

Crystal structure of $\text{Fe}_2(\text{AsO}_4)(\text{HAsO}_4)(\text{OH})(\text{H}_2\text{O})_3$, a dehydration product of kaňkite

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Abstract: We report the crystal structure of a dehydration product of the mineral kaňkite ($\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$). The structure was solved and refined by precession electron diffraction tomography. Initially, we believed that we solved the structure of kaňkite; this mineral, however, decomposes in vacuum to $\text{Fe}_2(\text{AsO}_4)(\text{HAsO}_4)(\text{OH})(\text{H}_2\text{O})_3$ ($= \text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). The crystal structure was solved in the space group Cc and the model was refined by the full-matrix least-squares method by Jana2006. The model converged to $R_{(\text{obs})} = 12.02\%$, $wR_{(\text{obs})} = 12.49\%$ (with $\text{GOF} = 6.39$) for 1139 observed reflections with $[I_{\text{obs}} > 3\sigma(I)]$. The structure of the dehydration product of kaňkite consists of corrugated heteropolyhedral sheets. Pairs of $\text{Fe}\phi_6$ octahedra, flanked by five adjacent arsenate tetrahedra, could be seen as the building units of the corrugated sheets. Variable-temperature powder X-ray diffraction showed that kaňkite dehydrates to $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ at 55–56 °C. Based on the similar topology of $\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$ and the mineral lausenite [$\text{Fe}_2(\text{SO}_4)_3 \cdot 5\text{H}_2\text{O}$], and the structural relationship between lausenite and kornelite [$\text{Fe}_2(\text{SO}_4)_3 \cdot 7.5\text{H}_2\text{O}$], we conjecture that the structure of kaňkite could be also built by corrugated sheets. One polyhedral linkage between an $\text{Fe}\phi_6$ octahedron and an $\text{As}\phi_4$ tetrahedron in the sheet of the dehydrated kaňkite needs to be broken to allow for stretching of the sheets, the introduction of an additional H_2O molecule into the sheet and perhaps also additional H_2O molecules in between the sheets.

Key-words: kaňkite; arsenate minerals; dehydration; crystal structure; precession electron diffraction.

Introduction

Kaňkite (nominally $\text{FeAsO}_4 \cdot 3.5\text{H}_2\text{O}$) is an elusive and seemingly uncommon mineral. The first description dates back to the 1970's (Čech *et al.*, 1976) from the type locality Kaňk near the municipality of Kutná Hora in the Czech Republic. This site is also the type locality of another arsenate mineral, bukovskýite, $\text{Fe}_2(\text{AsO}_4)(\text{SO}_4)(\text{OH}) \cdot 9\text{H}_2\text{O}$ (Novák *et al.*, 1967). At Kaňk, kaňkite can be found in the interstitial space between large rock fragments in the rocky dumps together with scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) and zýkaite ($\text{Fe}_4(\text{AsO}_4)_3(\text{SO}_4)(\text{OH}) \cdot 15\text{H}_2\text{O}$) (Čech *et al.*, 1978). Non-arsenate secondary minerals there include gypsum and jarosite. The clayey dumps at this site contain bukovskýite and very rare parascorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$) (Ondruš *et al.*, 1999). Other occurrences of kaňkite have been reported since then (Majzlan *et al.*, 2014) but, despite the fact that small, microscopic crystals of the mineral can be commonly found, the crystal structure is still unknown so far. This deficiency is mostly due to the fact that the crystals are essentially always twisted; in addition, kaňkite loses its crystal water rapidly and converts to another phase or assemblage of other phases. In our systematic research of sites contaminated with arsenic, we

identify kaňkite commonly under specific conditions, namely moderate temperature (~ 10 °C, typical for underground spaces) and high humidity (see Majzlan *et al.*, 2014; several papers in preparation). Therefore, it is of interest to determine the crystal structure of this phase.

In this contribution, we present an attempt to determine the crystal structure of kaňkite using precession electron diffraction tomography (PEDT). This method is an equivalent to standard single-crystal diffraction experiment with rotating crystal, but performed on a single microcrystal in a transmission electron microscope. The experiment involves rotating the selected crystal around the goniometer axis in small steps and taking an electron diffraction pattern at each step. The resulting data can be processed in a way similar to X-ray diffraction data, and an *ab initio* structure solution may be obtained. To suppress undesired multiple-scattering effects, which are always present in electron diffraction, the diffraction data may be collected in a precession mode, where the electron beam, instead of being stationary, rotates on the surface of a cone with vertex in the sample. This technique provides diffracted intensities more proportional to the square of the structure factor than standard electron diffraction with

stationary beam, and makes the structure solution and refinement easier (Mugnaioli *et al.*, 2009).

