

LETTER

## Hydrothermal synthesis and crystal structure of $\text{AlSO}_4(\text{OH})$ : A titanite-group member

ALAN J. ANDERSON,<sup>1</sup> HEXIONG YANG<sup>2,\*</sup> AND ROBERT T. DOWNS<sup>2</sup>

<sup>1</sup>Department of Earth Sciences, St. Francis Xavier University, Antigonish, Nova Scotia B2G 2W5, Canada

<sup>2</sup>Department of Geosciences, University of Arizona, Tucson, Arizona 85721-0077, U.S.A.

### ABSTRACT

Aluminum hydroxysulfate,  $\text{AlSO}_4(\text{OH})$ , is postulated to play a vital role in controlling the solubility of aluminum in sulfate-rich acidic soils and ground waters, but it has not yet been confirmed in nature. This study reports the synthesis of an  $\text{AlSO}_4(\text{OH})$  crystal at 700 °C and ~1.0 GPa in a hydrothermal diamond-anvil cell from a mixture of 95%  $\text{H}_2\text{SO}_4$  and  $\text{Al}_2\text{O}_3$  powder and its structure determination from single-crystal X-ray diffraction data.  $\text{AlSO}_4(\text{OH})$  is monoclinic with space group  $C2/c$  and unit-cell parameters  $a = 7.1110(4)$ ,  $b = 7.0311(5)$ ,  $c = 7.0088(4)$  Å,  $\beta = 119.281(2)^\circ$ , and  $V = 305.65(3)$  Å<sup>3</sup>. Its crystal structure is characterized by kinked chains of corner-sharing  $\text{AlO}_6$  octahedra that run parallel to the  $c$ -axis. These chains are linked together by  $\text{SO}_4$  tetrahedra and hydrogen bonds, forming an octahedral-tetrahedral framework. Except for the numbers and positions of H atoms,  $\text{AlSO}_4(\text{OH})$  is isostructural with the kieselite-type minerals, a subgroup of the titanite group of minerals. A comparison of powder X-ray diffraction patterns indicates that our  $\text{AlSO}_4(\text{OH})$  is the same as that obtained by Shanks et al. (1981) through hydrolysis of  $\text{Al}_2(\text{SO}_4)_3$  solutions at temperatures above 310 °C. To date,  $\text{AlSO}_4(\text{OH})$  has been synthesized only at temperatures above 290 °C, implying that it may not be stable in low-temperature environments, such as acidic soils and mine waters. The possible environments to find  $\text{Al}(\text{OH})\text{SO}_4$  may include places where sulfur-rich magma-derived fluids react with aluminous rocks under elevated temperature and pressure, and on Venus where a sulfur-rich atmosphere interacts with surface rocks at temperatures above 400 °C.

**Keywords:**  $\text{AlSO}_4(\text{OH})$ , aluminum hydroxysulfate, X-ray diffraction, crystal structure, Raman spectroscopy, high temperature

### INTRODUCTION

Aluminum hydroxysulfates are of great importance as precursor materials for preparation of various activated aluminas, catalysts,  $\alpha$ -aluminas, and quality ceramic products (MacZura et al. 1994 and references therein). Of the many compounds in the system  $\text{Al}_2\text{O}_3$ - $\text{SO}_3$ - $\text{H}_2\text{O}$  (Bassett and Goodwin 1949; Dyson and Scott 1965; Nordstrom 1982), only about a dozen are known to occur naturally in low-temperature environments, such as hydrobasaluminite  $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 9\text{H}_2\text{O}$ , felsobanyaite  $\text{Al}_4\text{SO}_4(\text{OH})_{10} \cdot 4\text{H}_2\text{O}$ , alunogen  $\text{Al}_2(\text{SO}_4)_3(\text{H}_2\text{O})_{12} \cdot 5\text{H}_2\text{O}$ , and jurbanite/rostitite  $\text{AlSO}_4(\text{OH}) \cdot 5\text{H}_2\text{O}$ . Numerous studies have shown that some aluminum hydroxysulfates play a vital role in controlling the solubility of aluminum in sulfate-rich acidic soils and ground waters (e.g., Van Breemen 1976; Nordstrom 1982; Jones et al. 2011). In particular, based on the observations on aluminum activities in 127 acid mine waters and acid sulfate soil waters, Van Breemen (1973) found, for a wide range of pH, pAl, and p $\text{SO}_4$ , that there was a fairly constant proportion of  $\text{Al}:\text{OH}:\text{SO}_4 = 1:1:1$ , and suggested that a basic aluminum sulfate mineral of this stoichiometry controlled the dissolved aluminum concentrations. Further evidence to support this unknown mineral as a control on dissolved aluminum in acid sulfate soils and acid mine waters was provided by Van Breemen (1976) and Nordstrom (1982). Consequently, a new approach, called the  $\text{AlSO}_4(\text{OH})$  approach or a constant solubility product of  $\text{AlSO}_4(\text{OH})$  (Ludwig et al. 1999), has been proposed to model

