LIBS CALIBRATION STANDARDS APPLICABLE FOR MARSCODE ONBOARD THE ROVER OF TIANWEN-1.

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Introduction: The first Mars exploration mission of China, Tianwen-1, has been successfully launched on 23 July 2020, and is expected to land in Utopia Planitia [1, 2]. The Mars Surface Composition Detector (MarsCoDe) is one of the payloads onboard the rover to determine chemical compositions of the surface materials relied on the Laser-induced breakdown spectroscopy (LIBS) technique.

The capability of LIBS technique could be significantly affected by the LIBS database of calibration standards, especially the representativeness and number of calibration standards [3, 4]. For instance, to resolve the geochemical limitations and improve the accuracies of ChemCam (LIBS onboard Curiosity), the ChemCam team developed a larger set of standards (408) based on the initial 66 geochemical standards, and excluded more than 100 additional samples due to their similar geochemistry or significantly different elemental compositions from most Martian rocks [4, 5].

Correspondingly, calibration standards for MarsCoDe should be carefully selected. The rules for the selection of LIBS calibration standards are as follows: 1) samples with chemical and mineralogical representative of Tianwen-1 landing site; 2) terrestrial rocks that have experienced characteristic geologic evolution; 3) samples with good quality and large size to be validated in the future. Accordingly, we have prepared 259 terrestrial geological rocks as calibration standards for MarsCoDe at Shandong University.

Standards Preparation: 259 terrestrial rocks were obtained from several mineral specimen companies, which are typical minerals and rocks from around the world. Igneous, sedimentary and metamorphic rocks were included for this work. These samples were subsequently crushed, ground, and sieved to obtain grains smaller than 38 μm for homogeneous in the beam scale size (Fig. 1). A total of 194 samples have been well prepared until Dec. 2020.

Chemical Compositions of Standards: The major elemental compositions of 71 calibration standards were measured using ARL Perfom'X 4200 XRF (X-ray fluorescence) spectrometry at the State Key Laboratory of ORE Deposit Geochemistry, Chinese Academy of Sciences. Fig. 2 displays the compositional distribution of the samples of SiO_2 (0.2~99.9 wt.%), TiO_2 (0~8.5 wt.%), Al_2O_3 (0~26.4 wt.%), Fe_2O_3 (0~50.9 wt.%), MgO (0~47.6 wt.%), CaO (0.1~55.7 wt.%), Na_2O (0.1~8.6 wt.%), K_2O (0 ~12.6 wt.%), which are comparable to the 408 standards of ChemCam [4].

On a total alkali-silica (TAS) diagram (Fig. 3), igneous rocks of 71 calibration standards lie along the boundary of alkaline and subalkaline compositions. Andesitic and felsic rocks with low Na_2O+K_2O component are lacking compared with 408 calibration standards of ChemCam. Besides, a large number of targets of ChemCam in 1-90 sols are ultramafic rocks. Therefore, more igneous rocks should be added to the calibration standards.

In the ternary diagram with Al_2O_3, $CaO+Na_2O+K_2O$, and FeO_T+MgO (A-CNK-FM, Fig. 4), most igneous rocks are plotted along the bisecting line of FeO_T+MgO corner. Sedimentary rocks are totally above the line, indicating a strong degree of chemical weathering, and most metamorphic rocks are below the line. The bisecting line of FeO_T+MgO corner may provide an accessible method to distinguish igneous, sedimentary, and metamorphic rocks. Most of the 408 calibration standards of ChemCam are above the line, which may be determined by the lacustrine deposit in Gale crater [6].
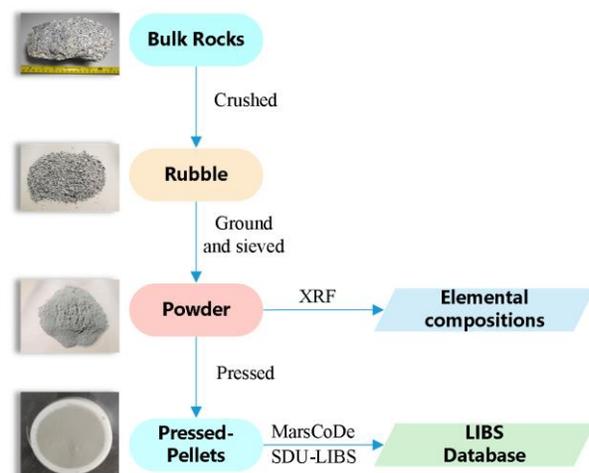