It turned out during the investigation that we could determine only the structure of a phase related to kaňkite, that is, its dehydration product. Based on this structure we conjecture what the structure of kaňkite may be.

Sample

The mineral sample of kaňkite was collected directly at the dump of Šafary mine at Kaňk in Czech Republic. Kaňkite forms pale green microcrystalline crusts in association with whitish zýkaite ($\text{Fe}_4(\text{AsO}_4)_3(\text{SO}_4)(\text{OH}) \cdot 15\text{H}_2\text{O}$) on a rock fragment (see Majzlan *et al.*, 2015).

Powder X-ray diffraction (XRD)

The *in situ* variable-temperature XRD patterns were collected using a Bruker D8 Advance diffractometer, equipped with a Cu X-ray source operated at 40 kV and 40 mA, a fixed divergence slit of 0.1° , a soller-slits of 2.5° , and a Lynx-Eye detector. The temperature stage was a model CHC+ Plus Cryo & Humidity Chamber (Anton-Paar GmbH, Graz, Austria) fitted with a platinum heater. A Pt 100 temperature sensor was integrated in the sample holder for accurate measurement and control of the temperature. The *in situ* diffraction data were collected from 20°C to 300°C by steps of 20°C . The XRD patterns were measured from 5° to $60^\circ 2\theta$, with a step of $0.02^\circ 2\theta$ and a counting time of 2.5 s per step.

Synchrotron powder data of the kaňkite sample were collected employing the diffractometer of the PDIFF beamline, ANKA synchrotron source (KIT, Karlsruhe, Germany) using monochromatic radiation ($\lambda = 1.0589 \text{ \AA}$). In order to determine the exact wavelength of the radiation, provided by the Si(111) double crystal monochromator, a silicon powder standard (NIST standard reference material 640) was measured. The kaňkite sample was loaded into a 0.5 mm glass capillary and spun during data acquisition. The intensity of the incoming beam was monitored during the data collection by an ion chamber, and the measured intensities of the diffracted beam were corrected for the decay and fluctuations of the primary beam. The XRD patterns were collected at room temperature with the scintillation counter and Ge (111) analyzer, over an angular range $7\text{--}57^\circ 2\theta$, with $0.01^\circ 2\theta$ steps and of 2 s per step counting time. When possible, powder XRD data were processed with the software package GSAS (Larson & von Dreele, 1994).

Precession electron diffraction tomography (PEDT)

For transmission electron microscope (TEM) experiments, a TEM instrument Philips CM 120 equipped with CCD

camera Olympus SIS Veleta (dynamic range 14 bits) was employed. The accelerating voltage used was 120 kV, corresponding to the wavelength of $0.0335 \text{ \AA}$. The device for precession electron diffraction DigiStar (NanoMegas) is coupled with the TEM. The electron diffraction data were processed by the programs PETS (Palatinus, 2011) and Jana2006 (Petříček *et al.*, 2014). Crystals of the sample provided diffraction patterns with sharp spots and it was possible to collect diffraction data of good quality. Structure was solved from the PEDT data by charge-flipping algorithm (Oslányi & Sütő, 2004; Oszlányi & Sütő, 2011; Palatinus, 2013) using the program Superflip (Palatinus & Chapuis, 2007).

Results

The symmetry analysis of the solution found by Superflip (Palatinus & van der Lee, 2008) indicated the space group *Cc*. The solution could indeed be easily interpreted in this space group and a complete structure model was built. The model was subsequently refined by the full-matrix least-squares method using Jana2006. The model converged to $R_{\text{(obs)}} = 12.02\%$, $wR_{\text{(obs)}} = 12.49\%$ (with $\text{GOF} = 6.39$) for 1139 observed reflections with $[I_{\text{obs}} > 3\sigma(I)]$. Details of the refinement and crystal data are given in Table 1. Atomic coordinates, displacement parameters are listed in Table 2, interatomic distances in Table 3, and bond-valence sums in

Table 1. Structural data and refinement for dehydrated kaňkite. All values correspond to the PEDT data collection except for the lattice parameters, which were obtained from the Rietveld refinement of the powder diffraction pattern measured at 75°C .

