LABORATORY SPECTROSCOPIC CHARACTERIZATION AND CLASSIFICATION OF NATURAL KAOLIN-GROUP MINERALS. Shangke Tian[1], Zongcheng Ling[1*], Changqing Liu[1], Hongchun Bai[1], Ping Liu[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).

Introduction: Kaolin-group minerals include kaolinite ($Al_2[Si_2O_5](OH)_4$), dickite ($Al_2[Si_2O_5](OH)_4$), halloysite ($Al_2[Si_2O_5](OH)_4 \cdot 2\text{-}4H_2O$), and nacrite ($Al_2[Si_2O_5](OH)_4$), which mainly formed by hydrothermal and weathering processes on Earth, and their formation environment is diverse (e.g. sedimentary, altered crustal rocks) [1]. They have also been found on Mars at Nili Fossae, Mawrth Vallis, Abrabia Terra and Leighton Crater [2]. The presense of smectite and carbonate near the kaolinite is observed on Mars [2]. Importantly, it can be the key tracer for the ancient aqueous alteration and pale environment of Mars.

The current researches about kaolin-group minerals on Mars mainly uses visible and near infrared (VNIR) orbital data (e.g. CRISM). In this work, we studied some natural minerals by VNIR, Laser-induced breakdown spectroscopy (LIBS), Laser Raman spectroscopy and X-ray diffraction (XRD), then analyzed the spectral charactrtistics of kaolin-group minerals and rocks. Moreover, all the data sets would be helpful for data interpretation of future Mars explorations.

Samples: Four kaolin-group minerals, two kaolinite clay minerals and three mixture samples (Table 1) were prepared in our study and all samples's partical size is less than 38 μm. We performed XRD measurements to determine the phases. The halloysite is divided into two series, one was dried for 6 hours at 105 ℃ in an oven before the spectral measurements. Considering the presence of smectite and carbonate near the kaolinite outcrop, and the bedrock is basaltic on Mars, we prepared binary mixtures of kaolinite with smectite, calcite and andesite basalt, respectively, to mimic the Martian surface mineral assemblages.

Experiments: The laboratory set-up of LIBS used a pulsed Nd:YAG laser at 1064 nm, 5 Hz pulse, ~91 mJ/pulse energy on target, and an integration time of 1 ms. Introducing the martian gas simulant (CO_2) at ~7 mbar before LIBS experiment. LIBS spectra were collected from five different points of the target, and 30 shots per point. All LIBS spectra were averaged to generate five spectra for a single sample (Fig. 1). LIBS spectra were processed by denoising and continuum removal, and the elements were determined according to the ChemCam quick element search tool (C-QuEST) [3] based on data sets from National Institute of Standards and Technology (NIST) and ChemCam team.

We used the FieldSpecR 4 Hi-Res VNIR spectrometer (Analytical Spectral Devices., Inc), and VNIR spectra ranging from 350 to 2500 nm (Fig. 2) were obtained for the <38 μm paticle size fraction of all samples.

The Raman spectra were obtained by inVia® Raman System using the 532 nm green laser. In addition, XRD measurements were performed to the samples for determining the phases of samples.

Table 1. Summary of all samples .

Samples	Type	Origin	Note
kaolinite_1	kaolinite	Suzhou, Jiangsu	
kaolinite_2	kaolinite	Tang County, Hebei	
dickite	dickite	Songyang, Zhejiang	
halloysite_nd	halloysite	Xuyong, Sichuan	
halloysite_d	halloysite	Xuyong, Sichuan	105℃, 6h
kaoliniteclay_1	Kaolinite clay	Suzhou, Jiangsu	
kaoliniteclay_2	Kaolinite clay	Lin'an, Zhejiang	
KS1_1	mixture		Equal mass mix
KC1_1	mixture		Equal mass mix
KAb1_1	mixture		Equal mass mix
smectites	smectites	Anji, Zhejiang	
calcite	calcite	Tai'an, Shandong	
andesite basalt	andesite basalt	Fuping, Hebei	

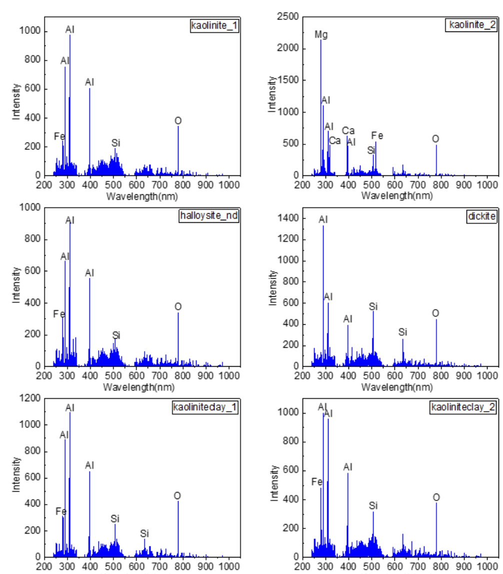

Fig. 1. LIBS spectra of four kaolin-group minerals and two kaolinite clays.

