

### Chemical and Spectroscopic Characteristics of Synthetic K-H<sub>3</sub>O-Na Alunite Solid-Solutions.

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**Introduction:** The ideal stoichiometry of alunite-supergroup minerals is described by the general formula  $AB_3(SO_4)_2(OH)_6$ , where A-sites are usually occupied by  $K^+$ ,  $Na^+$ ,  $H_3O^+$ ,  $NH_4^+$ , with B-sites being occupied by  $Al^{3+}$  or  $Fe^{3+}$ . The supergroup can be classified into various groups, among which the two simplest primary subdivisions are jarosite (B=  $Fe^{3+}$ ) and alunite (B=  $Al^{3+}$ ) on the basis of the B cations. Natural and synthesized solid-solutions with intermediate compositions between jarosite and alunite, as well as different endmembers, have been widely studied [1–7]. As a typical alteration production of Al-bearing minerals (e.g., feldspar), hydroxylated alunite usually occurs in weathering and hydrothermally acidic, perhaps habitable, environments [8, 9].

Previous work has focused on the B site (Fe/Al) substitutions of alunite-jarosite solid-solutions [6], here we examine spectral features of the K-H<sub>3</sub>O-Na (A-site) alunite solid-solutions with the intent to quantitatively correlate the chemical variations with their typical Raman peak positions. Three series of alunite solid-solutions (ASS) with hydronium substitutions of potassium and sodium (i.e.,  $[H_3O]_{1-x}K_xAl_3[SO_4]_2[OH]_6$ ,  $[H_3O]_{1-y}Na_yAl_3[SO_4]_2[OH]_6$ ,  $[Na]_{1-z}K_zAl_3[SO_4]_2[OH]_6$ ) are synthesized. Raman and infrared spectroscopy were then performed to acquire phase identifications and spectroscopic characteristics of ASS with varying  $H_3O^+$  substitutions of  $K^+$  or  $Na^+$ .

Alunite, as a common ferric sulfate mineral on Earth, has recently been suggested to be present on Mars on different locations by remote sensing studies, such as Cross crater [10], Eridania Basin [11], and NE Syrtis [12]. Specially, Jezero Crater, where Perseverer Rover will be landing in the coming month, has also proven to have alunite and jarosite distributions [12]. Three micro-miniaturized Raman spectrometers will soon be part of a suite of analytical tools on the surface of Mars with the landing of Perseverance and Rosalind Franklin Rovers. It is critically important to examine the Raman spectral information that could be forthcoming from attempts to discriminate various alunite phases under Mars' hostile surficial conditions.

Our research about the chemistry and spectra of K-H<sub>3</sub>O-Na alunites will provide a valuable database for alunite-group phase identifications on Mars for near-future Mars missions (i.e., Mars 2020 and ExoMars 2022).

**Methods and Samples:** *Synthesis methods:* Alunite samples are synthesized under a hydrothermal environment using similar methods to study [13–15]. Nine grams of  $Al_2(SO_4)_3 \cdot 18H_2O$  and various amounts of  $K_2SO_4$  were added to 80 mL deionized water. The solution was sealed in an autoclave and heated at 190 °C for 15 days. K-H<sub>3</sub>O alunite solid-solutions,  $K_{1-x}H_3O_xAl_3(SO_4)_2(OH)_6$ , were finally precipitated. Na-H<sub>3</sub>O alunite solid-solutions were synthesized using a similar method. Their homogeneity is examined using a multi-point check of Raman spectra.

*Chemistry:* Chemical composition was measured using an inductively coupled plasma mass spectrometer (ICP-MS, Perkin Elmer Nexion300). The average analytical accuracy and precision for each element are as follows: Al  $\pm 1.7\%$ , 0.7%; Na  $\pm 1.8\%$ , 0.7%; K  $\pm 1.4\%$ , 0.8%; and S  $\pm 1.9\%$ , 1.5%. The atomic percentages of potassium, sodium, and iron in A and B sites were normalized to two sulfur atoms per formula unit. For the K-H<sub>3</sub>O and Na-H<sub>3</sub>O alunite solid solutions, the  $H_3O$  content was obtained by assuming charge balance, full occupancy by  $Fe^{3+}$ , and no  $H_2O$  for OH- substitution [16].

