LIBS CHARACTERIZATION OF FELDSPAR: IMPLICATIONS FOR CHINA'S MARSCODE. Changqing Liu[1], Zongcheng Ling[1*], Kaichen Guo[1], Hongchun Bai[1], and Yanqing Xin[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 an atomic emission spectroscopy technique for rapid in-situ multi-elemental analysis. ChemCam is the first LIBS instrument for planetary exploration [1, 2], and China's first LIBS payload named MarsCoDe will be launched in 2020 to investigate Martian geochemistry [3].

One of the significant scientific discoveries obtained by ChemCam was the detection of alkali feldspar at Gale crater, which the bulk compositions of 67 wt.% SiO_2 and 14 wt.% Na_2O + K_2O [4, 5], greatly extending the magmatic diversity that was observed by previous Mars landing missions. Felsic minerals with medium Ca and low alkali compositions (e.g., andesine) were also discovered [5]. However, some elemental compositions of LIBS analysis points lied outside the general regions of feldspar in the ternary diagram (Ab-An-Or), resulting in uncertainty of feldspar identification. In this work, we preliminarily analyzed the LIBS spectra of four feldspar minerals with the intent to offer an available method for feldspar classification and element determination based on the LIBS spectra obtained by ChemCam and future MarsCoDe applications on Mars.

Method: Four feldspars used in our study were obtained from a commercial source. Powders of minerals were crushed in a zirconia shatterbox, sieved using a 320 mesh stainless-steel sieve, and pressed into pellets with a diameter of 40 mm under the pressure of 28 T. The major elements of samples were determined using an Energy 140 Dispersive Spectrometer (EDS, Ox-ford Aztec Xmax50) on the Scanning Electron Mi-croscopy (SEM, FEI Nova NanoSEM 450).

LIBS spectra were collected under the simulated Martian conditions (CO_2, 7 mbar). The laboratory set-up used a pulsed Nd:YAG laser at 1064 nm, 5 Hz pulse, 44.5 mJ/pulse energy on target, and an integration time of 1 ms. Feldspar pellets were placed in a vacuum chamber at a distance of ~ 0.6 m. LIBS spectra were collected from three different points, and each point conducted 50 shots. All LIBS spectra were averaged to generate one spectrum for a single sample.

LIBS spectra were denoised using a wavelet function, and continuum background were removed using a spline function. Radiometric calibration was conducted using a DH-3BAL-CAL light source from Ocean Optics and a fiber with a diameter of 1000 μm. Elements were identified via the ChemCam Quick Element Search Tool (C-QuEST, https://pds-geosciences.wustl.edu/workshops/ChemCam_Workshop_Mar15.htm). Ca(II) lines at 393.5 nm and 397.0 nm, Na(I) lines at 589.8 nm and 590.4 nm, and K(I) lines at 767.3 nm and 770.7 nm were selected in our study. The areas of LIBS emission lines were fitted using a Gaussian-Lorentz model.

Results: The compositions of four feldspars are shown in Table 1. Feldspar_01 has the most K content, Feldspar_02 is rich in Na, and Ca is the richest in Feldspar_04.

The intensities and areas of Ca and K emission lines increase with an increasing weight percentage of CaO, Na_2O and K_2O in feldspars (Fig. 1 and Fig. 2). However, Na emission lines exhibit a mussy trend with varying content, which may be due to the low signal-to-noise ratio and similar weight percentage of Na_2O in feldspars.

Table 1. Elemental compositions of feldspar minerals confirmed by SEM-EDS.

Oxide / wt.%	**CO_2**	**Na_2O**	**Al_2O_3**	**SiO_2**	**K_2O**	**CaO**
Feldspar_01	14.02	2.48	15.83	55.70	**11.84**	0.13
Feldspar_02	17.36	**6.24**	19.74	52.41	2.24	2.02
Feldspar_03	15.84	3.83	23.33	46.43	0.95	**9.61**
Feldspar_04	28.23	3.45	16.36	38.86	0.43	**12.68**

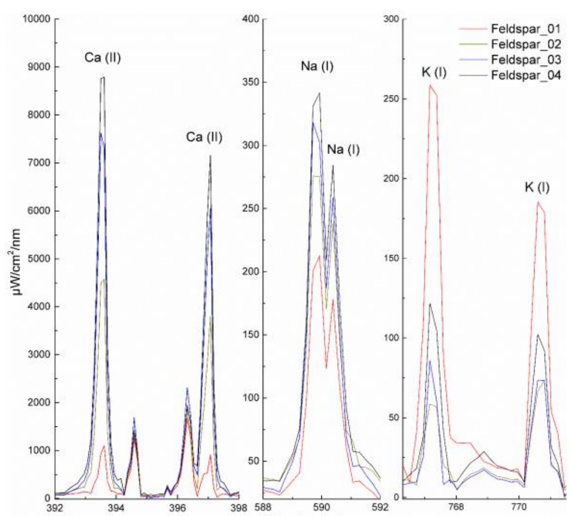

Fig. 1. LIBS spectra of feldspar mineral after radiometric calibration, and elements identification based on C-QuEST.