soil solution field data (Ludwig et al. 1999), as compared to the classical sorption isotherm approach (e.g., Alewell et al. 1997). Nevertheless, Van Breemen's conjectured mineral has not yet been discovered in nature, possibly because it may be very fine grained and amorphous (Van Breemen 1973; Nordstrom 1982). It should be pointed out that the compound  $\text{AlSO}_4(\text{OH})$  was also expressed as  $\text{Al}(\text{OH})\text{SO}_4$  or  $\text{AlOHSO}_4$  in the literature. However, to facilitate a direct comparison with the kieselite-group minerals, we have adapted the formula  $\text{AlSO}_4(\text{OH})$  throughout this paper.

Several experiments at temperatures above 100 °C, however, have produced other aluminum hydroxysulfates by hydrolysis of  $\text{Al}_2(\text{SO}_4)_3$  solutions (Bassett and Goodwin 1949; Dyson and Scott 1965; Shanks et al. 1981). Of special interest is "phase A" synthesized at 290 °C by Dyson and Scott (1965). This new phase has the composition  $\text{AlSO}_4(\text{OH})$  and does not appear at much lower temperatures (for example, 250 °C). It dehydrates upon heating above 550 °C. Shanks et al. (1981) obtained fine crystalline  $\text{AlSO}_4(\text{OH})$  from 127 and 336 g/L  $\text{Al}_2(\text{SO}_4)_3$  solutions at temperatures greater than 310 °C and suggested that the high-temperature hydrolysis product,  $\text{AlSO}_4(\text{OH})$ , could represent a possible state-of-the-art alternative to recovering alumina from  $\text{Al}_2(\text{SO}_4)_3$ . This study reports the first structure analysis of hydrothermally synthesized  $\text{AlSO}_4(\text{OH})$  with single-crystal X-ray diffraction and Raman spectroscopy.

### EXPERIMENTAL METHODS

The  $\text{AlSO}_4(\text{OH})$  crystal used in this study was synthesized in a hydrothermal diamond-anvil cell (HDAC) from a solution consisting of concentrated 95–98%

\* E-mail: hyang@email.arizona.edu

sulfuric acid (Alfa Aesar CAS: 7664-93-9) and  $\text{Al}_2\text{O}_3$  powder (~35g/L). The solution with an air bubble was enclosed in a cylindrical-shaped sample chamber (300  $\mu\text{m}$  in diameter and 40  $\mu\text{m}$  in height) that was milled into one of the diamond anvils (Anderson et al. 2002). The fluid sample was examined using a petrographic microscope as it was heated at a rate of 10  $^\circ\text{C}/\text{min}$ . The air bubble disappeared as the temperature reached 358  $^\circ\text{C}$ . At 700  $^\circ\text{C}$ , a single prismatic crystal measuring  $80 \times 20 \times 15 \mu\text{m}$  precipitated from the solution (Fig. 1). The pressure in the HDAC at 700  $^\circ\text{C}$  was estimated to be ~1.0 GPa using an isochore constructed from the equation of state of  $\text{H}_2\text{O}$ . The crystal was extracted from the HDAC after cooling to room temperature.

Because only one  $\text{AlSO}_4(\text{OH})$  crystal was synthesized, we did not prepare it for the quantitative chemical measurement with electron microprobe analysis. A qualitative chemical analysis of the crystal was conducted on a Hitachi 3400N scanning electron microscope equipped with an Oxford EDS/EBS system, revealing that Al, S, and O are the major constituents, with trace Cr, which results most likely from the interaction of  $\text{H}_2\text{SO}_4$  with nichrome wire used for resistance heating in the HDAC.

