

**RAMAN SPECTROSCOPIC STUDY OF THE K-NA JAROSITE SOLID SOLUTIONS** Zongcheng Ling<sup>1</sup>, Fengke Cao<sup>1</sup>, Yuheng Ni<sup>1</sup>, Zhongchen Wu<sup>1</sup>, Jiang Zhang<sup>1</sup>, Bo Li<sup>1</sup> <sup>1</sup> Shandong Provincial Key Laboratory of Optical Astronomy and Solar-Terrestrial Environment, Institute of Space Sciences, Shandong University, Weihai, 264209, P. R. China ([zcling@sdu.edu.cn](mailto:zcling@sdu.edu.cn))

## Introduction

The hydrated sulfate minerals are essential for identifying and determining the aqueous history for Mars. Terrestrial Jarosite ((K,Na,H<sub>3</sub>O)Fe<sub>3</sub>(SO<sub>4</sub>)<sub>2</sub>(OH)<sub>6</sub>) is a common mineral often associated with acid-mine waste on Earth. For Mars, Jarosite is the first definitely discovered sulfate mineral phases by Mossbauer spectrometer aboard Opportunity rover [1], indicating an acidic water-limited chemical weathering environment on this planet [2]. Jarosite has also been remotely detected as patchy exposures in the northern Mawrth Vallis region by Compact Reconnaissance Imaging Spectrometer for Mars (CRISM) aboard Mars Reconnaissance Orbiter (MRO)[3,4].

Raman spectroscopy has a great advantage for future Mars explorations due to its power in fast molecular (organic and inorganic) phase identification in mixtures, characterization of mineral chemistry, and the minimum-to-no sample preparation requirement, etc[5-7]. Three Raman units were selected as scientific payloads for 2018 ExoMars and 2020 Mars rover, with the mission goals of fine-scale definitive mineralogy and bio-signature detection. Calibrations have been done to extract compositional information from major igneous minerals using their Raman peak positions (e.g. Wang et al. (2001)[8] for pyroxene, Kuebler et al. (2006)[9] for olivine). There is a growing need for in-depth study of Raman spectra in the chemical characterization of martian related minerals (especially for secondary minerals like jarosite), as guidance for its possible applications in the coming Mars missions.

In this paper, we report our prediction of K content in K-Na jarosite solid solutions by using their characteristic Raman features. Our goal is trying to correlate the chemical variations (varying K/Na ratio) with their typical Raman peak positions, with intent to derive a reliable formula for the prediction of K content in K-Na jarosite solid solutions.

## Experiments

We synthesized the K-, Na-, H<sub>3</sub>O- jarosite endmembers and K-Na jarosite solid solutions following similar methods of Basciano and Peterson (2007, 2008)[10-11]. The elemental concentration (K, Na, Fe etc) of the samples are determined by the energy dispersive spectrometer (EDS, Oxford Aztec Xmax50) on the scanning electron microscopy (SEM, FEI Nova NanoSEM 450). The Raman measurements are performed on the newly installed state-of-art inVia® Raman System (Renishaw Company) in Shandong University, Weihai. The green laser (532 nm) is applied with a 50X objective during measurements, yielding spectral resolution better than

1cm<sup>-1</sup> and spectral repeatability of ± 0.2 cm<sup>-1</sup>.

## Results and Discussions

The chemical compositions of K-Na jarosite solid solutions are shown in Table 1. The occupancy of the alkali and Fe sites were determined in the solid samples based on the ratio of alkali and Fe to S. The percent of K, Na and Fe in these sites were normalized to 2 S per chemical formula based on the ideal chemical formula.

Table 1. The normalized chemical formula of K-Na jarosite solid solutions determined by SEM-EDS

ID	Formula
K-95	(K <sub>0.95</sub> Na <sub>0.05</sub> )Fe <sub>2.81</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
K-91	(K <sub>0.91</sub> Na <sub>0.09</sub> )Fe <sub>2.74</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
K-68	(K <sub>0.68</sub> Na <sub>0.27</sub> )Fe <sub>3.17</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
K-53	(K <sub>0.53</sub> Na <sub>0.44</sub> )Fe <sub>2.85</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
K-27	(K <sub>0.27</sub> Na <sub>0.67</sub> )Fe <sub>2.9</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
K-13	(K <sub>0.13</sub> Na <sub>0.8</sub> )Fe <sub>2.78</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
K-0	(K <sub>0.00</sub> Na <sub>0.95</sub> )Fe <sub>2.82</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>

