Crystal-chemistry of sulfates from the Apuan Alps (Tuscany, Italy). VIII. New data on khademite, Al(SO$_4$)F(H$_2$O)$_5$

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ABSTRACT

Khademite, ideally Al(SO$_4$)F(H$_2$O)$_5$, from the Monte Arsiccio mine (Apuan Alps, Tuscany, Italy) has been characterized through quantitative electron microprobe analysis, micro-Raman spectroscopy, and single-crystal X-ray diffraction. Khademite occurs as colorless to whitish tabular crystals, up to 5 mm across, or as sugary aggregates formed by colorless and shiny individuals less than 0.5 mm in size. Electron microprobe analysis (in wt% - average of twenty spot analyses) gave: SO$_3$ 35.43, Al$_2$O$_3$ 21.27, F 6.92, H$_2$O$_{calc}$ 39.73, sum 103.35, –O = F 2.92, total 100.43. On the basis of 10 anions per formula unit, assuming the occurrence of 5 H$_2$O groups and 1 (F+OH) atom per formula unit, its chemical formula can be written as Al$_{0.96}$S$_{1.03}$O$_4$(F$_{0.84}$OH$_{0.16}$)$_{21.00}$·5H$_2$O. The Raman spectrum of khademite is characterized by the occurrence of vibrational modes of SO$_4$ groups and by broad and strong bands due to the O–H stretching modes. Khademite is orthorhombic, space group Pcab, with unit-cell parameters $a = 11.1713(2)$, $b = 13.0432(3)$, $c = 10.8815(2)$ Å, $V = 1585.54(5)$ Å$^3$, $Z = 8$. The crystal structure refinement converged to $R_1 = 0.0293$ on the basis of 2359 unique reflections with $F_o > 4σ(F_o)$ and 152 refined parameters. The crystal structure of khademite is characterized by the alternation, along $b$, of two distinct kinds of {010} layers, one formed by [001] rows of isolated Al-centered octahedra, connected to each other through H-bonds, and the other showing isolated SO$_4$ groups. Along $b$, oxygen atoms belonging to SO$_4$ groups act as acceptor of H-bonds from H$_2$O groups coordinating Al atoms. The new data improved the description of the H-bonds in khademite and led us to discuss about the possible existence of its OH-analogue, rostitite. In addition, Raman spectroscopic data were collected on the same crystal used for the crystal-chemical characterization, allowing a comparison with previous results.

Keywords: khademite, fluorine, fluo-sulfate, crystal structure, hydrogen bonds, Raman spectroscopy, Monte Arsiccio mine, Apuan Alps.
Introduction

Sulfate minerals play a central role in governing the release and transport of acidity and potential environmentally critical elements following pyrite oxidation (e.g., Jerz and Rimstidt, 2003; Hammarstrom et al., 2003, 2005). Recently, the finding of high thallium contents in pyrite ore deposits from the southern Apuan Alps (northern Tuscany, Italy; D’Orazio et al., 2017) promoted the characterization of secondary mineral assemblages allowing the collection of mineralogical and geochemical data.

The presence of sulfate assemblages related to the weathering of pyrite ores has been known since the second half of the 19th Century (e.g., D’Achiardi, 1872). However, only in the last decade modern mineralogical data have been collected, with the identification of well-crystallized sulfates in the Fornovolasco and Monte Arsiccio mines. In the former locality, the new mineral species volaschuite, Fe₄(SO₄)O₂(OH)₆·2H₂O, as well as Tl-bearing varieties of alum-(K) and voltaite, were found (Biagioni et al., 2011, 2020). Moreover, Monte Arsiccio proved to be an extraordinary laboratory for the study of sulfate minerals, providing the mineral systematics with three new K-Fe sulfates (giacovazzinite, scordarite, and magnanelliite – Biagioni et al., 2019a; 2019b; 2019c), and several other species, among which world-class specimens of coquimbite (Mauro et al., 2020).

A peculiar feature of the Fornovolasco and Monte Arsiccio sulfate assemblages is represented by the rare occurrence of fluo-sulfates. Mauro et al. (2019) described wilcoxite from the Fornovolasco mine, reporting new crystal structure data and improving the knowledge of its H-bond system. Recently, another fluo-sulfate, khademite, was identified at the Monte Arsiccio mine. The current definition of khademite is the result of a long and debated history summarized by Košek et al. (2019). As a matter of fact, a modern and full characterization of khademite is still lacking, since Bachet et al. (1981) did not give any chemical analysis and no further crystal structure refinements were reported. The finding at the Monte Arsiccio mine permitted the collection of a new set of good-quality data, integrating electron microprobe, spectroscopic, and single-crystal X-ray diffraction analyses, along with a thoughtful discussion of previous available data.