Single-crystal X-ray diffraction data of  $\text{AlSO}_4(\text{OH})$  were collected on a Bruker X8 APEX2 CCD X-ray diffractometer equipped with graphite-monochromatized MoK $\alpha$  radiation and frame widths of 0.5 $^\circ$  in  $\omega$  and 30 s counting time per frame. All reflections with  $I > 2\sigma(I)$  were indexed based on a monoclinic unit cell (Table 1). No satellite or super-lattice reflections were observed. The intensity data were corrected for X-ray absorption using the Bruker program SADABS. The systematic absences of reflections suggest the possible space groups  $C2/c$  or  $Cc$ . The crystal structure was solved and refined using SHELX97 (Sheldrick 2008) based on the space group  $C2/c$ , because it yielded a better refinement statistics in terms of bond lengths and angles, atomic displacement parameters, and  $R$  factors. The positions of all atoms were refined with anisotropic displacement parameters, except for the H atom, which was refined isotropically. During the structure refinements, an attempt to refine the site occupancy of  $\text{Al}^{3+}$  vs.  $\text{Cr}^{3+}$  was made, showing no detectible Cr substitution for Al in the crystal. The ideal chemical formula,  $\text{AlSO}_4(\text{OH})$ , was thus assumed in the refinements. Final atomic coordinates and displacement parameters are listed in Table 2 and selected bond lengths and angles in Table 3. (CIF<sup>1</sup> available.)

The Raman spectrum of  $\text{AlSO}_4(\text{OH})$  was recorded from a random orientation on a Thermo-Almega microRaman system, using a solid-state laser with a frequency of 532 nm and a thermoelectrically cooled CCD detector. The laser is partially polarized with 4  $\text{cm}^{-1}$  resolution and has a spot size of 1  $\mu\text{m}$ .

## RESULTS AND DISCUSSION

The crystal structure of  $\text{AlSO}_4(\text{OH})$  is characterized by kinked chains of corner-sharing  $\text{AlO}_6$  octahedra that extend parallel to the  $c$ -axis. These chains are linked together by  $\text{SO}_4$  tetrahedra and hydrogen bonds, forming an octahedral-tetrahedral framework (Fig. 2a). Except for the numbers and positions of H atoms,  $\text{AlSO}_4(\text{OH})$  is isostructural with the kieserite-type minerals,  $M^{2+}\text{SO}_4 \cdot \text{H}_2\text{O}$ , where  $M = \text{Mg}, \text{Ni}, \text{Co}, \text{Fe}, \text{Mn}, \text{Zn}$  (Hawthorne et al. 1987; Wildner and Giester 1991) (Table 1, Fig. 2b), which have been further classified into the titanite group of minerals (Baur 1959; Hawthorne et al. 1987). The determination of the  $\text{AlSO}_4(\text{OH})$  structure has thus added a new subgroup to the titanite-type family.

<sup>1</sup> Deposit item AM-15-15160, CIF. Deposit items are stored on the MSA web site and available via the American Mineralogist Table of Contents. Find the article in the table of contents at GSW (ammin.geoscienceworld.org) or MSA (www.minsocam.org), and then click on the deposit link.

Nevertheless, there are some noticeable structural discrepancies between  $\text{AlSO}_4(\text{OH})$  and kieserite  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ . The most notable are the hydrogen bonding schemes, owing to the substitution of OH for  $\text{H}_2\text{O}$  (Fig. 2). In  $\text{AlSO}_4(\text{OH})$ , the H atom forms a bifurcated hydrogen bond with two O1 atoms, whereas in kieserite, the two H atoms form two normal asymmetrical hydrogen bonds with two O2 atoms. Moreover, the relatively strongly bonded and rigid  $\text{Al}^{3+}\text{O}_6$  octahedron in  $\text{AlSO}_4(\text{OH})$  is less distorted than the  $M^{2+}\text{O}_6$

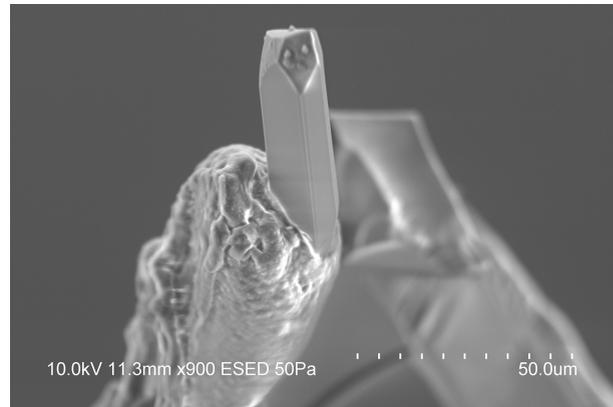


FIGURE 1. Secondary electron image of the  $\text{AlSO}_4(\text{OH})$  crystal mounted on a glass fiber with epoxy.

