

Laser-Induced Breakdown Spectroscopy for the Identification and Quantification of Volatiles and Highly Siderophile Elements in the Lunar Regolith. F. Diotte¹, M. Lemelin¹ and F. R. Doucet², ¹Department of applied geomatics, Université de Sherbrooke, Québec, Canada, J1K 2R1 (Frederic.diotte@usherbrooke.ca, Myriam.Lemelin@usherbrooke.ca), ²ELEMISSION Inc., Montréal, Québec, Canada, H4R 1V6 (fdoucet@elemission.ca).

Introduction: A high occurrence of scientific instruments is expected to survey the surface of the Moon by the end of the decade and will play a major role in refining our knowledge of its elemental and mineral compositions [1]. The poles are areas of high interest, as they likely contain abundant water ice resources [2]. Assessing the distribution of volatiles at the lunar surface is a milestone in better understanding the water cycles on airless bodies, including supply sources such as solar winds [3], past lunar volcanism [4] and meteorite influx history [5]. Highly siderophile elements are also indicators of the lunar impacting past. Due to their high affinity to iron, they have mostly segregated into the core of terrestrial planets during accretion. Their presence in the crust is therefore associated with meteorite influx after the solidification of the global magma ocean [6]. An instrument that could quantify both volatiles and highly siderophile elements abundances at the surface of the Moon could help provide geological constraints to lunar formation and impacting models.

This project aims to investigate the capabilities of a laser-induced breakdown spectroscopy (LIBS) hyperspectral imaging instrument, the “Coriosity”, to quantify both volatiles and highly siderophile elements. In this instance, we compare quantitative analysis models for the abundance of water in icy regolith simulants. We also present results of qualitative analysis of palladium in lunar regolith simulants.

Instrument: The Coriosity is a LIBS hyperspectral imaging instrument developed by Elemission Inc. in Montreal. Its spectrometer measures the spectral emission of laser induced plasma with a spectral range of 220 - 930 nm. With its frequency of acquisition of 1 kHz, it can scan 40 000 LIBS spectra in 40 seconds with a spatial resolution of 50 μm [7]. The resulting data are hyperspectral matrices of spectral emission, which contain spatially resolved signatures of the elemental composition of a target. Since the spectra are sampled from a grid over the analyte, the imaging device also allows to map the elemental abundance at the surface using wavelength-specific element atomic emission intensity.

Methods: Calibration standards of known elemental composition were prepared using the Lunar Highlands Simulant and the Lunar Mare Simulant from Exolith Lab (Center for Lunar & Asteroid Surface Science, University of Central Florida). Up to 40 wt. % of water

was added in known quantities to the samples, which were then mixed and frozen until analysis with LIBS. Spectra for each sample were averaged, and statistical methods were compared for the quantification of H_2O . Those algorithms include a univariate linear regression fitting the intensity of hydrogen peaks at 656.5nm (H_α) with H_2O concentration, as well as OLS (ordinary least squares), PLS1 (partial least squares), and PCR (principal components regression) for larger spectral window. Models were validated using ten-fold cross validation and independent validation on a test set containing 20% of the complete dataset.

LIBS response to highly siderophile elements was also tested using massive sulfide ore deposit rocks which were acquired from Vale-Sudbury Mine in Ontario, Canada. Bulk Pd concentration of 10 ppm was measured with ICP-MS. Rocks were crushed and pulverized to obtain particles of sizes inferior to 105 μm . Crushed samples that were not pulverized, with particle size below approx. 2 mm, were also mixed with the regolith simulant and analyzed with LIBS. Baseline was subtracted from Pd peaks at 340.5 nm for each spectrum. Then, the sum of baseline-corrected intensity of palladium was computed for each sample, excluding spectra devoid of Pd. The variation of the sum with Pd concentration was then analyzed.

Quantification of water ice: Intensity of emission decreases past the sample’s saturation point due to a weak laser-to-sample coupling in pure water. Regressions were therefore fitted for the full dataset as well as for two other ranges of concentrations: [0:10] wt. % and [0:15] wt. %, to better evaluate the plus-value of multivariate methods over univariate regression. Comparison of RMSEP (root-mean-square error of prediction) for the different models in figure 2 shows that PLS regression provides the best prediction accuracy for the complete dataset, with a RMSEP of 3.2 wt. %. RMSECV (root-mean-square error of cross validation) for OLS, PLS and PCR are very similar. Simple linear regression is the most accurate for concentrations below 10 wt. %, where water concentration varies linearly with hydrogen intensity of emission. Using the second definition of LOD (limit of detection) from Wiens et al. (2013) [8], it is estimated that concentrations of water superior to 1.1 wt. % could be detected in the regolith using the Coriosity.

