

POTENTIAL EXISTENCE OF AL-BEARING SULFATES ON MARS AND THEIR SPECTRAL CHARACTERISTICS. Yuhang Zhou and Alian Wang, Dept of Earth and Planetary Sciences and McDonnell Center for Space Sciences, Washington University in St. Louis, St. Louis, MO, 63130, USA (yuhang@wustl.edu, alianw@levee.wustl.edu)

Potential existence of Al-bearing sulfates on Mars: Hydrous Mg-, Ca-, and Fe-sulfates are one of the two main types of sedimentary minerals found on Mars by recent missions. The data from OMEGA instrument on Mars Express and CRISM instrument on MRO revealed the existences of kieserite ($\text{MgSO}_4 \cdot \text{H}_2\text{O}$), gypsum ($\text{CaSO}_4 \cdot 2\text{H}_2\text{O}$) and polyhydrated sulfates in layered terrains on Mars [1]. Calcium-rich sulfates, mostly like Gypsum are observed in the north polar region of Mars [2]. Mg-, Ca- sulfates, and especially ferric sulfates were found by two Mars Exploration rovers at Gusev and Meridiani Planum [3, 4].

On the other hand, data from orbiters, rovers, and landers all suggest that basalt is the major igneous rock type on Mars, composed mainly olivine, pyroxene and feldspar of various compositions [5]. When these minerals react with SO_4 -bearing fluids, the process with the lowest Gibbs free energy will be preferred. Thus, the weathering of olivine ($\Delta G_f^0 = -6.58$ to -4.0 Kcal/atom) and pyroxene ($\Delta G_f^0 = -2.72$ to -2.98 Kcal/atom) would happen earlier than the weathering of feldspar ($\Delta G_f^0 = -1.32$ to -0.32 Kcal/atom) [6]. The cations release by olivine and pyroxene weathering are mainly Mg, Fe, and Ca, as evidenced by the finding of Mg-, Fe-, and Ca-sulfates on Mars [1-4].

On Earth, Al-bearing sulfates are commonly formed in natural acidic sulfate-rich environments such as active crater lakes, fumaroles, and acidic hot springs, etc. Al-bearing sulfates were not yet reported on Mars but cannot be excluded, because the evidence of extensive weathering was observed on Mars [7-9]. During the late stage of weathering when feldspar altered, Al, K, Na and Ca can be released and can form (under suitable conditions) Al-sulfates and multi-cation-sulfates. Al-sulfates can also form from the acidic leaching of clay minerals [10], e.g., the OMEGA observation of sulfates in stratigraphic layer (in an acidic environment) formed post the formation of a layer of phyllosilicates [7]. In addition, the Inner Basin of Columbia Hills contains several features that likely have formed by volcanic processes [8]. The weathering process of volcanic ash can happen before the feldspar alteration, thus to release Al, K, Na and Ca and to form Al-sulfates and multi-cation sulfates.

Spectroscopic study of Al-bearing sulfates: In sorting of 101 species of Al-bearing sulfates in Dana's New Sulfates Classification [Web 1], we selected 6 groups of hydrated and anhydrous Al-bearing sulfates

for detailed structure and properties study. They are Alunogen group, Felsobanyaite group, Halotrichite group, Voltaite group, Alum group and Alunite group. From the 6 groups of Al-bearing sulfates commonly seen on Earth, we selected two for a preliminary spectroscopic study. The purpose is to learn their major spectral features and the differences from that of Mg-, Fe-, and Ca-sulfates.

The two selected Al-bearing sulfates are alum-(K) ($\text{KAl}(\text{SO}_4)_2 \cdot 12(\text{H}_2\text{O})$) and alunogen ($\text{Al}_2(\text{SO}_4)_3 \cdot 17(\text{H}_2\text{O})$). Laboratory chemicals were used as the samples of measurements. XRD analysis was first made to confirm their structures, then spectroscopic measurements were made using laser Raman, MIR-Attenuated Total Reflectance (ATR) and NIR-Diffuse Reflectance (DR). XRD measurement was made using a Rigaku Geigerflex X-ray diffractometer with Cu $\text{K}\alpha$ radiation. Raman measurements were made on single crystal grain under the microscope of KOSI HoloLab5000 Raman spectrometer, with $\sim 9\text{mW}$ of 532 nm laser power at the sample. MIR-ATR measurements were made on crashed grains using a GoldenGate ATR accessory of Nicolet Nexus 670 FTIR spectrometer. NIR-DR measurements were made on ground powder using Crocket accessory of the same FTIR spectrometer.

Results and discussion: Peaks in laser Raman and MIR-ATR spectra provide the information on the fundamental vibration modes of these Al-bearing sulfates, thus can be directly linked to the crystal structural character of the samples. The spectral peaks of NIR-DR are the overtones and combinational modes that have the highest application potentials for interpreting the data from planetary missions.

Figure 1 compares the Raman spectra of alum-(K) and alunogen with that of three typical hydrous Mg-, Fe-, and Ca-sulfates: epsomite ($\text{MgSO}_4 \cdot 7(\text{H}_2\text{O})$), melanterite ($\text{FeSO}_4 \cdot 7(\text{H}_2\text{O})$) and gypsum ($\text{CaSO}_4 \cdot 7(\text{H}_2\text{O})$). Those spectra were obtained by laboratory measurements under similar conditions. There are two most distinguished differences between Al-sulfates and others, the first one is in spectral range 2600-3600 cm^{-1} (Fig. 1a). The H_2O Raman peak of alunogen and alum-(K) is much broad than other three sulfates, extends from 3600 to 2800 cm^{-1} . This feature is probably due to the multi-sites occupied by structural water in Al-bearing sulfates and the large site differences.