TABLE 1. Comparison of crystal data and refinement results for  $\text{AlSO}_4(\text{OH})$  and kieserite

	Synthetic $\text{AlSO}_4(\text{OH})$	Kieserite
Ideal chemical formula	$\text{AlSO}_4(\text{OH})$	$\text{MgSO}_4 \cdot \text{H}_2\text{O}$
Crystal symmetry	Monoclinic	Monoclinic
Space group	$C2/c$	$C2/c$
$a$ ( $\text{\AA}$ )	7.1110(4)	6.981(2)
$b$ ( $\text{\AA}$ )	7.0311(5)	7.624(2)
$c$ ( $\text{\AA}$ )	7.0088(4)	7.645(2)
$\beta$ ( $^\circ$ )	119.281(2)	117.70(2)
$V$ ( $\text{\AA}^3$ )	305.65(3)	355.6(2)
$Z$	4	4
$\rho_{\text{calc}}$ ( $\text{g}/\text{cm}^3$ )	3.043	2.585
$\lambda$ ( $\text{\AA}$ , MoK $\alpha$ )	0.71073	0.7107
$\mu$ ( $\text{mm}^{-1}$ )	1.209	
$2\theta$ range for data collection	$\leq 65.18$	
No. of reflections collected	2037	
No. of independent reflections	556	598
No. of reflections with $I > 2\sigma(I)$	485	509 [ $I > 2.5\sigma(I)$ ]
No. of parameters refined	38	
$R(\text{int})$	0.029	
Final $R_1, wR_2$ factors [ $I > 2\sigma(I)$ ]	0.025, 0.057	0.023 [ $I > 2.5\sigma(I)$ ]
Final $R_1, wR_2$ factors (all data)	0.031, 0.061	
Goodness-of-fit	1.051	
Reference	This study	Hawthorne et al. (1987)

TABLE 2. Coordinates and displacement parameters in atoms in  $\text{AlSO}_4(\text{OH})$  and  $\text{FeSO}_4(\text{OH})$  for comparison

Atom	$x$	$y$	$z$	$U_{\text{eq}}$	$U_{11}$	$U_{22}$	$U_{33}$	$U_{23}$	$U_{13}$	$U_{12}$
Al	0	1/2	0	0.0045(2)	0.0045(3)	0.0048(3)	0.0042(3)	-0.0001(2)	0.0021(2)	-0.0008(2)
Fe1=Fe2*	0	1/2	0							
S	0	0.12284(8)	1/4	0.0058(2)	0.0052(3)	0.0053(2)	0.0063(2)	0	0.0024(2)	0
S*	0	0.116	1/4							
O1	0.1878(2)	-0.0026(2)	0.3465(2)	0.0105(3)	0.0068(5)	0.0095(6)	0.0132(6)	0.0015(4)	0.0033(5)	0.0022(4)
O1=O5*	0.183	0	0.3415							
O2	0.0037(2)	0.2427(2)	0.0798(2)	0.0102(3)	0.0165(6)	0.0069(6)	0.0092(6)	0.0015(4)	0.0079(5)	-0.0002(4)
O2=O3*	0	0.23	0.084							
O3	0	0.5861(3)	1/4	0.0090(3)	0.0141(8)	0.0062(8)	0.0078(8)	0	0.0062(7)	0
O4*	0	0.60	1/4							
H	0	0.684(7)	1/4	0.042(1)						

\* These data are for  $\text{FeSO}_4(\text{OH})$ , which were taken from Ventrucci et al. (2005) after the transformation (see the text for discussion).

octahedron in any of the kieserite-group minerals, as measured by the octahedral angle variance and quadratic elongation indices (OAV and OQE) (Robinson et al. 1971). The OAV and OQE values are 2.41 and 1.001, respectively, for the  $\text{AlO}_6$  octahedron in  $\text{AlSO}_4(\text{OH})$ , but 9.7–15.6 and 1.005–1.008 for the  $\text{MO}_6$  octahedron in the kieserite-group minerals.