a [$\text{\AA}$]	5.4930(5)
b [$\text{\AA}$]	20.3915(30)
c [$\text{\AA}$]	8.8122(10)
β [$^\circ$]	92.983(6)
V [$\text{\AA}^3$]	985.73
Z	4
Space group	<i>Cc</i>
Data collection	TEM Philips CM120
Temperature	293 K
Source, wavelength	TEM, $0.0335 \text{ \AA}$
Crystal dimensions	$1.00 \times 0.35 \text{ }\mu\text{m}$
Collection mode	electron diffraction tomography
Limiting θ angles	$0.14\text{--}1.34^\circ$
Limiting Miller indices	$-7 < h < 7, -20 < k < 21, -12 < l < 12$
No. of reflections	2885
No. of unique reflections	1578
No. of unique observed reflections	1139 [$I_{\text{obs}} > 3\sigma(I)$]
Data completeness	0.51
R_{int} (obs on F^2)	0.0615
Refinement by Jana2006	
Parameters refined	79
R , wR_{obs}	0.1202, 0.1249
R , wR_{all}	0.1506, 0.1259
GoFobs/all	6.39/5.42
Weighting scheme, details	$\sigma, w = 1/(\sigma^2(F) + 0.0001F^2)$

Table 2. Structural data for dehydrated kaňkite, as determined by the refinement of the model and the PEDT data.

Space group: Cc				
$a = 5.4930 \text{ \AA}$, $b = 20.3915 \text{ \AA}$, $c = 8.8122 \text{ \AA}$, $\beta = 92.983^\circ$, $V = 985.73 \text{ \AA}^3$				
Atom	x	y	z	U_{iso}
Fe1	0.1002(7)	0.2284(4)	0.0515(5)	0.035(2)
Fe2	0.3230(7)	0.0785(5)	0.2160(5)	0.035(2)
As1	0.0920(7)	0.1935(4)	0.4128(4)	0.033(3)
As2	0.8192(7)	0.0815(5)	0.0115(5)	0.037(3)
O1	0.8264(18)	0.1636(11)	0.0454(11)	0.019(2)
O2	0.0748(16)	0.1165(10)	0.3506(11)	0.014(2)
O3	0.603(2)	0.0447(12)	0.1037(13)	0.035(3)
O4	0.0532(18)	0.2496(11)	0.2741(11)	0.022(2)
O5	−0.1293(17)	0.2017(10)	0.5353(10)	0.018(2)
O6	0.3676(15)	0.2017(10)	0.4997(10)	0.012(2)
O7	1.084(2)	0.0469(13)	0.0609(14)	0.034(3)
Oh1	0.349(2)	0.1666(12)	0.1258(13)	0.031(3)
Oh2	0.774(2)	0.0777(15)	−0.1863(13)	0.037(3)
Ow1	0.7891(19)	0.4823(12)	0.2932(12)	0.030(3)
Ow2	0.635(2)	0.2996(12)	0.3330(13)	0.029(3)
Ow3	0.576(3)	0.0897(15)	0.4026(16)	0.048(4)

Table 3. Interatomic distances (in $\text{\AA}$) in the structure of dehydrated kaňkite.

As1	−O2	1.66	As2	−O3	1.65
	−O6	1.67		−O7	1.65
	−O5	1.68		−O1	1.70
	−O4	1.68		−Oh2	1.75
	−Oh1	1.95		−O7	1.95
Fe1	−O6	1.95	Fe2	−Oh1	1.97
	−O1	2.00		−O3	1.99
	−Ow2	2.03		−O2	2.01
	−O4	2.04		−Ow1	2.09
	−O5	2.07		−Ow3	2.11

Table 4. It should be noted that while the PEDT data are of sufficient quality for a finding a reliable structure model, the accuracy of the refined coordinates is limited and the quantities derived from the structure model, like interatomic distances or bond-valence sums, should be

Table 4. Bond-valence (b.v.) sums for the atoms in the structure of dehydrated kaňkite.

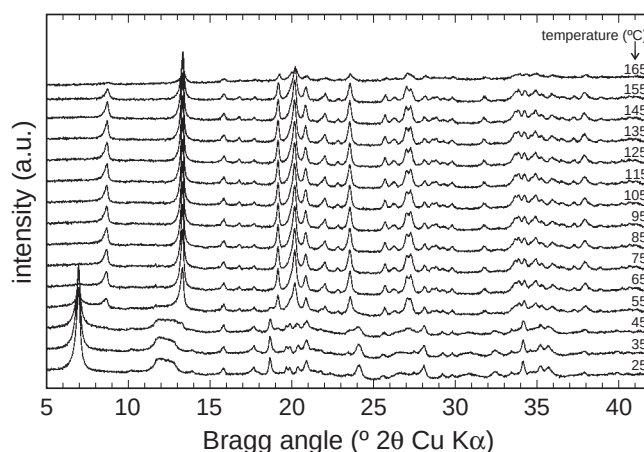
Atom	b.v. sum	Atom	b.v. sum
As1	5.17(11)	O5	1.68(4)
Fe1	2.90(5)	O6	1.86(4)
As2	4.96(12)	O7	1.91(6)
Fe2	2.79(6)	Oh1	1.09(5)
O1	1.69(8)	Oh2	1.05(4)
O2	1.79(8)	Ow1	0.38(3)
O3	1.85(6)	Ow2	0.454(17)
O4	1.71(6)	Ow3	0.363(15)