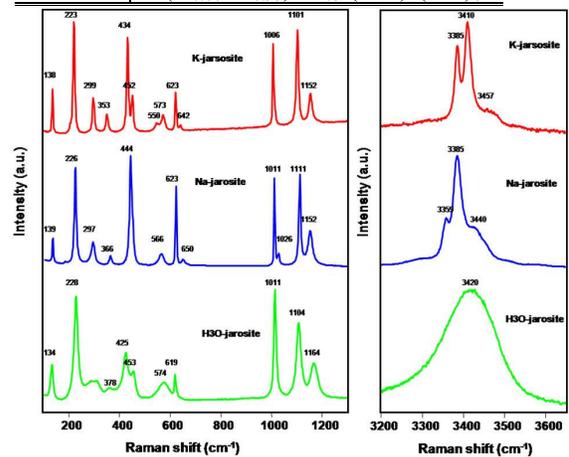


Fig.1. Typical Raman spectra of three end-members K-Na-H<sub>3</sub>O jarosites synthesized in laboratory

The Raman spectra of K-jarosite, Na-jarosite and H<sub>3</sub>O-jarosite end-members are shown in Fig.1. Although all three have similar major spectral features arising from the internal vibrational modes of SO<sub>4</sub> tetrahedra (ν<sub>1</sub> ~ ν<sub>4</sub>), their precise peak locations are different due to the different occupancies of A-site cations (K-, Na- and H<sub>3</sub>O-). The OH stretching region (3200~3650 cm<sup>-1</sup>) of three jarosite end-members also show distinct features (Fig.1). The major peaks are ascribed as the hydroxyl stretching (ν<sub>s</sub>) modes, which are sensitive with respect to different cation size in A site, i.e., from 3385 cm<sup>-1</sup> in Na-jarosite to 3410 cm<sup>-1</sup> in K-jarosite and 3420 cm<sup>-1</sup> in H<sub>3</sub>O-jarosite, thus this position can also be used as reference for their phase identifications. As shown in Fig. 2. The K-Na jarosite solid solutions show systematic variations of Raman peak positions with the changes of alkali content (i.e. K/Na ratio) in A site. The peak 1 (ν<sub>1</sub>,

$\sim 1010\text{cm}^{-1}$ ), Peak 2 ( $\nu_3$ ,  $\sim 1110\text{cm}^{-1}$ ) and Peak 3 ( $\nu_2$ ,  $\sim 440\text{cm}^{-1}$ ) have the largest variations due to the varying K/Na ratio, i.e., Peak 1 ( $\Delta=5\text{cm}^{-1}$  from  $1006$  to  $1011\text{cm}^{-1}$ ), Peak 2 ( $\Delta=11\text{cm}^{-1}$  from  $1100$  to  $1111\text{cm}^{-1}$ ) and Peak 3 ( $\Delta=10\text{cm}^{-1}$  from  $434$  to  $444\text{cm}^{-1}$ ).