Experimental

Study specimen

Khademite from the Monte Arsiccio mine occurs as colorless to whitish tabular crystals, up to 5 mm across (Fig. 1), associated with krausite, halotrichite, and coquimbite. These samples were carefully investigated during the present study.

Chemical analysis

Quantitative chemical data were collected on the same tabular crystal used for single-crystal X-ray diffraction study using a Superprobe JEOL JXA 8200 electron microprobe at the Eugen F. Stumpfl laboratory, Leoben University, Austria. The analytical conditions were: WDS mode, accelerating voltage 15 kV, beam current 10 nA, beam diameter 20 μm. Standards (element, emission line) were: pyrite (SKα), kaersutite (AlKα), and fluorite (FKα). Iron was sought but was found below the detection limit. ZAF routine was applied for the
correction of recorded raw data. Counting times were 20 s for peak and 10 s for left and right background, respectively. Quantitative chemical data are given in Table 1.

**Micro-Raman spectroscopy**

Micro-Raman spectra of khademite were collected on the same polished sample used for the quantitative chemical analysis using a Horiba Jobin-Yvon XploRA Plus apparatus, with a 50x objective lens and the 532 nm line of a solid-state laser attenuated to 25% (i.e., 6.25 mW). The spectra were collected in the range between 100 to 4000 cm⁻¹, through multiple acquisitions (3) with single counting times of 60 s. Backscattered radiation was analyzed with a 1200 gr/mm grating monochromator. Figure 2 shows the collected Raman spectrum, whereas Table 2 gives the observed Raman bands and their interpretation. Band fitting of the O–H stretching region was performed using *Fit2k* (Wojdyr, 2010).

**X-ray crystallography**

X-ray intensity data were collected using a Bruker Smart Breeze diffractometer (50 kV, 30 mA) equipped with a Photon II CCD detector. Graphite-monochromatized MoKα radiation was used. The detector-to-crystal working distance was 50 mm. Intensity data were integrated and corrected for Lorentz-polarization, background effects, and absorption, using the package of software Apex3 (Bruker AXS Inc., 2016), resulting in a set of 17,350 reflections. The refined unit-cell parameters are \(a = 11.1713(2), b = 13.0432(3), c = 10.8815(2) \, \text{Å}, V = 1585.54(5) \, \text{Å}^3, Z = 8\). Space group \(Pcab\) was suggested by the statistical tests on \(|E|\) values (\(|E^2-1| = 0.953\)) and by the examination of systematic absences. The crystal structure of khademite was refined using *SHELX-2018* (Sheldrick, 2015), starting from the atomic coordinates given by Bachet *et al.* (1981). Taking into account the results of the electron microprobe analysis, the site scattering at the Al, S, F, O, and H sites was modeled using neutral site scattering curves taken from the *International Tables for Crystallography* (Wilson, 1992). Although the coordinates of H atoms were given by Bachet *et al.* (1981), their positions for the sample from Monte Arsiccio have been sought in the difference-Fourier maps. Soft restraints were applied to O–H bonds, in order to avoid too short distances. The crystal structure refinement of khademite, after several cycles of anisotropic refinement (with the exception of H atoms, which were refined isotropically), converged to \(R_I = 0.0293\) for 2359 unique reflections with \(F_o > 4\sigma(F_o)\) and 152 refined parameters. Details of data collection and refinement are given in Table 3. Fractional atomic coordinates and isotropic or equivalent isotropic displacement parameters are reported in Table 4, whereas selected bond distances are shown in Table 5. Finally, the geometrical features of the hydrogen bonds are given in Table 6. Table 7 reports the bond-valence sum (BVS) calculations, performed using the bond parameters of Brese and O’Keeffe (1991) for Al–O, Al–F, and S–O bonds; simplified bond-valences, agreeing with Brown and Altermatt (1981), are reported for H-bonds.

**Results and discussions**

**Chemical data**

The occurrence of fluorine in the crystal structure of khademite has been debated for a long time. Indeed, the detection and quantification of this light element is not an easy task
(e.g., Stormer et al., 1993; Raudsepp, 1995; Ottolini et al., 2000). Quantitative chemical data of khademite, including F, have been reported by Žáček and Povondra (1988), Williams and Cesbron (1983), and Košek et al. (2019).

Data given in Table 1, recalculated on the basis of 10 anions per formula unit (pfu), assuming the occurrence of 5 H₂O and 1 (F+OH) pfu, in agreement with our structural data, allow to write the following chemical formula for khademite from the Monte Arsiccio mine: Al₉₀₋₉₁₀₂₁0₂₁₀₂(OH₁₀₋₁₂)₃₁₀₂·5H₂O. It agrees with the ideal formula Al(SO₄)F·5H₂O. The studied sample was chemically homogeneous and no significant F variations were observed among the twenty spot analyses, suggesting rather constant F/OH ratios.

