because the predicted abundances of MgO = 12-20 wt% and Fe_2O_3 = 16-17 wt% were more consistent with pyroxene than olivine (MgO = 15-18 wt%, Fe_2O_3 = 16-19 wt% for pyroxene; MgO = 29 wt%, Fe_2O_3 = 34 wt% for olivine). Furthermore, CaO was predicted to be 10.5 ± 1.4 wt% and 8.8 ± 1.4 wt%, both of which significantly higher than that expected for olivine (CaO < 1 wt %) [9]. These results demonstrate the capability of mineral classification with LIBS.

Third, Mg# (=Mg/(Mg+Fe) × 100) of one of the phenocrysts was 59 ± 5, which is consistent with the known Mg# = 55-66 within the mineral reported by [9]. This result indicates that Mg# of mafic minerals of a sub-millimeter scale can be measured accurately with LIBS. Although further calibration would improve the accuracy of the prediction model, our quantitative analyses using the actual lunar samples suggest the capability of LIBS as an in-situ quantitative analysis method for future lunar missions.

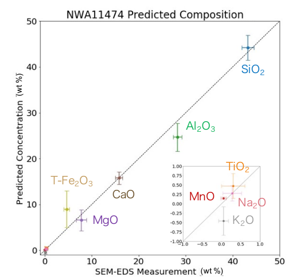

Figure 2: Predicted composition of NWA 11474. Error of horizontal axis represent standard deviation of SEM-EDS measurement.

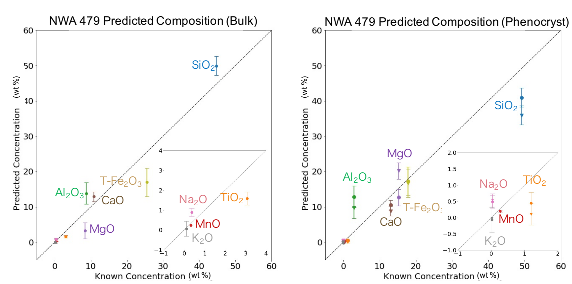

Figure 3: Predicted composition of both bulk (left) and phenocryst (right) of NWA 479. "Known Concentration" was from [9].

References: [1] Wiens R. C. et al. (2012) *Space Sci. Rev., 170*, 167-227. [2] Wiens R. C. et al. (2021) *Space Sci. Rev., 217*, 4. [3] Jia Y., Fan Y., Zou Y. (2018) *Chin. J. Space Sci., 38(5)*, 650-655. [4] Laxmiprasad A. S. et al. (2020) *Current Science, 118(4)*, 573-581. [5] Knight A. K. et al. (2000) *Appl. Spectrosc., 54*, 331-340. [6] Lasue J. et al. (2012) *JGR, 117,* E01002. [7] Warren P. H. and Taylor G. J. (2014) *Oxford: Elsiver*, 213-250. [8] Anderson R. B. et al. (2017) *Spectrochim. Acta B 129,* 49-57. [9] Fagan T. J. et al. (2002) *Meteoritics & Planet. Sci., 37,* 371-394. [10] Wiens R. C. et al. (2013) *Spectrochim. Acta B 82,* 1-27.