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**THE NETWORK OF HYDROGEN BONDING IN KINGITE,  
AS REVEALED BY A NEUTRON-DIFFRACTION INVESTIGATION  
OF ITS DEUTERATED ANALOGUE,  $\text{Al}_3(\text{PO}_4)_2\text{F}_3 \cdot 7\text{D}_2\text{O}$**

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ABSTRACT

The extensive hydrogen-bonding network of kingite is described for a specimen from Tom's Quarry, near Kapunda, South Australia. After deuteration, the triclinic structure was refined in space group  $P\bar{1}$ ,  $a$  9.318(1),  $b$  10.092(1),  $c$  7.108(1) Å,  $\alpha$  97.61(1),  $\beta$  100.56(1),  $\gamma$  95.97(1)°,  $V$  645.7(1) Å<sup>3</sup>,  $Z$  = 2. The formula of this modified specimen of kingite, refined using neutron powder-diffraction data, has been established as  $\text{Al}_3(\text{PO}_4)_2\text{F}_3 \cdot 7\text{D}_2\text{O}$ . We were able to locate the three atoms of fluorine.

*Keywords:* kingite, deuteration, Rietveld refinement, neutron, powder diffraction, hydrogen bond.

SOMMAIRE

Nous décrivons le réseau répandu de liaisons hydrogène dans la kingite; nos travaux ont porté sur un échantillon provenant de la carrière dite Tom's Quarry, près de Kapunda, en Australie du Sud. Une fois l'échantillon deutérié, la structure triclinique a été affinée dans le groupe spatial  $P\bar{1}$ ,  $a$  9.318(1),  $b$  10.092(1),  $c$  7.108(1) Å,  $\alpha$  97.61(1),  $\beta$  100.56(1),  $\gamma$  95.97(1)°,  $V$  645.7(1) Å<sup>3</sup>,  $Z$  = 2. La formule de cet échantillon ainsi modifié, affiné au moyen de données en diffraction neutronique sur poudre, serait  $\text{Al}_3(\text{PO}_4)_2\text{F}_3 \cdot 7\text{D}_2\text{O}$ . La position des trois atomes de fluor a été définie.

(Traduit par la Rédaction)

*Mots-clés:* kingite, deutération, affinement de Rietveld, diffraction de neutrons, liaisons hydrogène.

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## INTRODUCTION

Recently, Wallwork *et al.* (2003) reported a determination of the crystal structure of kingite,  $\text{Al}_3(\text{PO}_4)_2(\text{F},\text{OH})_2 \cdot 8(\text{H}_2\text{O},\text{OH})$ , from X-ray powder-diffraction data. The structure was found to contain finite strings of three corner-sharing  $\text{Al}\phi_6$  octahedra (where  $\phi$  represents either O, OH<sup>-</sup>, F<sup>-</sup> or H<sub>2</sub>O) that are cross-linked *via*  $\text{PO}_4$  tetrahedra to produce layers that are perpendicular to [100]. The layers are linked *via* hydrogen-bonding through H<sub>2</sub>O located in the interlayer space. This structural work led to revision of the formula of kingite from  $\text{Al}_3(\text{PO}_4)_2(\text{OH})_3 \cdot 9(\text{H}_2\text{O},\text{OH})$ , reported by Norrish *et al.* (1957), to  $\text{Al}_3(\text{PO}_4)_2(\text{F},\text{OH})_2 \cdot 8(\text{H}_2\text{O},\text{OH})$ .

However, several aspects of the crystal structure where left unresolved, in particular the nature of the H-bonding network and the locations of the F atoms. In order to fully characterize the crystal structure of kingite, we undertook a powder neutron-diffraction study of kingite using a deuterated sample.