taken only as approximate, with the e.s.d.s derived from the least-squares refinement most likely underestimated. Typically, errors in atomic positions derived from PEDT data are below $0.1 \text{ \AA}$, but occasionally they may be much larger (Kolb *et al.*, 2011; Palatinus *et al.*, 2015). Given the comparably low R_{obs} and generally well-behaved refinement, we believe the structure model is – for the standards of the PEDT data – relatively accurate, but errors in positions up to $0.1 \text{ \AA}$, especially for oxygen positions, must still be assumed.

Initially, we believed that the structure solved by PEDT is indeed the crystal structure of kaňkite. Yet, after repeated attempts, we failed to fit this structural model to the powder XRD data, either from the in-house diffractometer or a synchrotron. Therefore, we suspected a change of the kaňkite structure under high vacuum or elevated temperature and turned our attention to variable-temperature powder XRD experiments.

Variable-temperature powder X-ray diffraction

Variable-temperature powder XRD experiments served to monitor structural transformation of kaňkite. The results are summarized in Fig. 1, documenting clearly a fast transformation of the kaňkite sample to another phase at temperatures between 55 and 65°C . The transformation is marked by a gradual disappearance of the strongest peak of kaňkite at $d = 12.7 \text{ \AA}$. We note that the transformation seems to be of kinetic rather than thermodynamic nature. Thermodynamically driven transformations between hydrated salts are usually easily reversible, for example for the pair epsomite ($\text{MgSO}_4 \cdot 7\text{H}_2\text{O}$) – hexahydrate ($\text{MgSO}_4 \cdot 6\text{H}_2\text{O}$). For kaňkite, however, we were not able to reverse the transformation at lower temperatures and elevated relative air humidity. In addition, kaňkite spontaneously dehydrated even at laboratory conditions ($T = 20^\circ\text{C}$, relative humidity of $\sim 30\%$).

Fig. 1. Phase transformation of kaňkite as a function of temperature. Kaňkite dehydrates at temperatures of 55 – 65°C .

Thermodynamic data suggest that kaňkite is unstable with respect to scorodite (Majzlan *et al.*, 2012). Therefore, the transformation was most likely accelerated by the elevated temperature but not caused by this temperature variation. At a temperature of about 170 °C, the sample went amorphous and remained in this state up to the highest temperature achieved in our powder-diffraction study, *i.e.*, 200 °C.

The XRD pattern of the dehydration product bears little resemblance to the original kaňkite sample. It differs not only in the peak positions but also in the fact that all peaks are relatively sharp and the crystallinity of this phase seems to be much better than that of kaňkite initially. A full-profile fit with the structural model derived from PED confirmed that we solved the crystal structure of this, dehydrated phase.

Rietveld refinement of the structural model, using the powder XRD data, did not lead to an improved model for the structure of the dehydration product. Although the agreement between the measured data and calculated curve is good (Fig. 2), only the refinement of the heavy atom positions was possible. Attempts to refine the positions of the O atoms led to large variations in interatomic distances. Fixing the distances with heavy restraints was possible but the tetrahedra deformed considerably with that treatment. The powder XRD data confirm the validity of the model derived from PEDT, but lack the necessary quality to improve this model, especially with respect to the positions of the O atoms.