Wildner and Giester (1991) noted a strong inverse correlation between the  $M\text{-O}_3\text{-}M$  kinking angle within the octahedral chains in the kieserite-group minerals and the  $M^{2+}$  cation size. Our data on  $\text{AlSO}_4(\text{OH})$ , together with those for  $\text{FeSO}_4(\text{OH})$  (Ventruti et al. 2005), lend further support to this observation (Fig. 3). However, there is an obvious discontinuity in the trend of the  $M\text{-O}_3\text{-}M$  angle vs. the cation size, suggesting that some abrupt structural changes take place with the coupled substitution of ( $M^{3+} + \text{OH}$ ) for ( $M^{2+} + \text{H}_2\text{O}$ ) in the kieserite-type structures. It thus follows that there may be an immiscibility gap between  $M^{3+}\text{SO}_4(\text{OH})$  and  $M^{2+}\text{SO}_4 \cdot \text{H}_2\text{O}$ , due probably to the charge and size differences between  $M^{3+}$  and  $M^{2+}$ .

Shanks et al. (1981) reported a powder X-ray diffraction pattern for  $\text{AlSO}_4(\text{OH})$  obtained by the hydrolysis of  $\text{Al}_2(\text{SO}_4)_3$  solutions at temperatures above 310 °C. For comparison, we calculated the powder X-ray diffraction pattern for our  $\text{AlSO}_4(\text{OH})$  from the determined structure model using the program XPOW (Downs et al. 1993) (Fig. 4). The strong correlation of the two patterns indicates that the  $\text{AlSO}_4(\text{OH})$  obtained by Shanks et al. (1981) adopts the same crystal structure as ours.

Through the thermal decomposition of metahohmannite,  $\text{Fe}_3^+\text{O}(\text{SO}_4)_2 \cdot 4\text{H}_2\text{O}$ , Ventruti et al. (2005) obtained a compound with the composition  $\text{FeSO}_4(\text{OH})$  and measured its powder X-ray

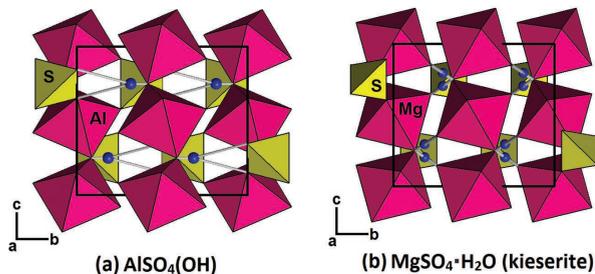
diffraction data at ~220 °C, which they claimed represents two distinct polymorphs. Phase 1, which is the same as that reported by Johansson (1962), is orthorhombic, with space group  $Pnma$  and unit-cell parameters  $a = 7.33$ ,  $b = 6.42$ , and  $c = 7.14$  Å, whereas phase 2 is monoclinic, with space group  $P2_1/c$  and unit-cell parameters  $a = 7.33$ ,  $b = 7.14$ ,  $c = 7.39$  Å, and  $\beta = 119.7^\circ$ . However, an inspection of the phase-2 structure reveals that it is actually isostructural with our  $\text{AlSO}_4(\text{OH})$ . Its true symmetry should be  $C2/c$ , rather than  $P2_1/c$ , with a transformation of their unit-cell parameters by the matrix  $[\bar{1}0\bar{1}, 010, 100]$ . The transformed cell parameters for  $\text{FeSO}_4(\text{OH})$  phase 2 are  $a = 7.394$ ,  $b = 7.14$ ,  $c = 7.33$  Å, and  $\beta = 119.75^\circ$ . Our conclusion has been validated by the PLATON program (Le Page 1987) and F. Scordari, the corresponding author for the work by Ventruti et al. (2005), agrees (personal communication). The transformed atomic coordinates for the phase-2 structure are listed in Table 2 for comparison with those for  $\text{AlSO}_4(\text{OH})$ . It is interesting to note that the similar compound  $\text{FeSO}_4(\text{OH})$  exhibits two polymorphs, one being orthorhombic (Johansson 1962) and the other monoclinic (Ventruti et al. 2005).