## EXPERIMENTAL METHODS

A sample of kingite from Tom's Quarry, near Kapunda, South Australia (South Australian Museum

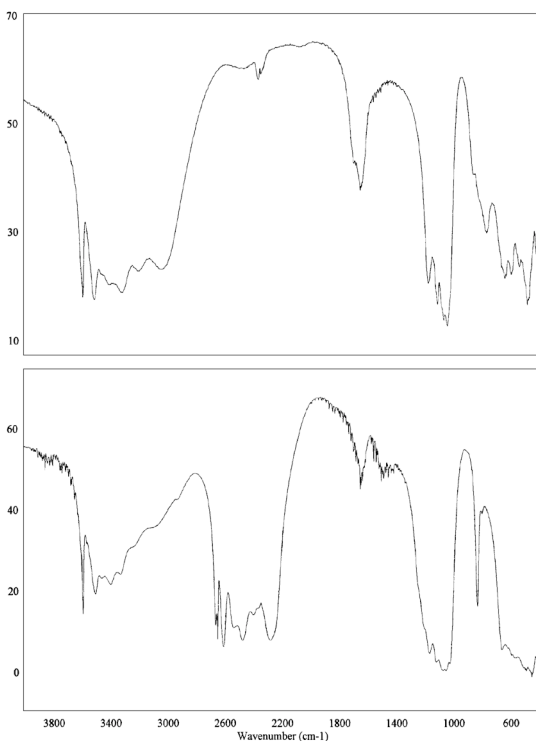


FIG. 1. Infrared spectra of kingite (pressed into KBr disks), a) before and b) after D exchange for seven days.

G12979) was selected for deuteration. This material was used by Wallwork *et al.* (2003) for the powder X-ray structure determination. The deuterated sample was prepared by warming a slurry of crushed kingite and D<sub>2</sub>O to *ca.* 40°C and stirring under an atmosphere of N<sub>2</sub> for seven days. The infrared spectra of the sample before and after D exchange are shown in Figure 1a and 1b. Note the shift in peaks from 3600–3000 cm<sup>-1</sup> (Fig. 1a) to 2700–2200 cm<sup>-1</sup> (Fig. 1b). The former indicates an OH stretch, and the latter an OD stretch; thus exchange has occurred. There was no further change in the infrared spectrum when treatment was continued for a longer time.

Powder neutron-diffraction data were collected on the deuterated sample at the Australian Nuclear Science and Technology Organisation's HiFlux Accelerator Reactor (HiFAR). The sample was loaded into a vanadium canister 8 mm in diameter. Data were collected for eleven days at the wavelength of 1.9090(4) Å. The flux at the sample was  $8 \times 10^4$  n.cm<sup>-2</sup>.s<sup>-1</sup>, and the beam size was 20 × 50 mm. Although good counting statistics were achieved, the data are still slightly affected by incoherent scattering due to the presence of some residual hydrogen.

## STRUCTURE SOLUTION AND REFINEMENT

The coordinates of the atoms, other than hydrogen, from Wallwork *et al.* (2003) were used as the basis for calculating the locations of the deuterium atoms. Deuterium atoms were placed geometrically in positions consistent with hydrogen-bonding. Initially, all non-phosphate O sites were treated as potential O–D donor sites. This gave a model that provided for the stoichiometric possibilities ranging from  $\text{Al}_3(\text{PO}_4)_2(\text{OD})_3 \cdot 7\text{D}_2\text{O}$  to  $\text{Al}_3(\text{PO}_4)_2\text{F}_3 \cdot 7\text{D}_2\text{O}$ . The neutron-scattering amplitude of deuterium,  $0.667 \times 10^{12}$  cm<sup>-1</sup> (International Tables of X-Ray Crystallography 1974) was used throughout the refinement; no adjustment was made for the small amount of hydrogen present.

The structure was refined from the neutron-diffraction data by the Rietveld method (Rietveld 1969), using the program GSAS (Larson & Von Dreele 1994). We used GSAS, as it allows the application of soft constraints to bond distances. The basic topology of the structure was confirmed. It was noted, however, that three of the deuterium atoms refined to positions that were not realistic locations if left unconstrained (*i.e.*, they moved too close to other atoms, such as Al). Attempts were made to restrain these atoms into chemically realistic sites, firstly, by constraining the length of the O–D bond concerned, and secondly by holding the displacement parameters (B) of those deuterium atoms at values consistent with those for the well-defined deuterium atoms in the structure, (*e.g.*, *ca.* 3.2 Å<sup>2</sup>), and their fractional coordinates were allowed to vary during the refinement. The first option caused the displacement

