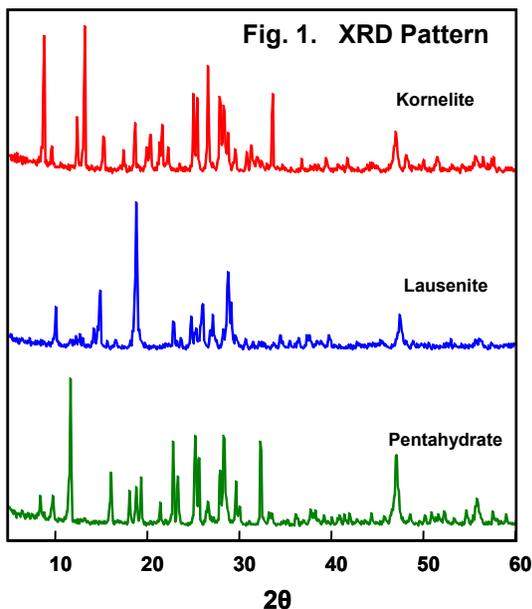


COMPARATIVE SPECTROSCOPIC STUDY OF THREE FERRIC SULFATES: KORNELITE, LAUSENITE AND PENTAHYDRATE, Z.C. Ling^{1,2,3}, Alian Wang³, Chunlai Li¹, ¹National Astronomical Observatories, Chinese Academy of Sciences, Beijing 100012, P R China, ²School of Space Science and Physics, Shandong University, Weihai, Shandong 264209, P R China; ³Department of Earth & Planetary Sciences and McDonnell Center for the Space Sciences, Washington University, St. Louis, MO, 63130 (zcling@sdu.edu.cn)

Introduction: Sulfates have been identified on Mars by orbital remote sensing (OMEGA and CRISM) and during surface exploration (Viking, MER) [1-4]. MER rovers have found Fe-sulfates at both landing sites. A ferric sulfate (jarosite) was identified with the Mössbauer spectrometer (MB) in Meridiani Planum outcrops (~10 wt.%) [5]. At Gusev Crater, light-toned salty soils are hydrous as seen by MiniTES[6], and could contain ferricopiapite, hydronium jarosite, fibroferrite, rhomboclase and paracoquimbite based on a Pancam spectral analysis [7]. To uncover the mysteries related to hydrologic stories of ferric sulfates on Mars, we have conducted a systematic spectroscopic study on hydrated ferric sulfates [8]. We prepared seven ferric sulfates from pure chemicals, confirmed their structures by XRD, and obtained their characteristic Raman spectra, which make the basis for non-invasive Raman identification in the study of stability studies and phase transition pathways under Mars-relevant environmental conditions, and will also be used during Raman-LIBS investigation on ESA's ExoMars mission. In this abstract, we report a set of Raman and Vis-NIR spectroscopic study on three hydrated ferric sulfates, kornelite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 7\text{H}_2\text{O}$), lausenite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$), and pentahydrate ($\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$).



Sample synthesis and XRD phase determination:

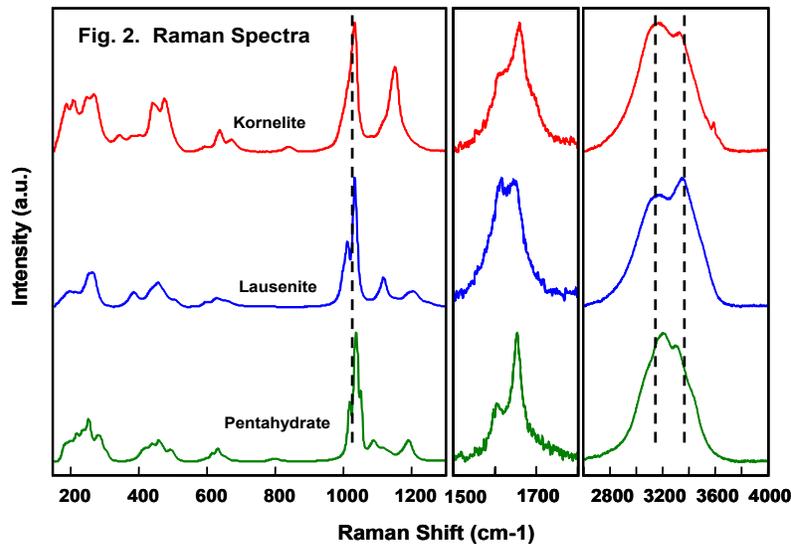
We used an amorphous ferric sulfate with five

structural waters as the starting material, to prepare the three ferric sulfates. When this material was put into a buffer of KI saturated solution at 95°C (~60%RH) for one day, it converted to kornelite with a purple pinkish color. When kornelite was put into a buffer of LiCl saturated solution at 95°C (~10%RH) for one more day, it changed into pentahydrate with a light pinkish color. By further experiment, a new yellowish crystalline phase was obtained from the amorphous ferric sulfate kept in NaI buffer at 95°C (~23%RH).

A Rigaku Geigerflex X-ray diffractometer with a $\text{CuK}\alpha$ radiation source was used in this study to verify the structures of the three produced ferric sulfates. The XRD patterns are shown in Figure 1. Our kornelite and pentahydrate were confirmed by corresponding XRD patterns in PDF2006 database, while the yellowish sample does not match with the XRD pattern of any phases in PDF 2006. It is apparently a new phase not reported before. Gravimetric measurements suggest that it has a molecular formula roughly $\text{Fe}_2(\text{SO}_4)_3 \cdot 5.75\text{H}_2\text{O}$. We also anticipate that it holds a intermediate number of structural water between kornelite and pentahydrate because this yellowish sample was prepared at an intermediate relative humidity environment (23%RH). Further experiments demonstrated that this yellowish phase dehydrated into pentahydrate when keeping it long enough in NaI buffer at 95°C. We concluded that it is lausenite ($\text{Fe}_2(\text{SO}_4)_3 \cdot 6\text{H}_2\text{O}$) which containing six molecules of structural water. Majzlan et al. (2005) determined the structure of pentahydrate and argued that pentahydrate should be called "lausenite" because they have not found a structure with six structural waters [9]. Hence further structural refinement of our newly found species may be of interest in order to validate their statement.