The Raman spectrum of  $\text{AlSO}_4(\text{OH})$  is displayed in Figure 5. The major band assignments (Table 4) are based on previous spectroscopic studies of similar hydrous sulfates, including kieserite and alunite (e.g., Frost et al. 2006; Kong et al. 2014). Ac-

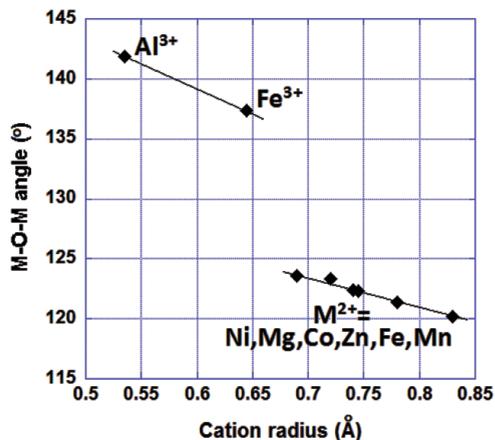
**TABLE 3.** Selected bond distances and angles in  $\text{AlSO}_4(\text{OH})$

	Distance (Å)
Al-O1	1.937(1) × 2
Al-O2	1.890(1) × 2
Al-O3	1.854(1) × 2
Avg. OAV	1.894
OQE	2.413
S-O1	1.461(1) × 2
S-O2	1.472(1) × 2
Avg. TAV	1.466
TQE	3.352
O3-H	1.001
O1...H	0.69(5)
O3...O1	2.49(4)
$\angle \text{O3-H}\cdots\text{O1}$	3.117(2)
	152.1(5)°

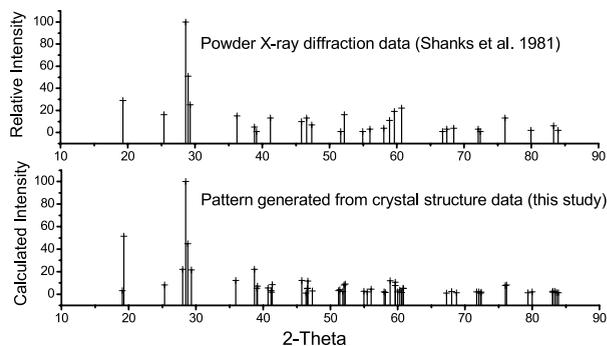
Note: OAV = octahedral angle variance; OQE = octahedral quadratic elongation; TAV = tetrahedral angle variance; TQE = tetrahedral quadratic elongation (Robinson et al. 1971).



**FIGURE 2.** Crystal structures of (a)  $\text{AlSO}_4(\text{OH})$  and (b) kieserite  $\text{MgSO}_4 \cdot \text{H}_2\text{O}$ . The small spheres represent the H atoms. (Color online.)



**FIGURE 3.** Variation of the  $M\text{-O-M}$  angle with the  $M$  cation size in the kieserite-type compounds. (Color online.)



**FIGURE 4.** Comparison of powder X-ray diffraction patterns of  $\text{AlSO}_4(\text{OH})$  obtained by the hydrolysis of the  $\text{Al}_2(\text{SO}_4)_3$  solutions at temperatures above 310 °C (Shanks et al. 1981) and that by hydrothermal synthesis done in this study.

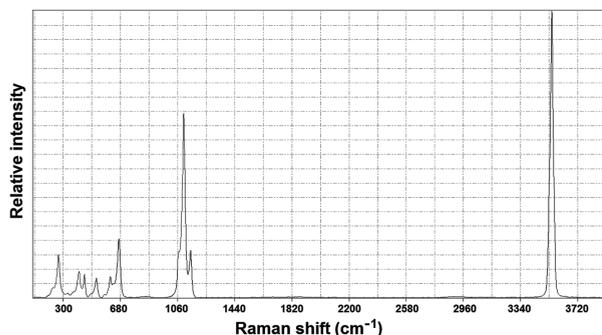


FIGURE 5. The Raman spectrum of  $\text{AlSO}_4(\text{OH})$ .