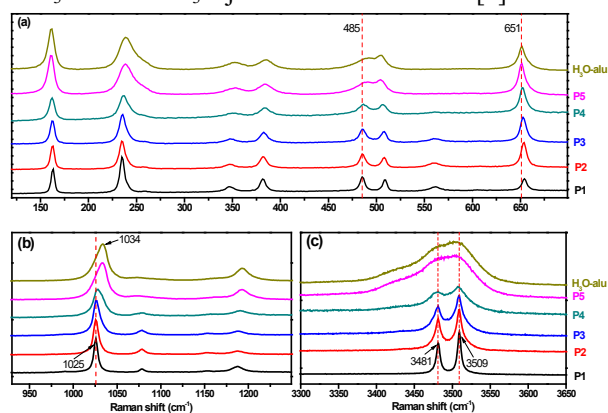
*Raman and infrared spectra:* Raman spectroscopic measurements were performed on the newly installed state-of-art inVia® Raman System (Renishaw Company) in Shandong University, Weihai. The Raman measurements employ a green 532 nm laser line for excitation and a 50×objective covering two spectral ranges of 100–1400  $cm^{-1}$  and 3000–4000  $cm^{-1}$  with a spectral resolution better than 1  $cm^{-1}$  and spectral repeatability of  $\pm 0.2$   $cm^{-1}$ . The infrared spectral measurements of alunite samples were collected using a Bruker vertex 70 Fourier Transform Infrared Spectrometer. The samples were analyzed in the mid-infrared spectral region (400–4000  $cm^{-1}$ ) in transmission mode by co-adding 32 scans with 2  $cm^{-1}$  spectral resolution. Near-infrared reflectance spectra were acquired in the 4000–8000  $cm^{-1}$  (2500–1250 nm) range with 128 scans at a resolution of 2  $cm^{-1}$ .

**Results:** The elemental abundance and chemical formula of each alunite sample are summarized in Table 1. Aluminum content within all the synthesized samples was generally smaller than 3mol/2mol of sulfur, indicating B site vacancies and the associated substitution of water molecules for part of the OH groups (protonation) [17–19].

**Table 1.** Chemical formulas of synthetic K-H<sub>3</sub>O-Na alunite solid-solutions determined by ICP-MS.

ID	Elemental abundance (atom %) and formula				Formula
	Al	K	Na	S	
P1	20.35	9.97	0	17.84	(K <sub>0.92</sub> H <sub>3</sub> O <sub>0.08</sub> )Al <sub>2.70</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
P2	20.58	9.10	0	18.31	(K <sub>0.82</sub> H <sub>3</sub> O <sub>0.18</sub> )Al <sub>2.66</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
P3	21.83	7.57	0	18.09	(K <sub>0.69</sub> H <sub>3</sub> O <sub>0.31</sub> )Al <sub>2.86</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
P4	22.33	4.25	0	19.54	(K <sub>0.36</sub> H <sub>3</sub> O <sub>0.64</sub> )Al <sub>2.71</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
P5	24.84	2.18	0	19.93	(K <sub>0.18</sub> H <sub>3</sub> O <sub>0.82</sub> )Al <sub>2.95</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
S1	20.58	0	5.57	18.47	(Na <sub>0.84</sub> H <sub>3</sub> O <sub>0.16</sub> )Al <sub>2.64</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
S2	20.53	0	5.38	17.70	(Na <sub>0.85</sub> H <sub>3</sub> O <sub>0.15</sub> )Al <sub>2.75</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
S3	24.02	0	4.90	19.84	(Na <sub>0.69</sub> H <sub>3</sub> O <sub>0.31</sub> )Al <sub>2.87</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
S4	27.17	0	3.18	23.87	(Na <sub>0.37</sub> H <sub>3</sub> O <sub>0.63</sub> )Al <sub>2.70</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
S5	25.58	0	1.66	22.09	(Na <sub>0.21</sub> H <sub>3</sub> O <sub>0.79</sub> )Al <sub>2.74</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
H1	18.52	0	0	16.71	H <sub>3</sub> OAl <sub>2.63</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
A1	23.38	1.96	5.12	19.41	(K <sub>0.17</sub> Na <sub>0.73</sub> )Al <sub>2.86</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
A2	23.07	3.63	4.09	18.05	(K <sub>0.33</sub> Na <sub>0.63</sub> )Al <sub>3.03</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
A3	20.58	4.85	2.76	16.71	(K <sub>0.48</sub> Na <sub>0.46</sub> )Al <sub>2.92</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
A4	22.46	7.72	1.59	18.62	(K <sub>0.68</sub> Na <sub>0.24</sub> )Al <sub>2.86</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>
A5	22.67	10.02	0.47	19.07	(K <sub>0.86</sub> Na <sub>0.07</sub> )Al <sub>2.82</sub> (SO <sub>4</sub> ) <sub>2</sub> (OH) <sub>6</sub>