In alunogen $[\text{Al}(\text{H}_2\text{O})_6]_2(\text{SO}_4)_3(\text{H}_2\text{O})_5$ unit cell, (SO_4) tetrahedra and $[\text{Al}(\text{H}_2\text{O})_6]$ octahedra are linked

together by hydrogen bonding. There are two kinds of sites for aluminum atoms marked as Al₁ and Al₂. The bond lengths from six H₂O to Al₁ (or Al₂) are all different, which will induce small frequency difference in H₂O vibrational peak. There are five types of interstitial H₂O groups that link to tetrahedral and octahedral through hydrogen bonds. Their site differences would also bring difference in H₂O vibration modes. In total, there are 17 types of H₂O groups that are sited or bonded differently in the unit cell of alunogen. Therefore H₂O Raman peak of alunogen can be viewed as a combination of many inequivalent H₂O fundamental vibration modes, with very broad peak width (Fig. 1a).

The 2600-3600 cm⁻¹ spectral range of alum-(K) can be viewed as composed by three sub-peaks and contributed by inequivalent H₂O fundamental vibration modes. The structure of Alum-(K), K[Al(H₂O)₆](SO₄)₂(H₂O)₆ consists of [Al(H₂O)₆], (H₂O), and (SO₄) groups linked by hydrogen bonding. All (H₂O) groups are coordinated with K or Al cations. In [Al(H₂O)₆] octahedra, the bond lengths from six (H₂O) to Al are all the same. The other six (H₂O) surrounding K form a distorted octahedra. These two groups of inequivalent H₂O can be the contributors of the two strong sub-peaks in 2600-3600 cm⁻¹ of alum (K).

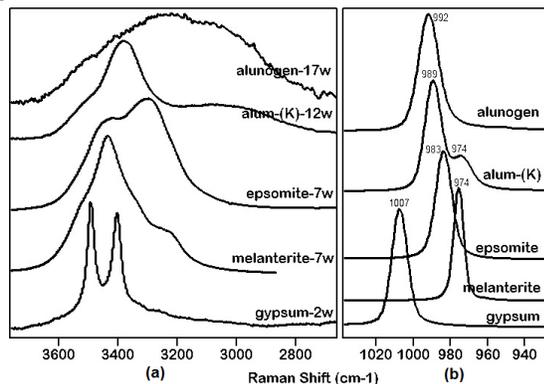


Figure 1. Comparison of the Raman spectra of Al-bearing sulfates with three typical Mg-, Fe-, Ca-sulfates. (a) H₂O modes in 2600-3600 cm⁻¹ spectral range, (b) ν_1 modes of (SO₄)₂⁻ in 1040-940 cm⁻¹ spectral range.

The second major spectral difference between Al-sulfates and typical Mg-, Fe-, Ca-sulfates is in 1200-100 cm⁻¹ region of fundamental vibration of [SO₄]²⁻ tetrahedra (Fig. 1b). The peaks with the highest intensity in the 900-1100 cm⁻¹ is contributed by the symmetrical stretching vibrational mode ν_1 of [SO₄]²⁻. The ν_1 peak position of the two Al-bearing sulfates is higher than the ν_1 of epsomite and melanterite but lower than that of gypsum. It is notable that the ν_1 peak of alum-(K) is a doublet (989 cm⁻¹ and 974 cm⁻¹). This doublet is caused by a specific structural disorder that produces two types of [SO₄]²⁻ tetrahedra with different orientations in crystal lattice [11]. Both (SO₄) tetrahedral are

distorted to have a 3-fold symmetry. The vertex along the 3-fold axis of a (SO₄) tetrahedron can either point towards or point away from an Al atom. The former tetrahedron is called a major (SO₄) tetrahedron, and the latter one is called a minor (SO₄) tetrahedron [11]. It is believed that the short distance between K atoms and O atoms in (SO₄) tetrahedron causes this disorder [12]. The ν_1 doublet in Alum (K) Raman spectrum is due to the different vibration frequencies contributed by the major and minor (SO₄) tetrahedra.

Figure 2 compares the NIR Diffuse reflectance spectra of alunogen and alum-(K), with those of epsomite, melanterite and gypsum. It appears that the absorption bands of these two Al-bearing sulfates have weaker spectral contrast than the corresponding bands of Mg-, Fe-, and Ca-sulfates. Further detailed analysis will be made and will be reported at conference.

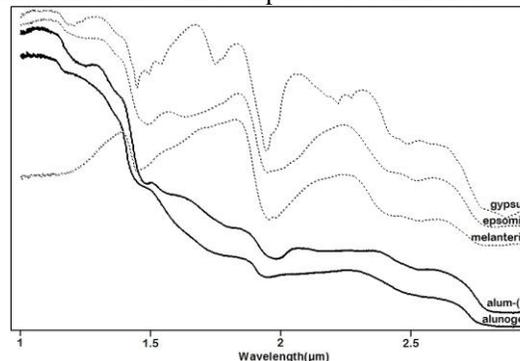


Figure 2. NIR-DF spectra of two Al-bearing sulfates in comparison with three typical Mg-, Fe-, Ca-sulfates.

Future work: The further in-depth study of the precipitation, preservation, and spectroscopic characters of Al-bearing sulfates will be conducted.

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