**Micro-Raman spectroscopy**

The Raman spectrum of khademite (Fig. 2) is characterized by the occurrence of the four fundamental modes of the SO₄ group and by the O–H stretching vibration modes due to the H₂O groups hosted in its crystal structure. Two spectral regions can be recognized, i.e., between 100-1200 cm⁻¹ and between 2500-3800 cm⁻¹. The former region (Fig. 2a) is characterized by bending and stretching modes of the SO₄ group, located between 400 and 1130 cm⁻¹, and by the vibration modes of Al–O (φ = O, F) bonds and/or to lattice vibration modes, below 400 cm⁻¹. The symmetric bending modes (ν₂) of the SO₄ group are characterized by bands at 417, 432, 499, and 523 cm⁻¹ whereas the bands due to the antisymmetric bending modes (ν₁) occur at 566, 587, 616, and 632 cm⁻¹. The strongest band at 993 cm⁻¹ is due to the symmetrical stretching mode (ν₁) of the SO₄ group. The weaker bands at 1079 and 1128 cm⁻¹ are attributed to the antisymmetrical stretching mode (ν₃) of the SO₄ group. In the region between 3000 and 4000 cm⁻¹ a broad multi-component band related to the O–H stretching modes of H₂O groups occur. This band can be compared with that observed by Košek et al. (2019) who established the peak position through a basic peak-finding routine, reporting the presence of three bands at 3040, 3177, and 3404 cm⁻¹; these values agree with those measured (using a similar peak-finding routine) in the sample of khademite from Monte Arsiccio, i.e., 3053, 3183, and 3406 cm⁻¹. In addition, a shoulder at 2967 cm⁻¹ was observed. In addition, a fitting of the spectrum using theoretical peak shapes (i.e., Voigt function) was performed from the sample from Monte Arsiccio, revealing the occurrence of at least four main bands, at 2966, 3047, 3197, and 3420 cm⁻¹ (Fig. 2b). These components are likely related to the occurrence of relatively strong H-bonds in khademite, as shown in Table 6 and discussed below. For instance, six out of the ten O···O distances reported in Table 6 range between 2.662 and 2.692 Å, corresponding to frequencies of 3053 and 3166 cm⁻¹ according to the relationship of Libowitzky (1999). The maxima of the broad Raman bands are in agreement with such an interpretation. Košek et al. (2019) interpreted the Raman band at 3404 cm⁻¹ as due to the hydroxyl stretching mode. However, this is not proved by structural data and disagrees with previous data reported for sulfate minerals. Indeed, the occurrence of the O–H stretching modes due to the hydroxyl group should be observed at higher wavenumber (e.g., Kong et al., 2011; Ventru et al., 2016). In addition, three bands at 3524, 3521, and 3584 cm⁻¹ were observed for not-symmetry related OH units occurring in the crystal structure of creedite, Ca₃Al₂(SO₄)(OH)₂F·2H₂O, by Frost et al., (2013a). Finally, as it will be discussed below, the possible occurrence of an OH-group in khademite may be related
to a relatively long O···O distances, giving rise to a band at wavenumbers higher than 3500 cm⁻¹.

Bending modes due to the H–O–H bonds were observed at 1606 cm⁻¹. On the contrary, Košek et al. (2019) did not observe any bending modes in their Czech sample, whereas Frost et al. (2015) reported two bending modes at 1605 and 1692 cm⁻¹ in rosite. Table 2 compares our results with available micro-Raman spectroscopic data collected on both khademite and its OH-analogue rosite. Data for the Monte Arsiccio sample are in good agreement, within experimental uncertainties, with those given by Frost et al. (2015) and Košek et al. (2019). On the contrary, the sample of khademite studied by Frost et al. (2013b) shows a fully different Raman spectrum; this disagreement is likely due to the fact that these authors studied a not fully-characterized specimen. It is very likely that their spectrum does not belong to khademite.

Single-crystal X-ray diffraction

Description of the crystal structure: cation coordinations and general features

Three cation sites, namely Al(1), Al(2), and S, and ten anion positions occur in the crystal structure of khademite, along with ten H sites.