TABLE 4. Tentative assignments of major Raman bands for  $\text{AlSO}_4(\text{OH})$

Bands ( $\text{cm}^{-1}$ )	Assignment
270	O-Al-O bending within $\text{AlO}_6$
405, 442	$\nu_2$ ( $\text{SO}_4$ ) symmetric bending
521	Al-O stretching within $\text{AlO}_6$
614, 670	$\nu_4$ ( $\text{SO}_4$ ) anti-symmetric bending
1102	$\nu_1$ ( $\text{SO}_4$ ) symmetric stretching
1148	$\nu_3$ ( $\text{SO}_4$ ) anti-symmetric stretching
3549	OH stretching

cording to Libowitzky (1999), the O-H stretching band at  $3549 \text{ cm}^{-1}$  corresponds to an estimated O...O distance of  $\sim 3.10 \text{ \AA}$ , which compares well with the O3...O1 distance ( $3.117 \text{ \AA}$ ) determined from the structure refinement (Table 3).

Until now,  $\text{AlSO}_4(\text{OH})$  has only been attained at temperatures above  $290 \text{ }^\circ\text{C}$  (Dyson and Scott 1965; Shanks et al. 1981; this study) and this is most likely one of the reasons why  $\text{AlSO}_4(\text{OH})$  has not been found in low-temperature environments, such as surface soils and mine waters. A question remains regarding the identity of the enigmatic mineral with  $\text{Al}:\text{OH}:\text{SO}_4 = 1:1:1$  that was postulated by Van Breemen (1973). From the solubility equilibrium calculations of aluminum sulfate minerals, Nordstrom (1982) found that the composition and solubility of Van Breemen's unknown mineral compares well with those of jurbanite/rostitite  $\text{AlSO}_4(\text{OH}) \cdot 5\text{H}_2\text{O}$ . In fact, except for  $\text{AlSO}_4(\text{OH})$ , jurbanite/rostitite is the only known aluminum hydroxysulfate having the ratio of  $\text{Al}:\text{OH}:\text{SO}_4 = 1:1:1$ . Yet, we cannot rule out the possible existence of a low-temperature polymorph of  $\text{AlSO}_4(\text{OH})$ , in addition to the C2/c form determined in this study.

### IMPLICATIONS

Newton and Manning (2005) suggested that a large proportion of solute sulfur in a mafic magma may partition into an exhalative saline fluid as sulfate. Given that sulfuric acid is an effective agent for removing aluminum from aluminous minerals, we suggest that the interaction of highly oxidized brines of juvenile/magmatic origin with aluminum-rich rocks could result in the formation of  $\text{AlSO}_4(\text{OH})$  at elevated pressure and temperature conditions in the Earth's crust. Another possible environment for  $\text{AlSO}_4(\text{OH})$  to occur is on the surface of Venus, where highly concentrated sulfuric acid in the atmosphere may interact with aluminum-bearing minerals on the surface at temperatures exceeding  $400 \text{ }^\circ\text{C}$ .

The method used for synthesis in this study may be further developed so that thermochemical measurements can be obtained. These data are requisite for understanding the stability of  $\text{AlSO}_4(\text{OH})$  in low-temperature environments and for predicting the occurrence of  $\text{AlSO}_4(\text{OH})$  in the deep sulfur cycle.