Results: It can be seen from the LIBS spectra that kaolin-group minerals mainly include Al and Si emission lines (Fig. 1). However, kaolinite_2 contains Fe, Mg and Ca, and its VNIR spectra (Fig. 2) with two features at 1.41 and 2.21 μm implying the mixture nature.

The VNIR spectra of our samples exhibit obvious double features at 2.21 μm OH combination band and 1.41 μm OH stretching overtone feature, which is consistent with typical spectral features of kaolinite from Ref. [4] (Fig. 2). For mixtures of kaolinite and andesite basalt, which exhibit overlapped features in these two positions, and the two absorption features of VNIR spectra are relative weak compared with kaolinite.

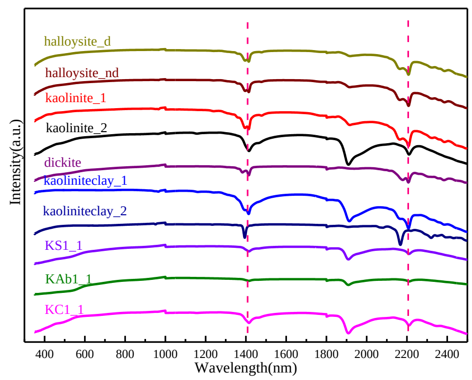

Fig. 2. VNIR spectra of ten samples. The two vertical dotted lines represent the features at 1.41 μm and 2.21 μm.

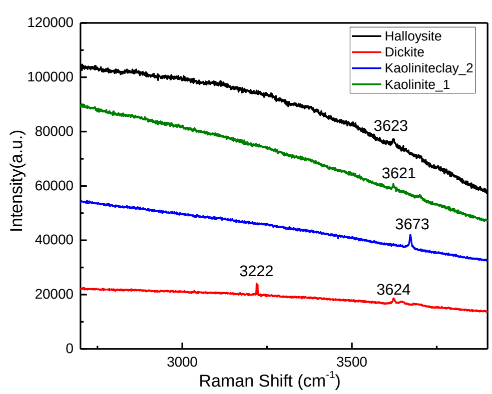

Fig. 3. Raman spectra of kaolin-group mineral and kaolinite clay from 2700 to 3900 cm^{-1}.

Raman spectra exhibit obvious fluorescence effect, which leads to weaker Raman features (Fig. 3). Raman features of kaolinite at 3622 cm^{-1} attributed as OH groups that coordinate with Al^{3+} in octahedral sites ($AlO_2(OH)_4$) of the kaolinite structure[5], which agree with above VNIR studies.

Applicatioin: LIBS spectra were applied to classify the endmembers and mixtures by principal components analysis (PCA), as shown in Fig. 4. The result shows that kaolin-group minerals, mixtures and rocks can be well distinguished. However, KAb1_1 is divided into kaolin-group minerals, the probable reason is that adding andesite basalt for kaolinite lead to negative PC2 values. Halloysite_d (105℃, 6 h) is different from halloysite_nd (no heating) in that the former is mixed with kaoliniteclay_2, KC1_1 and KS1_1. We will conduct more experiments to further explain the mechanism for this unexpected phenomenon.

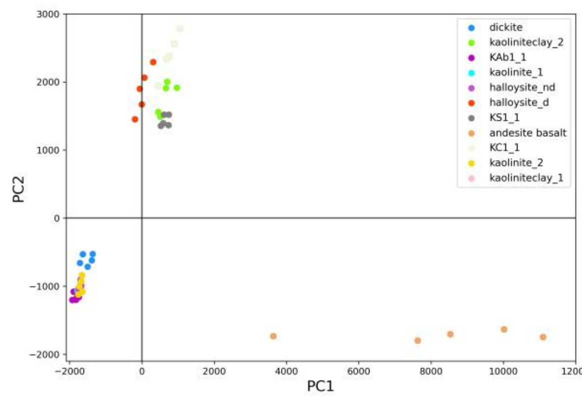

Fig. 4. Classification results of PCA.

Conclusion: In this work, LIBS, VNIR and Raman data of kaolin-group mineral and mixtures were acquired. We also find PCA analysis of LIBS data can classify endmembers and mixtures. In the future, *in-situ* explorations of Mars by VNIR, Raman and LIBS spectroscopy can be combined to distinguish kaolin-group minerals, and thus help to study the aqueous alteration on Mars.

Acknowledgments: We thank the fundings from the National Natural Science Foundation (U1931211, 11941001, 41972322), the Natural Science Foundation of Shandong Province (ZR2019MD008). This work is also supported by Physical-Chemical Materials Analytical & Testing Center of Shandong University at Weihai and the Pre-research project on Civil Aerospace Technologies No. D020102 funded by China National Space Administration (CNSA).

References: [1] Etienne Balan. et al., (2014) *ELEMENTS*, *10*, 183-188. [2] Bethany L. Ehlmann. et al., (2013) *Space Sci Rev*, *174*, 329-364. [3] Cousin, A. et al. (2011) *SAB*, 66, 805–814. [4] Javier Cuadros. et al., (2019) *Icarus*, *330*, 30-41. [5] Alian Wang. et al., (2015) *RAMAN SPECTROSCOPY*, *46*, 829-845.