Fig. 1. Scheme for calibration standards preparation applicable for China's MarsCoDe onboard Tianwen-1.
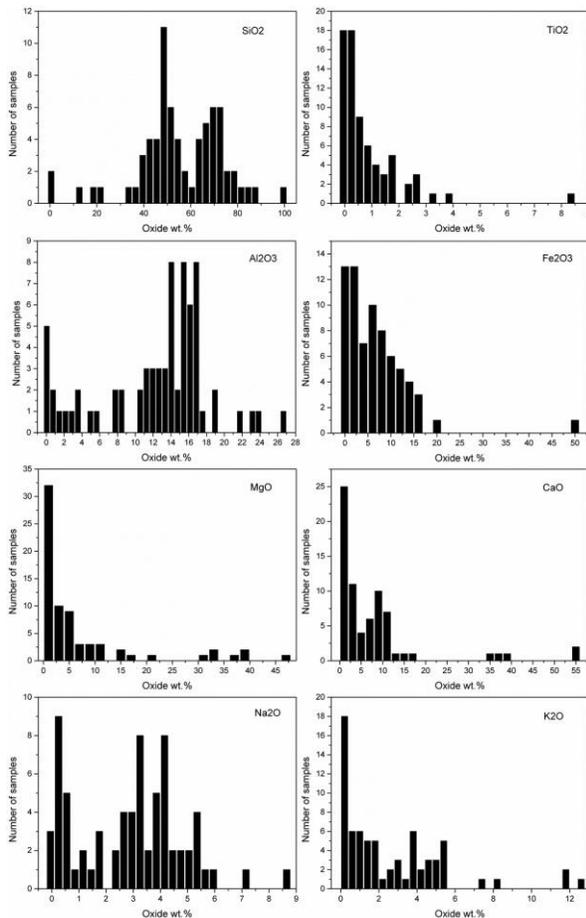
Fig. 2. The distribution of major elemental compositions (Si, Ti, Al, Fe, Mg, Ca, Na, and K) of the calibration standards.
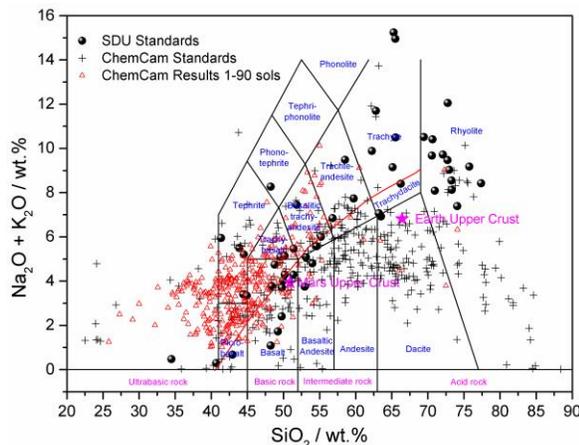

Fig. 3. TAS diagram of igneous rocks in SDU calibration standards, ChemCam 408 standards, and the results of ChemCam LIBS data in 1~90 sols. The red line is the distinction between alkaline and subalkaline compositions from [7].
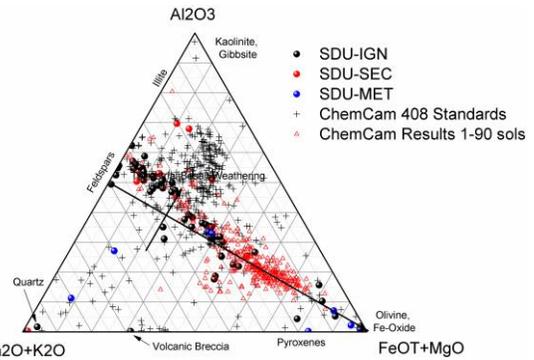

Fig. 4. A-CNK-FM diagram of chemical points of SDU standards, ChemCam 408 standards, and the results of ChemCam in 1~90 sols. The trend of typical terrestrial chemical weathering is modified from [8].

Conclusion: Calibration standards are crucial for MarsCoDe to obtain precise and accurate elemental compositions on Mars. We have prepared 259 terrestrial rocks, among which 194 samples have been crushed, ground, and sieved to obtain grains smaller than 38 μm. Chemical compositions of 71 standards have been determined by XRF. Several types of rocks should be included in the future such as intermediate and acid igneous rocks with low Na_2O+K_2O. The calibration standards will be finally applied to build a LIBS database and a model for elemental composition interpretation on Mars based on MarsCoDe.

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