Aluminum is hosted at the Al(1) and Al(2) sites. Both positions show an octahedral coordination; in the former site, Al atoms are coordinated by H₂O groups only, whereas in the Al(2) site, four H₂O groups and two F anions are bonded to Al. Bond distances at the Al(1) polyhedra range between 1.85 and 1.89 Å, in agreement with those previously reported by Bachet et al. (1981), i.e., 1.85 and 1.89 Å. The Al(2)-centered polyhedron is more distorted than the Al(1)-centered polyhedron with bond distances ranging from 1.73 and 1.95 Å. According to Bachet et al. (1981), the shortest distance can be attributed to the Al–F bond. The longest distance is the Al(2)–Ow(3). It is worth noting that this distance is longer than all the other Al–Ow distances observed in the crystal structure of khademite and it is related to the fact that the H₂O group at Ow(3) is the only H₂O group receiving an H-bond; in fact, the elongation of the Al–Ow distance favours a reduction of the BVS and the possibility to accept the additional H-bond from Ow(6) (Table 7). The average <Al–O> distances are 1.878 and 1.858 Å for Al(1) and Al(2) sites, respectively. The BVS for the Al(1) and Al(2) site (Table 7) are 3.26 and 3.14 valence units (v.u), respectively. The isolated SO₄ group has an average <S–O> distance of 1.472 Å, in agreement with those reported in sulfate minerals by Hawthorne et al. (2000), i.e., 1.473 Å. The corresponding BVS at the S site is 6.03 v.u (Table 7).

The crystal structure of khademite (Fig. 3) can be described as a layered structure. Indeed, it is characterized by the alternation of two different kinds of {010} layers. The first one (hereafter indicated as A) is formed by two independent isolated Al-centered octahedra, having chemical composition Al(H₂O)₁₀ and Al(H₂O)₄F₂, respectively. These octahedra are connected through H-bonds, forming rows running along [001]. Every A layer has chemical composition [Al₄(H₂O)₂₀F₄]ₖ⁺. The other layer (B layer) is formed only by isolated SO₄ groups; in each layer, four independent SO₄ groups occur. The connection between adjacent A and B layers occurs through the oxygen atoms of SO₄ groups that act as acceptor of H-bonds from H₂O coordinating Al atoms. In each unit cell, two A and B layers occur. Consequently, the unit-cell content is 2 × [Al₄(H₂O)₂₀F₄]ₖ⁺ + 2 × [(SO₄)₄]ₖ⁻ =
Al₈(SO₄)₉F₉(H₂O)₄₀ (Z = 1), corresponding to the end-member formula of khademite, Al(SO₄)F(H₂O)₅ (Z = 8).

**Hydrogen bonding**

Table 7 highlights that all the atoms hosted at the ten independent anion positions occurring in the crystal structure of khademite are underbonded. Two groups of anions can be distinguished; a first group has BVS of ~ 1.5 v.u, whereas a second group has BVS ranging between 0.4 and 0.6 v.u. This observation suggests that H-bonds play a key role in the stabilization of the crystal structure of khademite. The geometrical features of H-bonds given in Table 6 match those found by Bachet *et al.* (1981). On the basis of the O···O distances d, the ten H-bonds can be grouped into three types: (1) very strong [d = 2.52 Å – one H-bond], (2) strong [2.6 < d < 2.7 Å – eight H-bonds], and (3) weak [d ~ 2.9 Å – one H-bond]. All O atoms bonded to S have BVS ~ 1.5 v.u. and each of these O atoms receives two similar strong H-bonds. The valence sum rule therefore suggests each of these bonds be 0.25 v.u. in strength; this values is in agreement with Figure 2 of Brown and Altermatt (1985) as well as the relationship of Ferraris and Ivaldi (1988), giving BVS for these strong H-bonds ranging between 0.23 and 0.27 v.u. Consequently, in Table 7 all strong H-bonds can be assigned a bond strength of 0.25 v.u. On similar ground, the very strong H-bond can be assigned a value of 0.30 v.u., considering that the acceptor is F (see Figure 1 in Brown and Altermatt, 1985), whereas 0.15 v.u. are attributed to the weak H-bond.

In details, the H₂O groups coordinating the Al(1) and Al(2) sites, namely Ow(2)-Ow(5) act as donor in strong H-bonds to the O atoms belonging to the SO₄ group. The Ow(6) is donor of a strong H-bond to an oxygen atom belonging to the SO₄ group, i.e., O(2), and of a weak bond to Ow(3), as discussed above. The F atom is acceptor of a very strong H-bond from Ow(5). The role of F as acceptor of H-bonds agrees with the previous structural model proposed by Bachet *et al.* (1981) and was observed in other rare sulfate minerals [e.g., wilcoxite, MgAl(SO₄)₂F·17H₂O; Mauro *et al.*, 2019].

