CONTRIBUTION OF GRAIN SIZE, ATMOSPHERE PRESSURE, AND LASER ENERGY TO LIBS SPECTRA OF FELDSPAR: IMPLICATIONS FOR SPECTRA LIBRARY BUILDING FOR CHINA'S MARSCODE. Changqing Liu[1], Zongcheng Ling[1*], Kaichen Guo[1], and Hongchun Bai[1], [1]Shandong Provincial Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, Institute of Space Sciences, Shandong University, Weihai, Shandong, 264209, China. (zcling@sdu.edu.cn, liucq@mail.sdu.edu.cn).

Introduction: Laser-induced breakdown spectroscopy (LIBS) is a powerful technique for rapid in-situ multi-elemental analysis in planetary exploration missions. China's first Mars exploration mission (HX-1) will be launched in 2020, and the Mars Surface Composition Detection Package (MarsCoDe) is one payload onboard the rover, which will investigate elemental compositions of Martian soils and rocks at the distances from 1 to 7 m [1].

The accuracy and precision for determining elemental compositions on Mars based on LIBS spectra depend on the quality of the LIBS database built in laboratory [2]. However, the huge differences between Mars and the laboratory including environmental conditions, physical state of targets (e.g., grain size), and laser energy probably lead to the inaccuracy in quantitative elemental composition determination. Besides, the diverse grains of Martian soils can be smaller and/or larger than the laser beam, which may affect the coupling between the laser and targets. The primary aim of this study is to assess the effects of sample grain size, atmosphere pressure, and laser energy to LIBS spectra, and we intend to constrain the experiment parameters when building the LIBS database for MarsCoDe.

Method: An albite obtained from a commercial source was selected in our study. The albite was crushed in a zirconia shatterbox, sieved using stainless-steel sieves to obtain powers with different grain sizes (Table 1), and pressed into pellets with a diameter of 20 mm using the pressure of 12 T for 5 s. The major elements of the albite were determined using an Energy 140 Dispersive Spectrometer (EDS, Ox-ford Aztec Xmax50) on the Scanning Electron Mi-croscopy (SEM, FEI Nova NanoSEM 450).

Table 1. The grain sizes of power samples used in this study.

Sample ID.	Ab1	Ab2	Ab3	Ab4	Ab5
Grain Size / μm	29.7-46.4	46.4-74.2	74.2-98.9	98.9-185.4	> 185.4

All LIBS spectra used in this study were collected under the air condition. The laboratory set-up used a pulsed Nd:YAG laser at 1064 nm, 1 Hz pulse and an integration time of 1 ms. Targets were placed in a vacuum chamber at a distance of ~ 0.6 m. LIBS spectra were collected from five different points and 30 shots for each point. All spectra were averaged to obtain one spectrum for a single pellet to partially offset the heterogeneity of the sample. The noise and continuum background were removed using a wavelet function and a spline function, respectively. Elements were identified from LIBS emission lines via ChemCam Quick Element Search Tool (C-QuEST, https://pds-geosciences.wustl.edu/workshops/ChemCam_Workshop_Mar15.htm).

Results: The albite is richer in Ca compared with K and Na based on the results of SEM-EDS. Hence, Ca(II) emission lines at 393.39 nm and 396.85 nm, and Ca(I) lines at 422.76 nm were selected in our study.

Effect of different grain sizes. To investigate the effect of grain size on LIBS spectra, ~23 mJ laser energy on target and 1 atm pressure were selected.

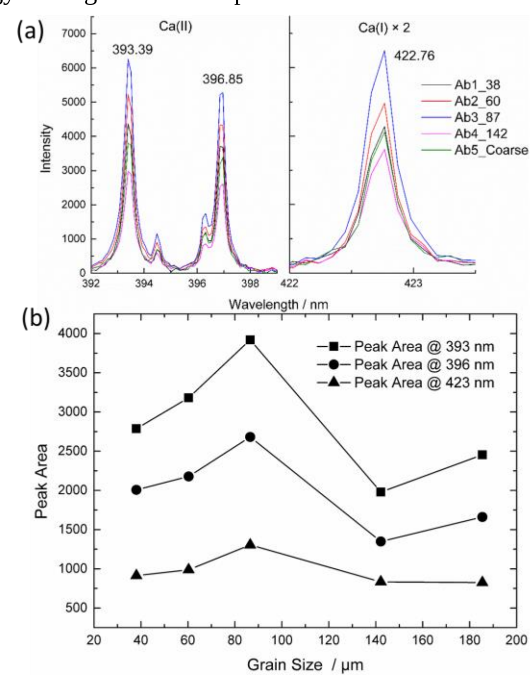

Fig. 1. (a) Ca(II) and Ca(I) LIBS emission lines, and (b) their areas with averaged grain sizes (the grain sizes of Ab5 was selected as 185.4 μm).

The areas of Ca emission lines (Fig. 1) exhibit functions of grain sizes consistent with previous studies [3, 4]. For samples with small grain sizes (Ab1, Ab2, and Ab3), the areas of Ca emission lines increase with increasing grain sizes. However, the LIBS features of

Ab4 are less intense than Ab3. The various trend of the emission line areas may be produced by the different breakdown threshold irradiance due to diverse surface properties [3, 5]. Some coarse grains in Ab5 may be larger than the diameter of the laser beam (~ 400 μm), and one LIBS plasma may be produced by a single grain, resulting in more intense LIBS emission lines for both Ca(I) and Ca(II) [3, 4].