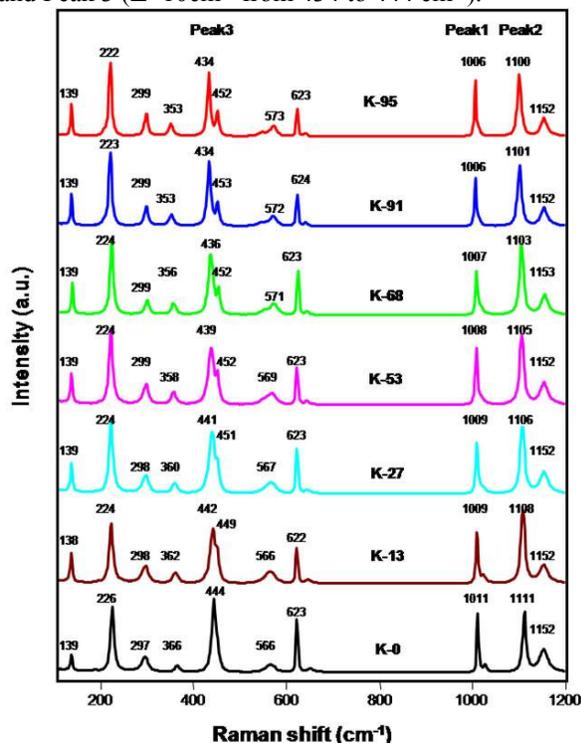


Fig. 2. Raman spectra of K-Na jarosite solid solutions

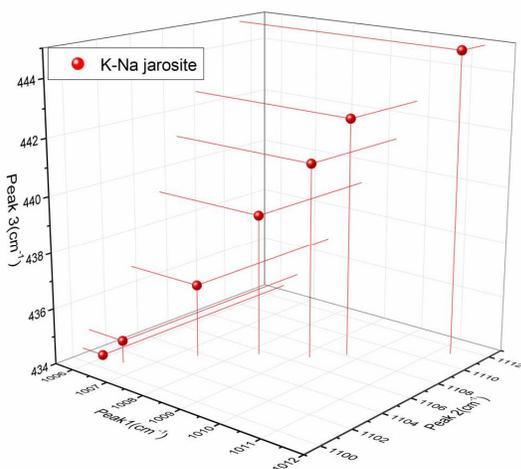


Fig. 3. The 3D scatter plot of peak 1, peak 2 and peak 3 for K-Na jarosite solid solutions.

The precise peak positions of Peak 1, Peak 2 and Peak 3 were obtained by spectral deconvolution using the Renishaw WiRE 3.4 software package with a mixed Gaussian-Lorentzian algorithm. As shown in the 3D scatter plot for K-Na jarosite solid solutions (Fig. 3), the Peak 1, Peak 2 and Peak 3 have very good linear rela-

tionship between each other (with Pearson's correlation coefficients  $> 0.99$ ). This indicates they are good candidate parameters for the evaluation of chemical variations of K-Na jarosite solid solutions. Based on multiple linear regression of these parameters, we can derive the calculation formula as follows,

$$K\text{-content} = 9.37 \times \text{Peak1} - 0.32 \times \text{Peak2} - 13.32 \times \text{Peak3} - 3195 \quad (1)$$

Where the K-number is the molar ratio  $K/(K+Na) \times 100$  of K-Na jarosite solid solutions, Peak1 ( $\sim 1010\text{cm}^{-1}$ ), Peak2 ( $\sim 1110\text{cm}^{-1}$ ) and Peak3 ( $\sim 440\text{cm}^{-1}$ ) are Raman peak positions of K-Na jarosite solid solutions in the unit of Raman shift ( $\text{cm}^{-1}$ ). As shown in Fig. 4, the data points of measured and predicted K-number of K-Na jarosite solid solutions distribute equally along the 1:1 line, suggesting a good model of K-number has been achieved. The standard deviation between measured and predicted K-number is  $\pm 4$ . This formula can be used as the first principle for the prediction of K contents in K-Na jarosite solid solution series.

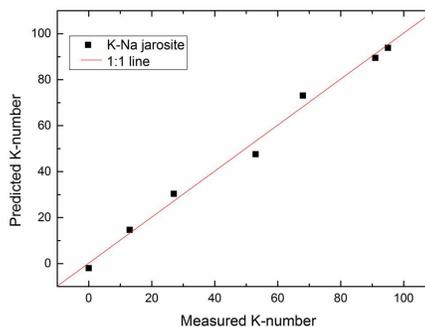


Fig. 4. The scatter plot of measured K-number versus predicted K-number by using equation 1.

### Conclusions and Future work

We have synthesized the endmember K-jarosite, Na-jarosite and  $\text{H}_2\text{O}$ -jarosite and the K-Na jarosite solid solutions in laboratory. The Raman peak positions of Na-K jarosites show systematic variations in concert with the K-content for the solid solutions. We derived a formula applicable for the prediction of K content in jarosite, which is meaningful for the future Raman payloads of Mar's missions. Future work will focus on the refinement of the K-number formula and we will extend our calibration work to the ternary K-Na- $\text{H}_2\text{O}$  jarosite solid solutions.

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**References:** [1] Klingelhöfer G. et al. (2004) *Science*, 306, 1740. [2] Madden M. E. et al. (2004) *Nature*, 431, 821-823. [3] Farrand W.H. et al. (2009) *Icarus*, 204, 478-488. [4] Michalski J.R. et al. (2013) *Icarus*, 226, 816-840. [5] Wang A. et al. (2003) *JGR*, 108(E1), 5005. [6] Sharma S.K. et al. (2003) *Spectrochim. Acta Part A*, 59(10), 2391-2407. [7] Rull F. et al. (2014) *GeoRaman*, 11th, 5056. [8] Wang A. et al. (2001) *Am. Miner.*, 86,790-806. [9] Kuebler K.E. et al. (2006) *GCA*, 70(24), 6201-6222. [10] Basciano L.C. and Peterson R.C. (2007) *Am. Miner.*, 92, 1464-1473. [11] Basciano L.C. and Peterson R.C. (2008) *Am. Miner.*, 93, 853-862.