Detection of palladium: We analyze Pd as non-equivocal signal at 340.5 nm is observed in certain

spectra, contrary to Pt peaks which couldn't be discriminated because of spectral interference. The scatter plot of the sums of Pd intensities varying with concentration in ppm is shown in Figure 1. The positive trend seems to indicate a correlation, indicating that the lowest Pd concentration measured (2.6 ppm) is above its LOD. New observations will be integrated in the dataset to evaluate the significance of the correlation and estimate the limit of detection.

In finely pulverized minerals (105 microns), no signal of palladium was observed. This recovery issue could indicate that Pd was diluted in fine powders, increasing the non-uniformity of the sample, or was lost in the crushing/sieving sample preparation process. The investigation of the latter issue will also be discussed. Thus, wet sieving of the pulverized rocks will also be attempted, with an expected effect of breaking potential

bonds between Pd and the coarse fraction, allowing those particles to be sieved and included in the samples.

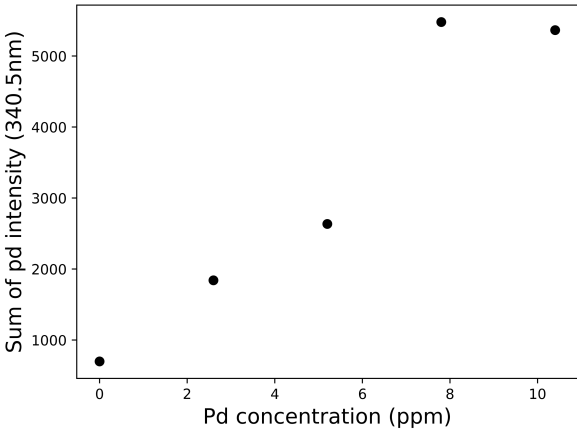


Figure 1. Variation of Pd intensity at 340.5nm with Pd concentration.

[H2O] (wt. %)	Simple linear regression		OLS (Multivariate)		PLS1		PCR	
	RMSECV	RMSEP	RMSECV	RMSEP	RMSECV	RMSEP	RMSECV	RMSEP
All	11	11	3.3	3.2	3.2	3.2	3.8	23
<15	2.2	1.5	1.2	2.1	1.2	1.4	1.2	8.4
<10	1.1	0.40	1.1	1.0	0.73	0.62	0.77	8.5

Figure 2. Cross validation and independent testing accuracies of statistical methods applied to LIBS data for the quantification of water ice in lunar regolith simulants.

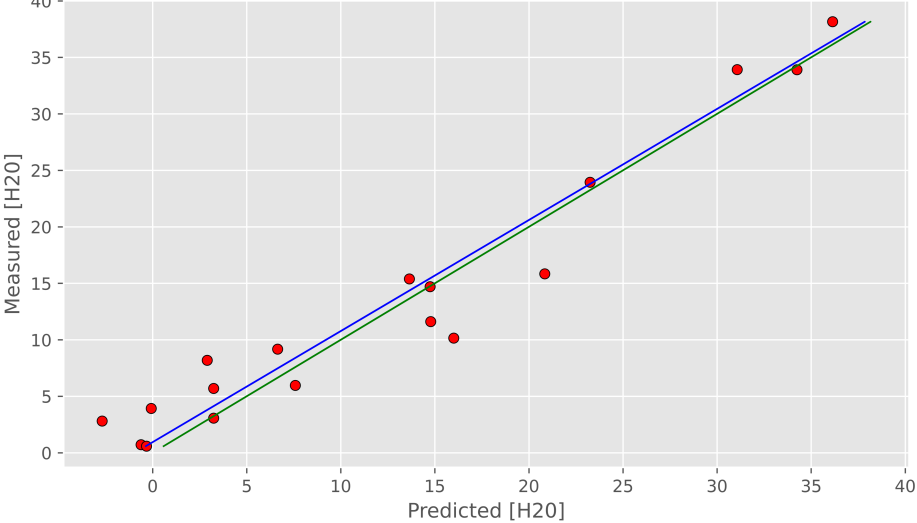


Figure 3. Predicted concentration of H₂O vs the measured concentration using an independent dataset with PLS1 regression. Green line is the ideal 1:1 line, blue line is the best fit. R² (prediction) is 0.93.

References: [1] ISECG (2020) *Global exploration roadmap supplement*. [2] Li S. et al. (2018) *PNAS*, 115(36), 8907-8912. [3] Farrell W.M. et al. (2017) *JGR Planets*, 122(1) 269-289, [4] Needham D.H. and Kring D. (2017) *Earth Planet. Sci. Lett.*, 478, 175-168. [5] Costello, E.S. (2020) *JGR Planets*, 125(3) [6] Brenan J.M. et al. (2019) *Nat. Geosci.*, 12, 701-706 [7] Rifai K. (2020) *Miner.*, 10(3). [8] Wiens R.C. et al. (2013) *Spectrochim. Acta B*, 82, 1-27.