THE MICRO RAMAN SPECTROSCOPY FOR ANALYSIS OF THE GYPSUM DEHYDRATION BY SIMULATED SPACE WEATHERING. Zhongchen Wu1,2, Yuheng Ni1, Zongcheng Ling1, Hong Wu1. 1School of Space Science and Physics & Shandong Provincial Key Laboratory of Optical Astronomy & Solar-Terrestrial Environment, Shandong University at Weihai, Shandong 264209, China; 2Key Laboratory of Planetary Sciences, Chinese Academy of Sciences, Shanghai 200030, China. (z.c.wu@sdu.edu.cn)

Introduction: Due to low atmospheric pressure, frequently windy and very dry carbon dioxide environment of the Mars, the dust on the Martian surface is susceptible to triboelectric charging [1] and subsequent glow discharge which is easy to generate the low temperature plasma (LTP) by exciting the martian atmosphere.

LTP (at room temperature) contains abundant high-energy electrons in the range of 1–10eV [2] with higher density of 10^2–10^5 cm^-3 [3] which may cause space weathering of solid particles in air and the fine surface soil of the Mars by electron-impact reactions. LTP could be one of the most important chemical weathering factors except for the UV radiation.

Herein, a simulated space weathering of hydrated sulfates by CO2 LTP was reported. The dehydration is a significant process of weathering analyzed by micro Raman spectroscopy.

Analytical Experiments: CaSO₄.2H₂O (mixed with small amount of CaSO₄.0.5H₂O) was grinded into fine powder with over 200 mesh and then pressed into tablets (thickness 2mm) which were analyzed by micro Raman spectroscopy (inVia, Renishaw) equipped with 532 nm laser as unweathered samples. The spectra were recorded from 200 to 4000cm⁻¹ with a resolution better than 1.0cm⁻¹ under ambient air conditions.

LTP was generated between CO2 gas tube (iron tube, 2.0 mm i.d., 3.0 mm o.d) end (as anode) and iron plate electrode (as cathode) which was sealed in a shelfmade air-tight chamber to keep the ambient air out of the plasma excitation source. The distance between two discharge electrodes was set to be 10 mm. And the sample tablets were placed on the iron plate electrode just blow the gas tube end.

When the two electrodes were connected to high-voltage power supply at a voltage of ~4000V and the working gas (High purity CO₂, 99.99%) was inducted into this plasma generator at a fixed flow rate of 1.0 L.min⁻¹, the generated LTP jet can be observed outside of the tube and directly impacted on the gypsum tablets.

After electrons bombardment for 30 min, the weathered gypsum tablets were analyzed by micro Raman spectroscopy. The spectroscopic fingerprints of weathered samples were compared to those of unweathered samples.

Results: The surface appearance of one weathered gypsum tablet was shown in Fig.1. The area marked with the letter A or D (fracture surface of gypsum tablet) had not been weathered by CO2 LTP. The area marked with the letter C or B had been weathered for 30 min. A thin layer of dark material in the area labeled C was identified as magnetite[4] by its Raman spectrum (as shown Fig.2) which is the oxidation products of iron electrodes in CO2 LTP. The area labeled B was detected by micro Raman spectroscopy without interferences of magnetite particles and one fingerprint spectrum was shown in Fig.3B. The crack in this area was due to LTP electrons bombardment and the impingement of high flow rate of CO2 gas.

Fig.1 The surface appearance figure of the weathered gypsum tablet obtained by micro Raman imaging system. Labels A and B refer to collected Raman spectra in Fig. 2 A and B.

Fig.2 The Raman spectrum of the dark material in the area labeled C

The representative Ramam spectra of unweathered and weathered sample were shown in Fig.3.

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Fig. 3 Representative Raman spectra of unweathered (a) and weathered (b) CaSO$_4$.2H$_2$O samples

The spectral bands from 400 cm$^{-1}$ to 800 cm$^{-1}$ (Fig. 3A) are mainly assigned to SO$_4^{2-}$ (both CaSO$_4$.2H$_2$O and CaSO$_4$.0.5H$_2$O) which have very similar spectral features. The band at 1007 cm$^{-1}$ (Fig. 3B) is assigned to SO$_4^{2-}$ of CaSO$_4$.2H$_2$O ($\nu_1$ mode) and the band at 1014 cm$^{-1}$ is assigned to SO$_4^{2-}$ of CaSO$_4$.0.5H$_2$O ($\nu_1$ mode). As seen in Fig. 3C, the band at 3406.9 cm$^{-1}$ and 3494.1 cm$^{-1}$ are due to 2H$_2$O($\nu_1$ mode). And the bands at 3554.1 cm$^{-1}$ and 3614.8 cm$^{-1}$ are due to 0.5H$_2$O ($\nu_1$ mode). By contrasting the spectral data of Fig. 3, we could see that 2H$_2$O rather than 0.5H$_2$O was lost by CO$_2$ LTP weathering. And gypsum dehydration is the significant process of CO$_2$ LTP weathering. However, the other changes in composition and structure of samples were not detected using our Raman method.

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