parameters to become very large, indicating that the sites of the D atoms were incorrect. Option two resulted in the D atoms again moving to positions near Al or O atoms. These three deuterium atoms were subsequently removed from the refinement, and the associated oxygen atoms were thereafter refined as fluorine atoms. By this means, it was confirmed that the bridging anions of the cluster of three corner-linked aluminum octahedra (F1 and F2 in the X-ray refinement) are indeed F atoms. The identity of O12 in the X-ray refinement was established as predominantly F, and is herein denoted F3. Note that the neutron-scattering amplitude of oxygen and fluorine are  $0.575 \times 10^{12} \text{ cm}^{-1}$  and  $0.57 \times 10^{12} \text{ cm}^{-1}$  (International Tables of X-Ray Crystallography 1974), respectively, thus interchange of these atoms has little impact on the calculated pattern. A greater effect is observed, however, through the presence or absence of spurious deuterium atoms.

The chemical analyses undertaken by Wallwork *et al.* (2003) gave the composition of this specimen of kingite as  $\text{Al}_{3.2}(\text{PO}_4)_2(\text{F}_{1.7}\text{OH}_{0.3}) \cdot 7.5(\text{H}_2\text{O}, \text{OH})$ . The formula, calculated on the basis of two  $\text{PO}_4$  groups, accounts for only half the number of F atoms required to fully occupy the three F sites located in this refinement. This indicates that some of these sites are partially oc-

cupied by OH and that the protons were not replaced by deuterium during deuteration. This finding is consistent with some remnant OH absorption in the infrared spectrum shown in Figure 1b.

Constraints were applied to the structural model in order to impose some regularity on the aluminum-bearing octahedra and the phosphate tetrahedra. Oxygen–deuterium distances were constrained to 1.00(2) Å, aluminum–oxygen, to 1.90(2) Å, aluminum–fluorine, to 1.80(2) Å and phosphorus–oxygen, to 1.52(2) Å. Removal of the constraints did not alter the overall topology of the structure other than to cause the loss of regularization of the polyhedra, and the residuals demonstrated a 10–15% improvement. One single displacement parameter was refined for each atom type (*i.e.*, Al, O or F, P and D), and was refined in alternative cycles to the profile and background parameters. A summary of the refinement is presented in Table 1. The final coordinates of the atoms are listed in Table 2, and the structure of the deuterated kingite, including the D atoms, is presented in Figure 2, with atom labels. The final difference neutron-diffraction pattern is shown in Figure 3.

#### DESCRIPTION OF THE NETWORK OF HYDROGEN BONDS

The basic topology of the kingite structure is illustrated in Figures 4 and 5. The structure consists of chains of three  $\text{Al}\phi_6$  octahedra (highlighted in Fig. 4) that are cross-linked by  $\text{PO}_4$  tetrahedra, forming layers perpendicular to [100]. The layers, shown in Figure 5a, are linked by H-bonds, as indicated by interatomic distances between coordinated ( $\text{F}^-$ ,  $\text{OD}^-$  and  $\text{D}_2\text{O}$ ) species. Two uncoordinated  $\text{H}_2\text{O}$  molecules in the interlayer space are H-bonded to both adjoining layers (Fig. 5b).

The Al–(O,F) distances in the  $\text{Al}\phi_6$  octahedra and phosphate groups are not significantly different from those reported by Wallwork *et al.* (2003), and need not be further discussed. All of the non-phosphate O atoms (*i.e.* O4, O5, O9, O12, O13, O14, O15) are within a reasonable H-bonding distance of at least two potential H-bond acceptors, as shown in Table 3.