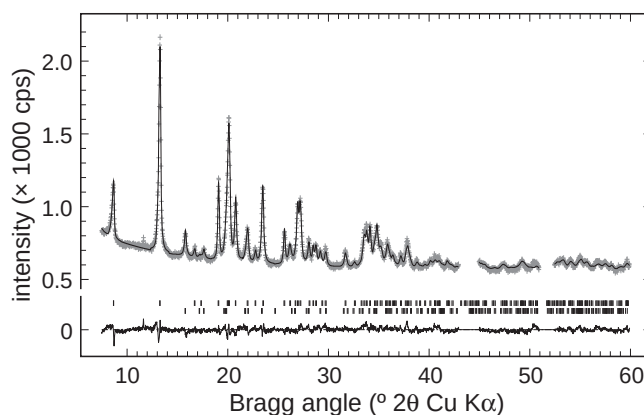


Fig. 2. Rietveld refinement of a structural model of the dehydration product of kaňkite with the powder XRD data. Grey crosses represent the data, the thick solid line the model. The ticks below the pattern show the expected positions of the peaks; the upper row for the dehydrated kaňkite, the lower row for scorodite ($\text{FeAsO}_4 \cdot 2\text{H}_2\text{O}$). The lowermost curve is the difference curve ($I_{\text{measured}} - I_{\text{calculated}}$). Parts of the powder profile were excluded due to the presence of peaks arising from the sample holder.

Description of the solved structure

The structure of the dehydration product of kaňkite consists of corrugated heteropolyhedral sheets (Figs. 3 and 4). Arsenic is coordinated tetrahedrally, iron octahedrally. Within the corrugated sheets, there are

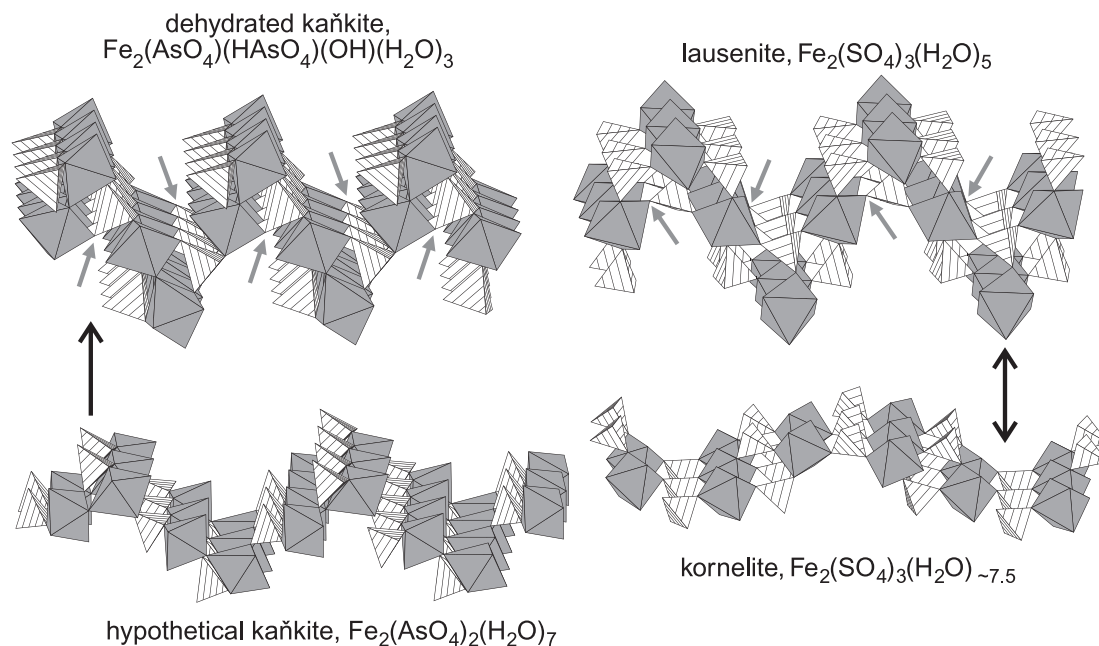


Fig. 3. Crystal structures of the lausénite (Majzlan *et al.*, 2005), kornelíte (Robinson & Fang, 1973), dehydrated kaňkite (this work), and a hypothetical model of the possible kaňkite structure. The transformation between kornelíte and lausénite is reversible (Kong *et al.*, 2011), as shown by the double arrow. The transformation between kaňkite and dehydrated kaňkite cannot be probably reversed, as shown by the single arrow. Small grey arrows indicate the points where the As-O-Fe or S-O-Fe bridges must be broken in the dehydrated forms to obtain the sheet of the hydrated form.