**Can rosite be a valid mineral species?**

Khademite and its (OH)-analogue rosite have a troubled history, as summarized by Košek *et al.* (2019). These authors stated that the crystal structure study of khademite performed by Bachet *et al.* (1981) “found that the atomic positions in the structure were so small that they require the presence of fluorine, and that the presence of OH in the structure was not possible.” It is not clear what Košek *et al.* (2019) mean when they state that “the atomic positions [...] were so small”. A critical reading of the original paper by Bachet *et al.* (1981) reveals the actual reason leading the authors to hypothesize the occurrence of F, without the support of any chemical data. Indeed, Bachet *et al.* (1981) were not able to locate the H atom related to the OH group and they observed a slight electron density residual on that O atom, supporting the occurrence of a slightly heavier atom. In this hypothesis, Bachet *et al.* (1981) were supported by the association of khademite with another fluo-sulfate, wilcoxite. Finally, the examination of the H-bond system around F suggested the impossibility to locate an OH group at this position.

The impossibility to locate an OH group in the crystal structure of khademite could have some implications for the actual existence of its OH-analogue, rosite, ideally
Al(SO₄)(OH)(H₂O). Indeed, to the best of our knowledge, only a sample of rostite from the Cetine di Cotorniano mine (Tuscany, Italy) has been reported in literature, with OH slightly dominant over F (Sabelli, 1984). However, in agreement with Košek et al. (2019), the correctness of the chemical data of Sabelli (1984) is questionable.

Bachet et al. (1981) described the coordination environment of F atoms, highlighting that they are acceptor of H-bonds from Ow(5). If F is replaced by OH, then OH would be donor to Ow(2), with a bond distance of ~3.19 Å but with a too small Ow(5)–OH–Ow(2) angle of ~55°. For this reason, Bachet et al. (1981) wrote that it was impossible to replace F with OH groups in khademite. Taking into account the result of the refinement performed on the sample from Monte Arsiccio, the structural features described by Bachet et al. (1981) are confirmed (Fig. 4a). As regards the possible existence of the OH-analogue, we argue that the replacement of F by OH might favour an increase in the Al–O distance, e.g., up to 1.84 Å, in order to supply a similar BVS (0.60 v.u.). The strong contribution from H(52) could be retained; taking into account a similar H···O distance as observed in khademite, a bond strength of ~0.35 v.u. can be proposed on the basis of Brown and Altermatt (1985). In order to have a BVS of ~2 v.u. at the O atom occurring at the OH position, a strong donor contribution (e.g., ~0.95 v.u.) is required. This would necessitate a distant O acting as acceptor, that would receive a weak H-bond (e.g., ~0.05 v.u.). In the crystal structure of khademite there are two possible O anions, Ow(2) (as proposed by Bach et al., 1981) and O(4). Whereas Ow(2) was excluded by Bachet et al. (1981) in order to avoid too small Ow(5)–OH–Ow(2) angle (i.e., ~55°), a reasonable angle of ~95° can be formed with O(4). Figure 4b shows a hypothetical H-bond scheme involving these atoms. The BVS at O(4) would be 2.06 v.u.; if one consider the distance measured in the crystal structure of khademite (~3.25 Å), a bond strength of 0.10 v.u. can be calculated using the relationship of Ferraris and Ivaldi (1988), whereas a value close to 0 v.u. can be hypothesized following Brown and Altermatt (1985). Minor structural changes could likely be associated with the F-OH replacement, improving the structural fitting with respect to this chemical substitution.

This discussion does not aim to prove that rostite actually exist. Indeed, as written above, the only available data are those of Sabelli (1984) and they are questionable. On the contrary, we aim at demonstrating that there are no apparent impediment to the occupation of univalent anion site by OH within the khademite structure, in disagreement with the hypothesis of Bachet et al. (1981). Rostite may be a valid mineral species, but more sound chemical data are required to confirm its existence.

**Conclusions**

The occurrence of khademite at the Monte Arsiccio mine allowed the collection of high-quality single-crystal X-ray diffraction data and electron microprobe analyses, improving the crystal-chemical knowledge of this rare fluo-sulfate and confirming previous results reported by Bachet et al. (1981). Taking into account that all H₂O groups are bonded to Al atoms, the chemical formula of khademite could be written as Al(SO₄)F(H₂O)₅.

In addition, the critical examination of available Raman spectroscopic data highlighted some discrepancies in the published spectra. Indeed, whereas the data reported by Frost et al. (2015) for rostite from Le Cetine di Cotorniano (Italy) and Košek et al. (2019) for khademite
from Libušín (Czech Republic) agree, within experimental uncertainties, with those collected on the Monte Arsiccio sample, the Raman spectrum of khademite reported by Frost et al. (2013b) does not fit with previous and current results. These observations have a two-fold implication. On the one hand, the strong similarity between the Raman spectra of rosite and khademite confirms the uncertain distinction between these two phases, although current structural data do not show any impediment to the existence of the OH-analogue of khademite. On the other hand, the discrepancy observed between the spectra of khademite and the data published by Frost et al. (2013b) highlights the importance of using crystal-chemically well-characterized samples during Raman studies.