TABLE 2. DEUTERATED KINGITE: ATOM PARAMETERS AND ISOTROPIC-DISPLACEMENT PARAMETERS<sup>1</sup>

	x	y	z	B (Å <sup>2</sup> )
Al1	0.6813(11)	0.8497(10)	0.6135(15)	0.8(1)
Al2	0.4498(10)	0.7107(10)	0.1777(15)	0.8(1)
Al3	0.2307(12)	0.6272(11)	-0.2785(15)	0.8(1)
P1	0.3367(11)	0.8649(10)	0.5218(14)	1.6(1)
P2	0.5720(11)	0.6002(11)	-0.1945(15)	1.6(1)
F1	0.6004(12)	0.7385(12)	0.3876(15)	0.8(1)
F2	0.2966(13)	0.6986(13)	-0.0236(14)	0.8(1)
F3	0.0434(12)	0.6331(13)	-0.2605(18)	0.8(1)
O1	0.4948(10)	0.9008(12)	0.6371(19)	0.8(1)
O2	0.7203(14)	0.9998(10)	0.4918(16)	0.8(1)
O3	0.6801(13)	0.7022(11)	0.7500(17)	0.8(1)
O4	0.7425(14)	0.9649(12)	0.8612(16)	0.8(1)
O5	0.8808(11)	0.8268(13)	0.6131(19)	0.8(1)
O6	0.3193(11)	0.7892(11)	0.3169(14)	0.8(1)
O7	0.5684(12)	0.6373(12)	0.0189(15)	0.8(1)
O8	0.3736(13)	0.5365(9)	0.2238(19)	0.8(1)
O9	0.5074(13)	0.8805(10)	0.1059(17)	0.8(1)
O10	0.2416(14)	0.7981(10)	-0.3580(16)	0.8(1)
O11	0.4183(11)	0.5960(13)	-0.3188(17)	0.8(1)
O12	0.1737(15)	0.5580(13)	-0.5497(15)	0.8(1)
O13	0.1911(14)	0.4469(10)	-0.2338(19)	0.8(1)
O14	0.9008(15)	0.9434(13)	0.2111(16)	0.8(1)
O15	1.0171(13)	0.7065(13)	0.1338(18)	0.8(1)
D4a	0.7492(17)	1.0642(13)	0.8614(22)	4.0(1)
D4b	0.8154(15)	0.9584(16)	0.9779(21)	4.0(1)
D5a	0.9645(16)	0.9048(15)	0.6507(19)	4.0(1)
D5b	0.9377(18)	0.7537(15)	0.6618(23)	4.0(1)
D9a	0.5117(19)	0.9708(13)	0.1898(23)	4.0(1)
D9b	0.5860(17)	0.8894(14)	0.0280(22)	4.0(1)
D12a	0.0945(17)	0.4828(14)	-0.6119(23)	4.0(1)
D12b	0.2429(16)	0.5366(15)	-0.6379(22)	4.0(1)
D13a	0.0981(16)	0.4064(15)	-0.2047(24)	4.0(1)
D13b	0.2684(16)	0.4029(14)	-0.1600(23)	4.0(1)
D14a	0.8377(17)	0.9461(14)	0.3123(21)	4.0(1)
D14b	0.9480(16)	0.8598(14)	0.1994(22)	4.0(1)
D15a	1.1244(14)	0.7198(14)	0.2011(21)	4.0(1)
D15b	1.0340(17)	0.6921(15)	-0.0030(20)	4.0(1)

<sup>1</sup> Fractional coordinate values >1 are given in order to present a connected set of atoms.

TABLE 3. SUMMARY OF HYDROGEN-BONDING INTERACTIONS IN DEUTERATED KINGITE

O–D...X	O–D (Å)	O...X (Å)	D...X (Å)	D–O–D (°)	O–D...X (°)
O4–D4a...O6	0.997(8)	2.99(2)	2.145(17)	102.5(2)	141.8(2)
O4–D4b...O14	0.985(8)	2.70(2)	1.736(18)		164.2(2)
O5–D5a...O14	1.019(8)	2.90(2)	1.907(16)	98.0(2)	163.3(2)
O5–D5b...F3	1.014(8)	2.74(2)	1.727(18)		176.6(2)
O9–D9a...O1	1.014(8)	2.68(2)	1.679(17)	107.5(2)	167.2(2)
O9–D9b...O4	1.000(8)	3.15(2)	2.180(17)		164.3(2)
O12–D12a...F3	0.996(8)	2.67(2)	1.680(18)	96.3(2)	172.9(2)
O12–D12b...O8	0.998(8)	2.68(2)	1.700(17)		167.6(2)
O13–D13a...O15	0.988(8)	2.61(2)	1.674(17)	104.6(2)	157.9(2)
O13–D13b...O7	0.991(8)	2.75(2)	1.778(17)		166.3(2)
O14–D14a...O2	1.008(8)	2.87(2)	1.890(16)	112.4(2)	164.6(2)
O14–D14b...O15	0.992(8)	2.76(2)	1.775(16)		169.7(2)
O15–D15a...O6	1.013(8)	2.86(2)	1.871(16)	97.0(2)	165.6(2)
O15–D15b...F3	1.007(8)	2.86(2)	1.869(17)		168.9(2)