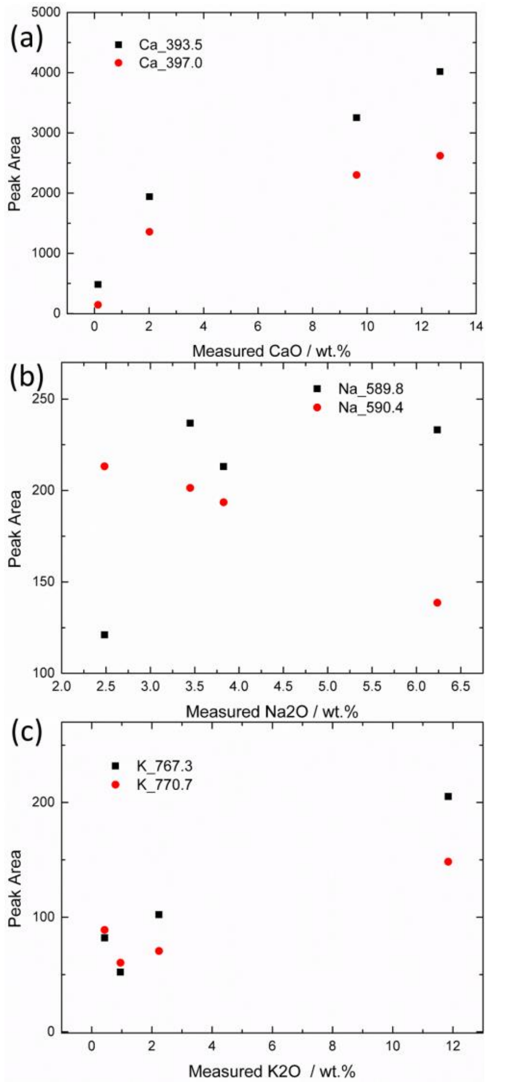

Fig. 2. Emission line areas of Ca, Na and K with the mass fractions of CaO, Na_2O, and K_2O in feldspars.

We used three polynomials to predict the weight percentage of CaO, Na_2O, and K_2O in samples based on areas of LIBS emission lines, which can be expressed as follows:

$CaO = 0.0099 \times Ca\_393.5 - 0.0086 \times Ca\_397.0 - 3.95$ (1)

$Na_2O = 0.0042 \times Na\_589.8 - 0.044 \times Na\_590.4 + 11.38$ (2)

$K_2O = 0.073 \times K\_767.3 + 0.0093 \times K\_770.7 - 5.04$ (3)

where Ca_393.5 means the area of Ca emission line at 393.5 nm. As shown in Fig. 3, all predicted results are monotone increasing as increasing measured mass fractions of CaO, Na_2O, and K_2O. The R-squared of these equations are 0.960, 0.999, and 0.937 respectively, and the RMSE values are 1.04 wt.%, 0.05 wt.%, and 1.17 wt.%, indicating good calibrations for predicting the percentages of CaO, Na_2O, and K_2O in feldspar minerals. The RMSE values of CaO and K_2O prediction are larger than that of Na_2O due to lager content regions for them in feldspars. Besides, a bigger database is required to build more reliable models.

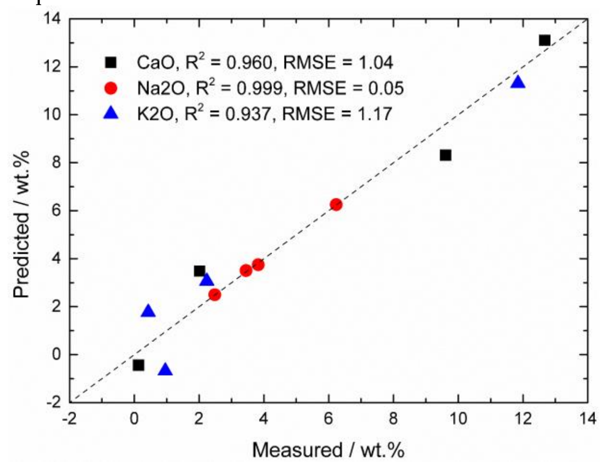

Fig. 3. The scattered plot of predicted weight percentage of CaO, Na_2O, and K_2O based on the equations above versus measured results by SEM-EDS. All points are approximately along with a 1:1 line (the dashed line).

Conclusion: The weight percentage of CaO, Na_2O, and K_2O can be predicted using areas of Ca, Na and K emission lines based on polynomials. However, this method greatly depends on the LIBS database built in laboratory and the sample selection, and four points are limited to make the models valable to determine elemental compositions of feldspar on Mars based on LIBS spectra collected by ChemCam and MarsCoDe. In the future, we will choose more igneous minerals and rocks to enrich our database and build more reliable models to quantitatively identify elements of Martian soils and rocks.

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