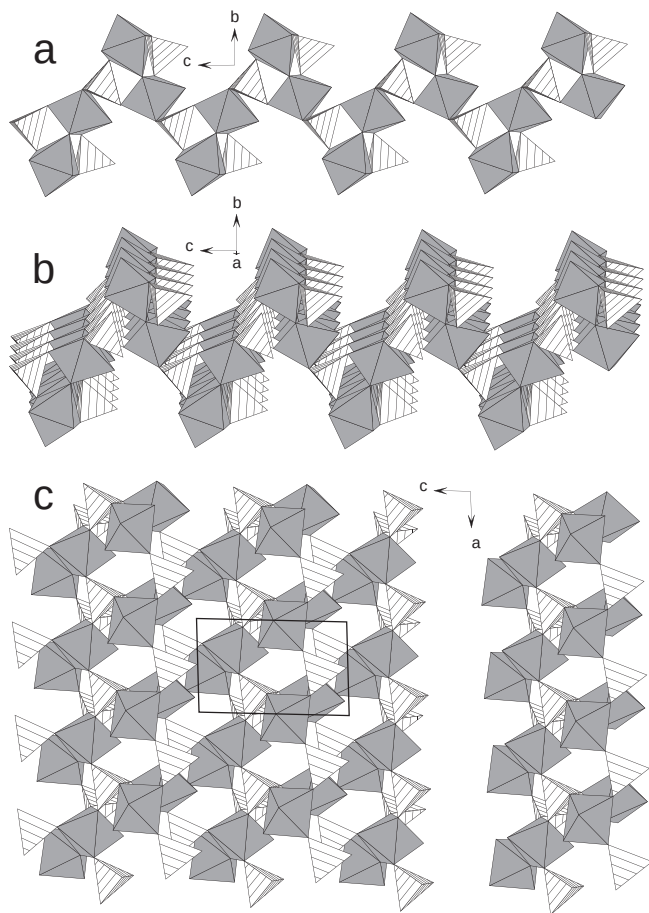


Fig. 4. Views of the crystal structure of the dehydration product of kaňkite: a) side view of the corrugated sheets (projection onto 100), b) side view, projection slightly off 100, c) top view of the corrugated sheets (projection onto 010). In c), unit cell is shown by thin black lines; some of the polyhedra are erased in the right-hand part of the figure for a better visualization of the polyhedral linkages. In all figures, FeO_6 octahedra are grey, AsO_4 tetrahedra are white and hatched.

pairs of Fe^{3+} octahedra connected *via* a common corner. This corner, according to the bond-valence calculations (see below), is an OH group. Each pair of octahedra is connected to five adjacent arsenate tetrahedra, also *via* corners. The geometry of two of these arsenate tetrahedra can be described as bidentate-binuclear, that of the other three as monodentate-mononuclear. The corrugated sheets are constructed by connecting the octahedral pairs by their arsenate neighbors to the other octahedral pairs. The topology of the corrugated sheets is also shown in Fig. 5 and discussed below.

According to the bond-valence calculations (Table 4, the accuracy of the bond-valence sum is limited by the lower accuracy of interatomic distances obtained from PEDT),

the oxygen atoms Oh1 and Oh2 should represent OH groups and oxygen atoms Ow1, Ow2 and Ow3 correspond to H_2O molecules, leading to the formula $\text{Fe}_2(\text{AsO}_4)(\text{HAsO}_4)(\text{OH})(\text{H}_2\text{O})_3$ for the dehydration product of kaňkite.

Discussion

We did not succeed in the solution of the crystal structure of kaňkite, because the poor crystallinity of the powder prevented solution from XRPD data and the mineral spontaneously dehydrated in the vacuum of the transmission electron microscope. The dehydrating effect of high vacuum prevents often the successful structure analysis of hydrated oxysalts. A comparison of the structure of dehydrated kaňkite to similar structures among ferric sulfates may, however, provide some insight into what the structure of kaňkite may be.

The crystal structure of lausenite, $\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_5$, consists of corrugated heteropolyhedral sheets (Figs 3 and 5) (Majzlan *et al.*, 2005) with a somewhat similar topology to the dehydrated kaňkite. A perfect analogy between the two sheets cannot be expected because of the different charge of the sulfate and arsenate groups.

Lausenite can hydrate to kornelite, $\text{Fe}_2(\text{SO}_4)_3(\text{H}_2\text{O})_7$, and this transformation is reversible (Kong *et al.*, 2011), indicated by the double arrow in Fig. 3. The structure of kornelite is also built of sheets (Robinson & Fang, 1973), which are almost flat and can be obtained from the corrugated sheets of lausenite by breaking a connection between two corner-sharing polyhedra – an SO_4 tetrahedron and FeO_6 octahedron. The relationship between the topology of the lausenite and kornelite sheets is shown as a polyhedral model and as schematic topology in Fig. 5.