The area of Ca(I) and Ca(II) lines exhibit similar trends as increasing grain sizes for Ab1, Ab2, and Ab3, indicating that the number of different ionized atoms increases simultaneously in LIBS plasma. For Ab4 with the grain sizes of 98.9-185.4 μm, the areas of Ca(II) lines decrease more rapidly than that of Ca(I), indicating decreasing ionization ratio in LIBS plasma with increasing grain sizes due to the rough surface.

Effect of pressure. We selected Ab2 with the laser energy of ~23.1 mJ on target to investigate the effect of atmosphere pressure to LIBS spectra. The areas of Ca emission lines exhibit increasing trend as increasing pressure (Fig. 2), which is consistent with previous studies (e.g., Cousin et al., 2011) [6] except the pressure of 1 atm where the most intense lines are shown in this study. More intense LIBS plasma lines in higher atmosphere pressure may be on account that more atmosphere can provide adequate confinement to plasma [7], and more excited atoms can be produced due to greater density of collisions in the plasma. Meanwhile, the plasma shielding effect on laser energy may not greatly contribute to the LIBS spectra in our study.

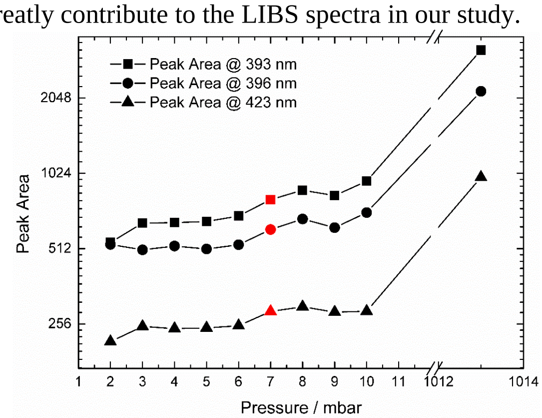

Fig. 2. The areas of Ca(II) and Ca(I) emission liens with the atmosphere pressure. Red points are Martian simulated pressure of 7 mbar.

Effect of laser energy. Lasers with the energy of 10.1, 12.9, 14.9, 16.4, 17.6, 20.1, 21.6, 23.1, 24.8, and 26.5 mJ were selected in this study using the Ab2 sample and 1atm pressure.

The areas of Ca emission lines increase with increasing laser energy (Fig. 3), which considerably depends on the degree of atom ionization [3]. The emission lines of Ca(II) show a steeper trend than Ca(I), which can be explained by an increasing ionization ratio in LIBS plasma with increasing laser energy.

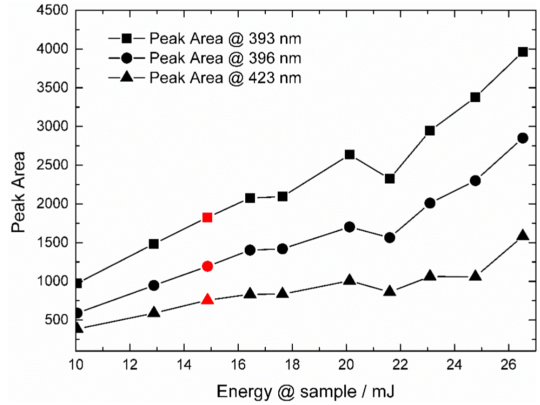

Fig. 3. The areas of Ca(II) and Ca(I) emission liens with the laser energy on target. Red points are laser energy of 14 mJ, which are similar to ChemCam [8].

Conclusion: The areas of LIBS emission lines and different ionized atoms ratios considerably change depending on sample grain size, atmosphere pressure and laser energy, which would result in inaccuracy of Martian element determination based on the LIBS database built in laboratory. Hence, similar pressure and laser energy with MarsCoDe performed on Mars should be constrained, and the grain sizes of the samples used to build the database should not be lager than 98.9 μm to keep the homogeneity of samples in the laser beam scale. Besides, further studies are required to constraint more effects (e.g., distance between LIBS system and targets) and reduce the influence of multiple grain sizes of real Martian geologic samples.

Acknowledgments: This work is supported by the Pre-research project on Civil Aerospace Technologies No. D020102 funded by China National Space Administration (CNSA). We also thank the fundings from the National Natural Science Foundation (11941001, 41972322, U1931211), the Natural Science Foundation of Shandong Province (ZR2019MD008), Qilu (Tang) Young Scholars Program of Shandong University, Weihai (2015WHWLJH14).

References: [1] Ren X. et al., (2018) *EPSC 2018*, Abstract #2018-759-2. [2] Maurice S. et al., (2016) *J. Anal. At. Spectrom.*, *31*, 863. [3] Schröder S. et al., (2019) *Icarus*, *325*, 1-15. [4] Gottlieb C. et al., (2018) *Spectrochimica Acta Part B*, *142*, 74-84. [5] Cremers D. A. et al., (2006) *John Wiley & Sons*. [6] Cousin A. et al., (2011) *Spectrochimica Acta Part B*, *66*, 805-814. [7] Effenberger A. J. et al., (2010) *Sensors*, *10*, 4970-4925. [8] Wiens R. C. et al., (2013) *Spectrochimica Acta Part B*, *82*, 1-27.