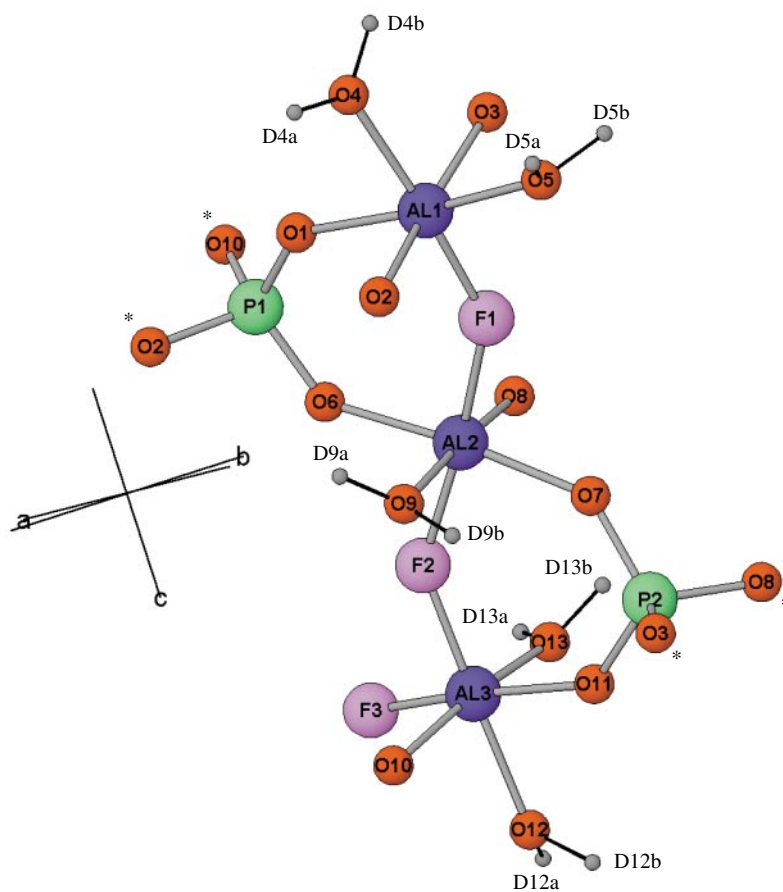


FIG. 2. Atom arrangement in deuterated kingite, refined with neutron-diffraction data, showing atom sites. Symmetrically equivalent atoms are designated with \*.

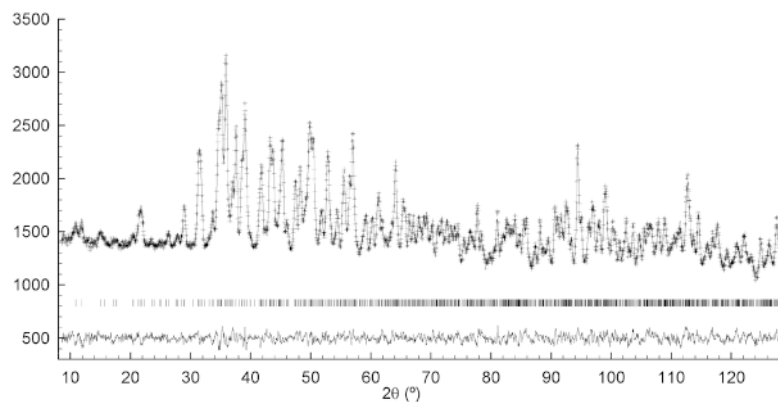


FIG. 3. The neutron powder-diffraction pattern of deuterated kingite refined at the wavelength 1.9090(4) Å. The observed (+) and calculated (-) patterns are shown, as are the Bragg reflection markers (|), with the difference pattern below these. The y-scale is in arbitrary count-units.