We suspect that the structural relationship between kaňkite and its dehydration product is similar to that between lausenite and kornelite. Assuming this similarity, we constructed a possible model of the kaňkite sheet by breaking one of the connections between the AsO_4 and FeO_6 polyhedra (bridge As1–O4–Fe1, dashed lines in Fig. 6) so that the sheet can be stretched out. This breaking and stretching can be obtained by adding one molecule of water per formula unit into the sheet. This tentative model is shown in Figs. 3 and 6. The topology of the sheets, shown in Fig. 6, is more difficult to interpret and visualize in a projection. Yet, it can be seen that the sheet of the hypothetical structure of kaňkite retains the corner-shared pairs of two FeO_6 octahedra. These pairs of octahedra are bonded to five adjacent arsenate tetrahedra, just like in the structure of the dehydration product of kaňkite. The bonding topology, however, changes; only one tetrahedron is bonded now in a bidentate-binuclear fashion, the remaining four tetrahedra in the monodentate-mononuclear

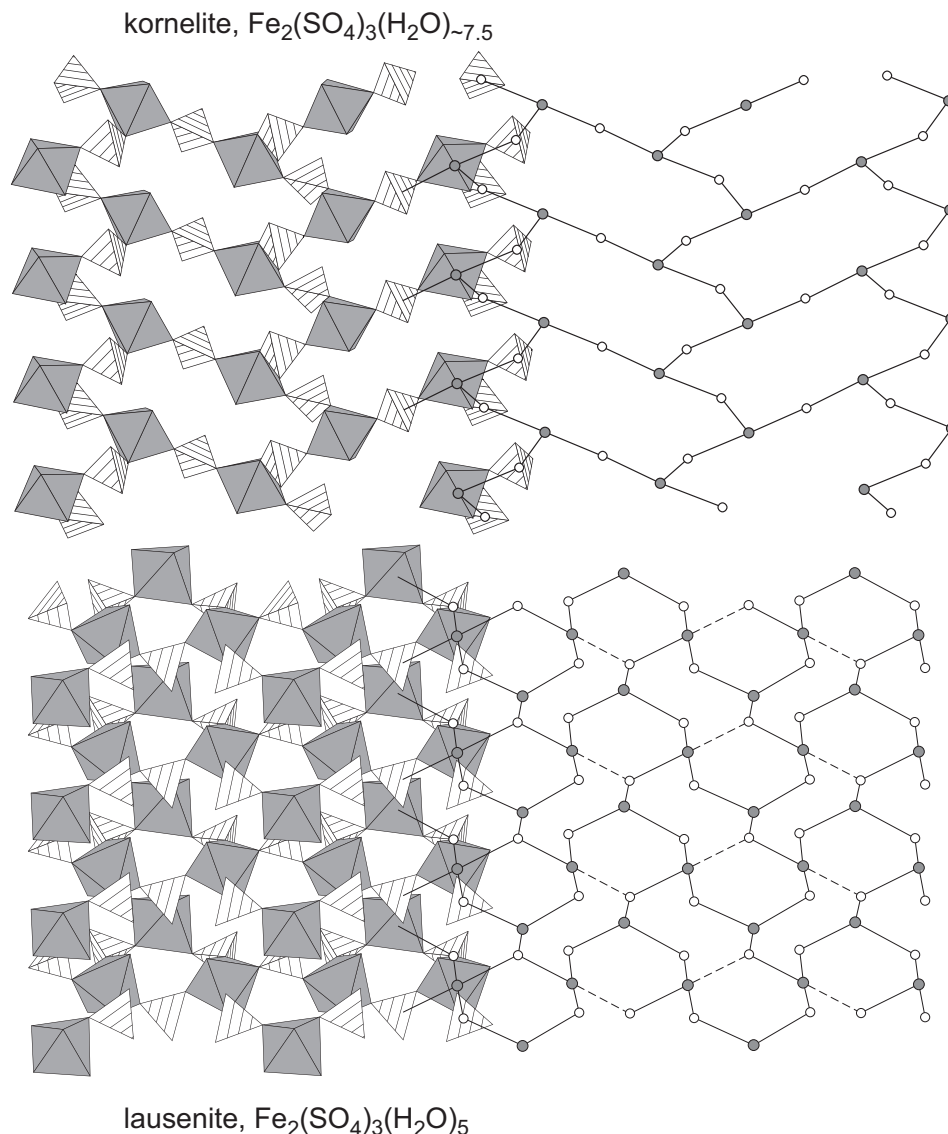


Fig. 5. Top view of the crystal structures of kornelite and lausenite, shown as polyhedral models (left) and topological schemes (right). In the topological schemes, only the cations are shown, Fe^{3+} as grey circles and S^{6+} as white circles. Dashed lines in the scheme of lausenite show the polyhedral linkages that need to be broken in order to allow the transformation from lausenite to kornelite.