### ACKNOWLEDGMENTS

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### REFERENCES CITED

- Alewell, C., Bredemeier, M., Matzner, E., and Blanck, K. (1997) Soil solution response to experimentally reduced acid deposition in a forest ecosystem. *Journal of Environmental Quality*, 26, 658–665.
- Anderson, A.J., Jayanetti, S., Mayanovic, R.A., Bassett, W.A., and Chou, I-M. (2002) X-ray spectroscopic investigations of fluids in the hydrothermal diamond anvil cell: The hydration structure of  $\text{La}^{3+}$  from ambient to  $300 \text{ }^\circ\text{C}$  and 1600 bars. *American Mineralogist*, 87, 262–268.
- Bassett, H., and Goodwin, T.H. (1949) The basic aluminum sulfates. *Journal of the Chemical Society*, 2239–2279.
- Baur, W.H. (1959) Die Kristallstruktur des Edelmetallygonits  $\text{LiAlPO}_4(\text{OH},\text{F})$ . *Acta Crystallographica*, 12, 988–994.
- Downs, R.T., Bartelmehs, K.L., Gibbs, G.V., and Boisen, M.B. Jr. (1993) Interactive software for calculating and displaying X-ray or neutron powder diffractometer patterns of crystalline materials. *American Mineralogist*, 78, 1104–1107.
- Dyson, N.F., and Scott, T.R. (1965) New phases in the system  $\text{Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  at temperatures above  $100 \text{ }^\circ\text{C}$ . *Nature*, 205, 358–359.
- Frost, R., Wills, R.-A., Weier, M., Martens, W., and Klopogge, T. (2006) A Raman spectroscopic study of alunites. *Journal of Molecular Structure*, 785, 123–132.
- Hawthorne, F.C., Groat, L.A., Raudsepp, M., and Ercit, T.S. (1987) Kieserite,  $\text{Mg}(\text{SO}_4)(\text{H}_2\text{O})$ , a titanite-group mineral. *Neues Jahrbuch für Mineralogie, Abhandlungen*, 157, 121–132.
- Johansson, G. (1962) On the crystal structure of  $\text{FeOHSO}_4$  and  $\text{InOHSO}_4$ . *Acta Chemica Scandinavica*, 16, 1234–1244.
- Jones, A.M., Collins, R.N., and Waite, D. (2011) Mineral species control of aluminum solubility in sulfate-rich acidic waters. *Geochimica et Cosmochimica Acta*, 75, 965–977.
- Kong, W.G., Zheng, M.P., Kong, F.J., and Chen, W.X. (2014) Sulfate-bearing deposits at Dalangtan Playa and their implication for the formation and preservation of martian salts. *American Mineralogist*, 99, 283–290.
- Le Page, Y. (1987) Computer derivation of the symmetry elements implied in a structure description. *Journal of Applied Crystallography*, 20, 264–269.
- Libowitzky, E. (1999) Correlation of O-H stretching frequencies and O-H...O hydrogen bond lengths in minerals. *Monatshefte für Chemie*, 130, 1047–1059.
- Ludwig, B., Khanna, P., and Prenzel, J. (1999) Some equilibrium approaches to study the retention and release of sulfate in some highly acid German subsoils. *Journal of Environmental Quality*, 28, 1327–1335.
- MacZura, G., Moody, K., Anderson, E.M., and Kunka, M.K. (1994) Alumina. *American Ceramic Society Bulletin*, 73, 76–78.
- Newton, R.C., and Manning, C.E. (2005) Solubility of anhydrite,  $\text{CaSO}_4$ , in  $\text{NaCl-H}_2\text{O}$  solutions at high temperatures and pressures: applications to fluid rock interactions. *Journal of Petrology*, 46, 701–716.
- Nordstrom, D.K. (1982) The effect of sulfate on aluminum concentrations in natural waters: some stability relations in the system  $\text{Al}_2\text{O}_3\text{-SO}_3\text{-H}_2\text{O}$  at  $298 \text{ K}$ . *Geochimica et Cosmochimica Acta*, 46, 681–692.
- Robinson, K., Gibbs, G.V., and Ribbe, P.H. (1971) Quadratic elongation: A quantitative measure of distortion in coordination polyhedra. *Science*, 172, 567–570.
- Shanks, D.E., Eisele, J.A., and Bauer, D.J. (1981) Recovery of aluminum hydroxyl sulfate from aluminum sulfate solution by high temperature hydrolysis. Report of Investigations, U.S. Dept. of the Interior, Bureau of Mines, vol. 8550, 10 p.
- Sheldrick, G.M. (2008) A short history of *SHELX*. *Acta Crystallographica, A*, 64, 112–122.
- Van Breemen, N. (1973) Dissolved aluminum in acid sulfate soils and in acid mine waters. *Soil Science Society of America Proceedings*, 37, 694–697.
- (1976) Genesis and solution chemistry of acid sulfate soils in Thailand. *Agriculture Research Reports*, 848, 263 pp. Ph.D. thesis.
- Ventrucci, G., Scordari, F., Schingaro, E., Gualtieri, A.F., and Meneghini, C. (2005) The order-disorder character of  $\text{FeOHSO}_4$  obtained from the thermal decomposition of metahohmannite,  $\text{Fe}_2^+(\text{H}_2\text{O})_2[\text{O}(\text{SO}_4)_2]$ . *American Mineralogist*, 90, 679–686.
- Wildner, M., and Giester, G. (1991) The crystal structures of kieserite-type compounds. I. Crystal structures of  $\text{Me}(\text{II})\text{SO}_4 \cdot \text{H}_2\text{O}$  ( $\text{Me}=\text{Mn, Fe, Co, Ni, Zn}$ ). *Neues Jahrbuch für Mineralogie, Monatshefte*, 296–306.