Acknowledgements

Mario Bianchini is thanked for providing us with the specimen of khademite from the Monte Arsiccio mine. CB acknowledges financial support from the University of Pisa through the project P.R.A. 2018-2019 “Georisorse e Ambiente” (Grant No. PRA_2018_41). The authors are grateful to the University Centrum for Applied Geosciences (UCAG) for the access to the E. F. Stumpfl electron microprobe laboratory. The authors wish to thank Mark Cooper for his critical revision, that greatly improved the discussion of the H-bonds in khademite and suggested a comparison with rosite. The comments of other two anonymous reviewers were also appreciated.
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Table captions

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Fig. 1. Colorless tabular crystals of khademite, up to 5 mm in size, associated with halotrichite. Monte Arsiccio mine, Apuan Alps, Italy.
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Table 1. Electron microprobe data of khademite.

| Oxide     | wt% (n = 20) | range         | σ  |
|-----------|--------------|---------------|----|
| SO$_3$    | 35.43        | 34.05-36.41   | 0.69 |
| Al$_2$O$_3$| 21.27        | 20.40-22.01   | 0.44 |
| F         | 6.92         | 6.54-7.16     | 0.20 |
| H$_2$O$_{calc}$* | 39.73 |                |     |
| Sum       | 103.35       |               |     |
| -O = F    | -2.92        |               |     |
| Total     | 100.43       |               |     |

*Calculated in agreement with structural data. $\sigma$ = estimated standard deviation.
Table 2. Raman bands (cm\(^{-1}\)) of khademite and their assignments.

| This study | Frost et al. (2013b) | Frost et al. (2015) | Košek et al. (2019) | Assignments |
|------------|----------------------|----------------------|---------------------|-------------|
| 127 vw, 150 w, 300 w, 337 w | 113 vw, 150 vw, 192 vw, 226 vw, 253 vw, 324 vw | 169 vw, 203 vw, 216 vw, 281 vw, 295 vw, 307 vw, 319 vw, 340vw | 130 w, 150 vw, 168 vw, 216 vw, 294 vw, 306 vw, 342 vw | Al–O and lattice modes |
| 420 w, 432 vw, 499 w, 523 vw | 455 w, 505 vw, 534 vw | 420 w, 434 vw, 504 m, 530 vw | 420 w, 433 vw, 504 m, 528vw | \(v_2(\text{SO}_4)\) |
| 566 w, 587 m, 616 m, 632 w | 618 w | 570 w, 590 m, 620 w, 632w | 569 w, 589 m, 619 w, 632w | \(v_4(\text{SO}_4)\) |
| 993 vs | 975 m, 991 vs | 991 vs | 990 vs | \(v_1(\text{SO}_4)\) |
| 1079 m, 1128 w | 1104 vw, 1132 w | 1070w, 1083 m, 1131 w, 1145vw | 1081 m, 1131 m | \(v_1(\text{SO}_4)\) |
| 1606 w | 1609 vw | 1605 w, 1692 w | - | \(v_2(\text{H}_2\text{O})\) |
| 2967, 3053, 3183, 3406 | 2991, 3146, 3380 | 2764, 2948, 3082, 3155, 3322, 3295 | 3040, 3177, 3404 | \(v_1\) and \(v_3(\text{H}_2\text{O})\) |
Table 3. Summary of crystal data and parameters describing data collection and refinement for khademite.

| Crystal data                      |                |
|-----------------------------------|----------------|
| Structural formula                | AlSO$_4$F(H$_2$O)$_5$ |
| Crystal size (mm$^3$)             | 0.18 × 0.15 × 0.13 |
| Cell setting, space group         | Orthorhombic, Pcab |
| $a$(Å)                            | 11.1713(2)     |
| $b$(Å)                            | 13.0432(3)     |
| $c$(Å)                            | 10.8815(2)     |
| $V$ (Å$^3$)                       | 1585.54(5)     |
| $Z$                                | 8              |

| Data collection and refinement    |                |
|-----------------------------------|----------------|
| Radiation, wavelength (Å)         | MoKα, λ = 0.71073 |
| Temperature (K)                   | 293            |
| Maximum observed 2θ (°)           | 63.04          |
| Measured reflections              | 17350          |
| Unique reflections                | 2600           |
| Reflections $F_o > 4\sigma(F_o)$ | 2359           |
| $R_{	ext{int}}$ after absorption correction | 0.0196     |
| $R_{\sigma}$                      | 0.0133         |
| Range of $h$, $k$, $l$             | -16 ≤ $h$ ≤ 16, -19 ≤ $k$ ≤ 16, -13 ≤ $l$ ≤ 15 |
| $R$ [$F_o > 4\sigma(F_o)$]        | 0.0293         |
| $R$ (all data)                    | 0.0332         |
| $wR$ (on $F_o^2$)                 | 0.0858         |
| Goof                               | 1.138          |
| Number of least-squares parameters | 152            |
| Maximum and minum residual peak (e/Å$^3$) | 0.32 [at 0.71 Å from O(2)] |
|                                    | -0.49 (at 0.36 Å from S) |
Table 4. Sites, fractional atom coordinates and isotropic (*) or equivalent isotropic displacement parameters in khademite.