fashion. This slight depolymerisation allows the sheets to stretch, to accommodate more H_2O groups within the sheets, and perhaps also to house more H_2O molecules between the sheets. The chemical formula of this hypothetical kaňkite sheet is $\text{Fe}_2(\text{AsO}_4)(\text{HAsO}_4)(\text{OH})(\text{H}_2\text{O})_4$. If the bulk formula $\text{Fe}_2\text{As}_2\text{O}_8 \cdot 7\text{H}_2\text{O}$ suggested for kaňkite by Čech *et al.* (1976) is correct, then the kaňkite structure would contain two additional water molecules per formula unit in the interlayer space.

Unfortunately, we cannot confirm the tentative model of the kaňkite structure, because our attempts to index

the powder XRD sets failed, namely due to poor diffraction patterns provided by natural kaňkite samples. The data from a synchrotron source are of a higher quality than the in-house data; particularly, the broad hump at $\sim 12^\circ 2\theta$ (for $\text{Cu K}\alpha$ radiation) is resolved as a relatively sharp peak in the synchrotron data (Fig. 7). Even with this and some other minor improvements, the indexing did not succeed. Once lattice parameters for kaňkite will be available, the knowledge of the structure of its dehydration product, presented in this work, may help to solve the structure of kaňkite, perhaps even from powder XRD data.

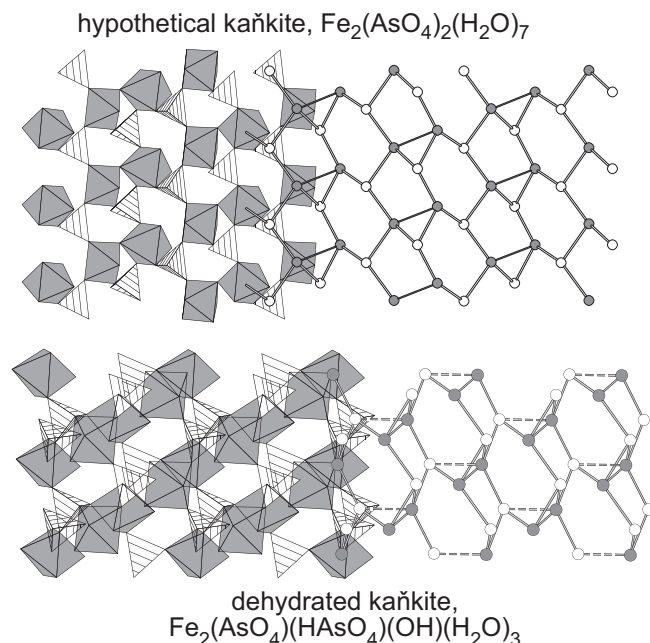


Fig. 6. Top view of the crystal structure of the dehydration product of kaňkite and the hypothetical structure of kaňkite, shown as polyhedral models (left) and topological schemes (right). In the topological schemes, only the cations are shown, Fe^{3+} as grey circles and As^{5+} as white circles. Dashed lines in the scheme of the dehydrated kaňkite show the polyhedral linkages that need to be broken in order to allow the transformation from dehydrated kaňkite to the hypothetical structure of kaňkite.

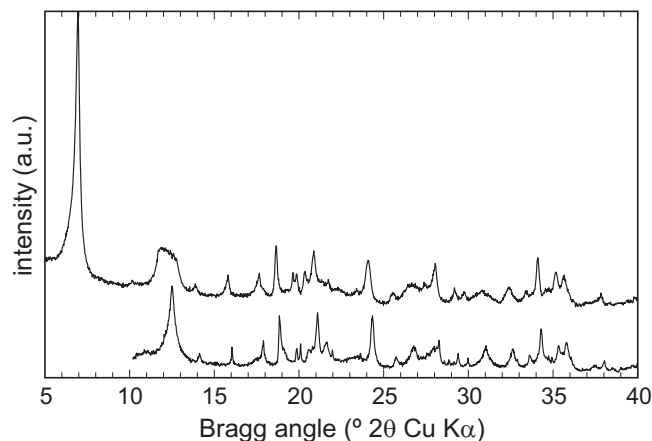


Fig. 7. A comparison of the in-house powder XRD data (upper curve) and synchrotron-source powder XRD data (lower curve) for kaňkite. For the purpose of this comparison, the synchrotron data were recalculated to $\lambda = 1.54056 \text{ \AA}$.

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