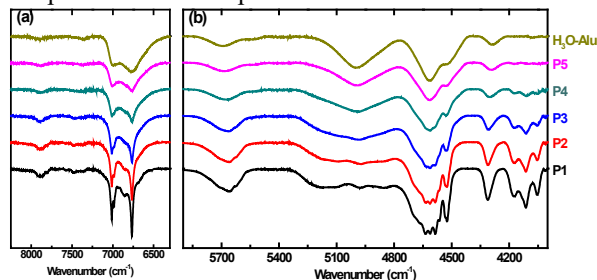
**Raman:** K-H<sub>3</sub>O alunite solid-solutions show systematic Raman spectral variations with varying hydronium content (Fig. 1). When chemical ratios of K/(K+H<sub>3</sub>O), increase from 0 % to 92 % (mol. %) in K-H<sub>3</sub>O alunite solid-solutions, Raman spectral peaks exhibit systematic shifts:  $\nu_2(\text{SO}_4)^{2-}$  (from 491.4 to 485.3 cm<sup>-1</sup>),  $\nu_4(\text{SO}_4)^{2-}$  (from 651.4 to 654.1 cm<sup>-1</sup>),  $\nu_1(\text{SO}_4)^{2-}$  (from 1,034.8 to 1,025.7 cm<sup>-1</sup>) and  $\nu_3(\text{SO}_4)^{2-}$  (from 1,193.1 to 1,187.3 cm<sup>-1</sup>). Hydronium alunite (H1) has one overlapped and broad peak in the 3,450–3,550 cm<sup>-1</sup> spectral range (assigned to  $\nu(\text{OH})$ ), and with increasing K content, there is a transition to double peaks. A similar phenomenon was reported in K-H<sub>3</sub>O and Na-H<sub>3</sub>O jarosite solid-solutions [2].



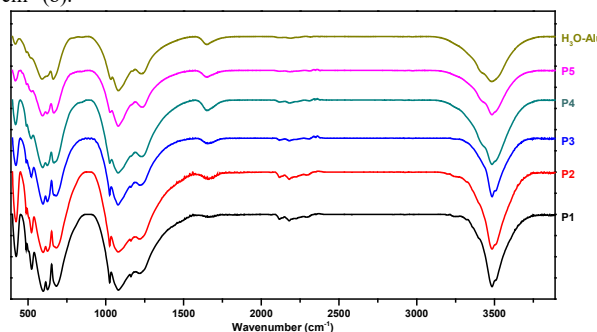
**Fig. 1.** Raman analysis of synthetic K-H<sub>3</sub>O alunite solid-solutions. Raman peaks in the (a) spectral range of fundamental vibrations and lattice modes (100–700 cm<sup>-1</sup>). (b) The spectral range of SO<sub>4</sub><sup>2-</sup> fundamental vibrations (900–1200 cm<sup>-1</sup>). (c) OH/H<sub>2</sub>O spectral range (3400–3600 cm<sup>-1</sup>).

Furthermore, the Raman peak width in the range becomes broader with increasing hydronium, which

may to some extent imply the poorer crystallization for the intermediates near hydronium alunite (e.g., P4 and P5 in Fig. 1c). Infrared spectra are shown in Fig. 2 and Fig. 3. H<sub>3</sub>O-alunite has some spectral bands that are dampened or lost compared to endmember K-alunite.



**Fig. 2.** Near-infrared (NIR) reflectance spectra for synthetic K-H<sub>3</sub>O alunite solid-solutions in the range of 6300–8200 cm<sup>-1</sup> (a), 4000–6000 cm<sup>-1</sup> (b).



**Fig. 3.** Mid-infrared Transmission spectra of synthetic K-H<sub>3</sub>O alunite solid-solutions in the range of 400–4000 cm<sup>-1</sup>.

**Acknowledgments:** This research was supported by the National Natural Science Foundation of China (U1931211) and the Natural Science Foundation of Shandong Province (ZR2019MD008). We thank Dr. Huajun Jiang for his skillful and meticulous chemical analysis of alunite samples.

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