| Site | x/a  | y/b   | z/c   | Ueq (Å²) |
|------|------|-------|-------|----------|
| Al(1) | 0    | ½     | ½     | 0.01120(11) |
| Al(2) | 0    | ½     | 0     | 0.01252(11) |
| S     | 0.23846(3) | 0.24741(2) | 0.24697(2) | 0.01431(9) |
| O(1)  | 0.16892(9)  | 0.25489(6)  | 0.13246(8)  | 0.02521(19) |
| O(2)  | 0.30519(10) | 0.14999(8)  | 0.24632(7)  | 0.0313(2)   |
| O(3)  | 0.15860(9)  | 0.25014(6)  | 0.35448(8)  | 0.0247(2)   |
| O(4)  | 0.32053(9)  | 0.33547(8)  | 0.25373(7)  | 0.0288(2)   |
| F     | 0.02937(7)  | 0.50938(5)  | 0.15592(6)  | 0.02092(15) |
| Ow(2) | 0.01006(7)  | 0.37567(6)  | 0.58852(7)  | 0.01751(16) |
| Ow(3) | 0.14302(7)  | 0.41497(6)  | -0.02101(7) | 0.01918(16) |
| Ow(4) | -0.09380(8) | 0.38237(6)  | 0.02869(8)  | 0.02325(18) |
| Ow(5) | 0.06920(8)  | 0.43591(6)  | 0.36595(7)  | 0.01916(17) |
| Ow(6) | -0.15403(7) | 0.46351(7)  | 0.44224(7)  | 0.01960(17) |
| H(21) | -0.0520(15) | 0.3324(14)  | 0.6011(17)  | 0.042(5)*   |
| H(22) | 0.0662(16)  | 0.3610(17)  | 0.6476(16)  | 0.050(6)*   |
| H(31) | 0.1498(17)  | 0.3608(13)  | 0.0315(16)  | 0.042(5)*   |
| H(32) | 0.148(2)    | 0.3879(16)  | -0.0974(15) | 0.054(6)*   |
| H(41) | -0.1181(16) | 0.3395(12)  | -0.0305(14) | 0.036(5)*   |
| H(42) | -0.1231(19) | 0.3699(16)  | 0.0968(19)  | 0.049(6)*   |
| H(51) | 0.0907(19)  | 0.3690(13)  | 0.3631(19)  | 0.057(6)*   |
| H(52) | 0.0576(18)  | 0.4617(16)  | 0.2911(14)  | 0.045(5)*   |
| H(61) | -0.2242(17) | 0.4922(15)  | 0.468(2)    | 0.060(7)*   |
| H(62) | -0.161(2)   | 0.4245(15)  | 0.3723(15)  | 0.055(6)*   |
Table 5. Selected bond distances (Å) in khademite.

|        | Bond Distance |        |
|--------|---------------|--------|
| Al(1)  | Al(1) – Ow(5) | 1.8505(7) x2 |
|        | Al(1) – Ow(2) | 1.8894(7) x2 |
|        | Al(1) – Ow(6) | 1.8927(8) x2 |
|        | <Al(1) – O>   | 1.878  |
| Al(2)  | Al(2) – F     | 1.7324(6) x2 |
|        | Al(2) – Ow(4) | 1.8841(8) x2 |
|        | Al(2) – Ow(3) | 1.9584(8) x2 |
|        | <Al(2) – O>   | 1.858  |
| S      | S – O(4)      | 1.4714(9)  |
|        | S – O(1)      | 1.4716(9)  |
|        | S – O(3)      | 1.4717(8)  |
|        | S – O(2)      | 1.4732(9)  |
|        | <S – O>       | 1.472   |
Table 6. Hydrogen-bond lengths (Å) and angles (°) for khademite.