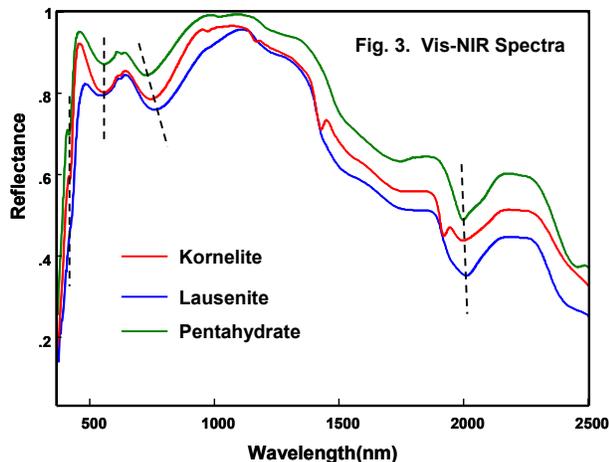
Raman and Vis-NIR spectroscopic studies:

HoloLab5000-532 laser Raman spectrometer (Kaiser Optical Systems Inc.) was used to obtain Raman spectra of the three ferric sulfates ($150\text{-}4000\text{cm}^{-1}$). As shown in Figure 2, the symmetric stretching vibration ν_1 mode of SO_4 tetrahedra in kornelite is a broad peak located at 1032 cm^{-1} ; the similar peak splits into two peaks at 1032 and 1012 cm^{-1} for lausenite; for pentahydrate, ν_1 splits into three peaks at 1051 , 1038 , and 1018 cm^{-1} , respectively. Different splitting of ν_1 suggest various distortion of SO_4 tetrahedra in their crystal structure, i.e., the larger the distortion, the more splitting peaks would be expected. This is also supported by the fact that most



of the other modes for SO_4 (ν_2, ν_3, ν_4) tend to have more peaks following the decreasing of their hydration states. Therefore, lausénite seems to have a medium distortion of SO_4 tetrahedra among the three ferric sulfates. Kornelite and pentahydrate have librational modes of H_2O near 800 cm^{-1} , while lausénite does not show this peak, indicating a restriction of water molecules in lausénite structure.

As shown in Figure 2 from 1500 to 1800 cm^{-1} , the peak widths for water bending mode appears gradually reduce as the hydration state decreases from kornelite to pentahydrate. For the stretching modes of H_2O in 2600 to 4000 cm^{-1} range, it is easy to find that the width of water peak of lausénite and kornelite are larger than that of pentahydrate due to higher hydration state. The relative intensity of anti-stretching modes of H_2O is larger than that of overtones of bending modes ($2\nu_2$) for kornelite. However, reversed relative intensities were observed for lausénite, which indicate a different lattice environment for structural waters in



lausénite.

Analytical Spectral Device (ASD) was used to obtain the reflectance spectra (0.4 – $2.5 \mu\text{m}$) of the three ferric sulfates. As shown in Figure 2, three samples have very different spectral patterns. The lausénite show the lowest albedo among the three. The major spectral variations for Fe^{3+} absorption in the visible region can be described as follows: (1) The peak near 418 nm for kornelite and pentahydrate red shift to become a shoulder. (2) In the 500 – 700 nm region, the absorption band of lausénite seems to blue shift than the other two and be broadened. (3) In the 700 – 1000 nm region indicated by a black dashed

line in Figure 3, the major absorption band shows a red shift and becomes broad for lausénite. The abnormality may be due to the lattice environment of Fe^{3+} , which is very different from the other two as indicated by Raman spectra (Fig.2), leading into a different selection rule for electron transitions. In the NIR region, the combination modes of water near $1.9 \mu\text{m}$ for lausénite is similar to that of pentahydrate but wider, unlike that of kornelite that shows a double peak.

Conclusions:

We have synthesized a ferric sulfate with six structural waters. Its XRD, Raman and Vis-NIR spectral patterns are distinct from those of kornelite and pentahydrate. Our study suggests that lausénite has considerable structural differences from the other two, such as the lattice environment of Fe^{3+} in lausénite. Structural refinement of this lausénite sample is needed to fully understand its spectroscopic features. Those features are useful for data interpretation of current and future missions to Mars.

Acknowledgement: This study is supported by a collaborative project between the Dept. of Space Sciences and Applied Physics at Shandong University and Dept. of Earth and Planetary Sciences at Washington University, and by a Mars Fundamental Research grant NNX07AQ34G.

References: [1] Bibring et al. (2005), *Science*, V307, 1576-1580. [2] Morris et al. (2007) Seventh International Conference on Mars #3393. [3] Clark et al. (1982) *JGR*, V87, 10059-10067. [4] Haskin et al. (2005) *Nature*, V436, doi:10.1038. [5] Klingelhöfer et al., *Science*, (2004) V306, 1740-1746. [6] Ruff et al., (2006) *JGR*, V111, E12S18. [7] Johnson et al. (2007) *JGR*, V34, L13202. [8] Ling et al. (2008) *LPS XXXIX*, #1463. [9] Majzlan et al., (2005) *Am. Mineral.*, 90, 411-416.