| Donor ($D$) | $D$--$H$ | Acceptor ($A$) | $H$···$A$ | $D$--$H$···$A$ Angle | $D$···$A$ |
|-------------|---------|---------------|----------|----------------------|--------|
| Ow(2)--H(21) | 0.905(15) | O(1) | 1.765(15) | 176.9(18) | 2.6696(12) |
| Ow(2)--H(22) | 0.918(15) | O(4) | 1.745(15) | 177(2) | 2.6624(11) |
| Ow(2)--H(31) | 0.912(14) | O(1) | 1.778(14) | 177.8(19) | 2.6892(11) |
| Ow(2)--H(32) | 0.905(15) | O(4) | 1.793(15) | 172(2) | 2.6925(11) |
| Ow(4)--H(41) | 0.895(14) | O(3) | 1.771(14) | 176.5(18) | 2.6654(11) |
| Ow(4)--H(42) | 0.83(2) | O(2) | 1.83(2) | 176(2) | 2.6669(12) |
| Ow(5)--H(51) | 0.906(16) | O(3) | 1.728(16) | 169(2) | 2.6237(11) |
| Ow(5)--H(52) | 0.891(15) | F | 1.627(15) | 175(2) | 2.518(10) |
| Ow(6)--H(61) | 0.912(16) | Ow(3) | 2.000(16) | 167(19) | 2.8961(12) |
| Ow(6)--H(62) | 0.919(15) | O(2) | 1.722(15) | 172(2) | 2.6351(11) |
Table 7. Bond-valence sums (in valence unit) for khademite.

|       | Al(1) | Al(2) | S  | Σanion | H(21) | H(22) | H(31) | H(32) | H(41) | H(42) | H(51) | H(52) | H(61) | H(62) | Σanions* |
|-------|-------|-------|----|--------|-------|-------|-------|-------|-------|-------|-------|-------|-------|-------|---------|
| O(1)  | 1.51  | 1.51  | 0.25 | 0.25   |       |       |       |       |       |       |       |       |       |       | 2.01    |
| O(2)  | 1.50  | 1.50  | 0.25 | 0.25   | 0.25  | 0.25  |       |       |       |       |       |       |       |       | 2.00    |
| O(3)  | 1.51  | 1.51  | 0.25 | 0.25   | 0.25  | 0.25  |       |       |       |       |       |       |       |       | 2.01    |
| O(4)  | 1.51  | 1.51  | 0.25 | 0.25   | 0.25  | 0.25  |       |       |       |       |       |       |       |       | 2.01    |
| F     | 0.60  | 0.75  | 0.75 | 0.75   | 0.75  | 0.75  |       |       |       |       |       |       |       |       | 2.09    |
| OW(2) | 0.53  | 0.53  | 0.53 | 0.53   | 0.53  | 0.53  |       |       |       |       |       |       |       |       | 2.03    |
| OW(3) | 0.44  | 0.44  | 0.44 | 0.44   | 0.44  | 0.44  |       |       |       |       |       |       |       |       | 2.09    |
| OW(4) | 0.53  | 0.53  | 0.53 | 0.53   | 0.53  | 0.53  |       |       |       |       |       |       |       |       | 2.03    |
| OW(5) | 0.58  | 0.58  | 0.58 | 0.58   | 0.58  | 0.58  |       |       |       |       |       |       |       |       | 1.93    |
| OW(6) | 0.52  | 0.52  | 0.52 | 0.52   | 0.52  | 0.52  |       |       |       |       |       |       |       |       | 2.12    |
| Σcations | 3.26 | 3.14 | 6.03 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00 | 1.00    |

Note: right superscripts indicate the number of equivalent bonds involving anions. The bond-valence sums at H sites have been simplified. The symbol * indicates the BVS at anion sites after correction for H-bonds.
Fig. 1. Colorless tabular crystals of khademite, up to 5 mm in size, associated with halotrichite. Monte Arsicchio mine, Apuan Alps, Italy.
Fig. 2. Raman spectrum of khademite and band positions in the regions 100-1200 cm$^{-1}$ (a) and 2500-3800 cm$^{-1}$ (b); in (b) the cumulative curve is shown in green whereas fitted bands are red. The plot of residuals and the $R^2$ value are also shown.

$R^2 = 0.9985$
Fig. 3. The crystal structure of khademite (a), as seen down a; letters A and B indicate the two different {010} layers. Dashed and dotted blue lines represent F···O distances and H···O distances shorter than 1.95 Å, respectively. Unit cell is shown as dashed black lines. Polyhedra: light blue = Al(1)-centered octahedra; violet = Al(2)-centered octahedra (c); yellow = S-centered tetrahedra; Circles: red = O atoms of the SO₄ group; light blue = O atoms of the H₂O groups; pink = H atoms; light green = F atoms. Details of the coordination of Al(1) and Al(2) are shown in (b) and (c), respectively; bond distances (in Å) are shown.
Fig. 4. The H-bond system around F atom in khademite (a) and an hypothetical configuration with F replaced by OH (b). Same symbols as in Figure 3. Bond strengths around the monovalent anion are shown in italics (in v.u.).

(a)

(b)