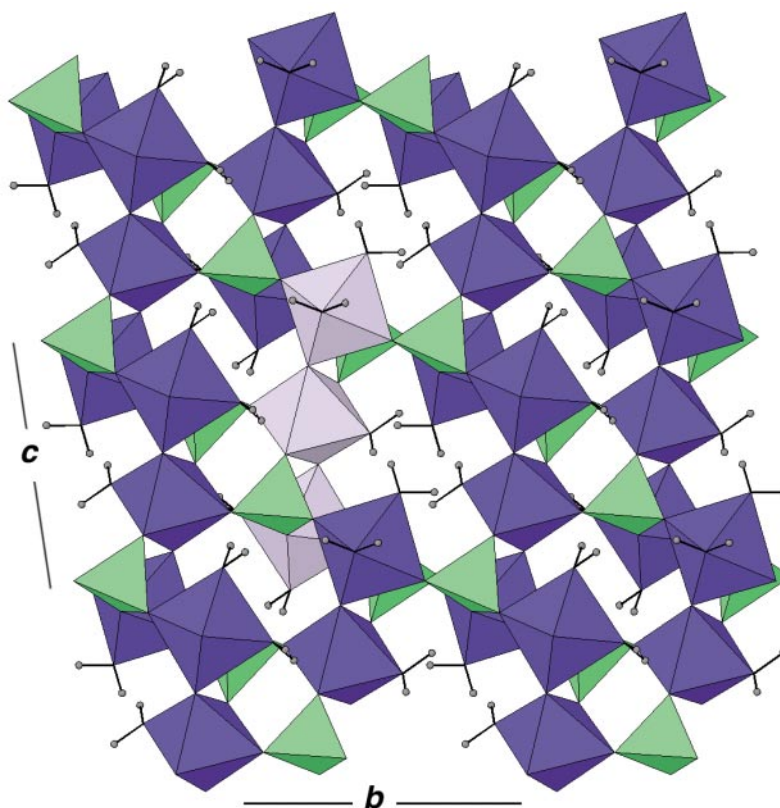


FIG. 4. A layer in the deuterated analogue of kingite viewed down the  $a$  axis, with stoichiometry  $\text{Al}_3(\text{PO}_4)_2\text{F}_3 \cdot 5\text{D}_2\text{O}$ . One triad is highlighted.

TABLE 3. SUMMARY OF HYDROGEN-BONDING INTERACTIONS IN DEUTERATED KINGITE

O–D...X	O–D (Å)	O...X (Å)	D...X (Å)	D–O–D (°)	O–D...X (°)
O4–D4a...O6	0.997(8)	2.99(2)	2.145(17)	102.5(2)	141.8(2)
O4–D4b...O14	0.985(8)	2.70(2)	1.736(18)		164.2(2)
O5–D5a...O14	1.019(8)	2.90(2)	1.907(16)	98.0(2)	163.3(2)
O5–D5b...F3	1.014(8)	2.74(2)	1.727(18)		176.6(2)
O9–D9a...O1	1.014(8)	2.68(2)	1.679(17)	107.5(2)	167.2(2)
O9–D9b...O4	1.000(8)	3.15(2)	2.180(17)		164.3(2)
O12–D12a...F3	0.996(8)	2.67(2)	1.680(18)	96.3(2)	172.9(2)
O12–D12b...O8	0.998(8)	2.68(2)	1.700(17)		167.6(2)
O13–D13a...O15	0.988(8)	2.61(2)	1.674(17)	104.6(2)	157.9(2)
O13–D13b...O7	0.991(8)	2.75(2)	1.778(17)		166.3(2)
O14–D14a...O2	1.008(8)	2.87(2)	1.890(16)	112.4(2)	164.6(2)
O14–D14b...O15	0.992(8)	2.76(2)	1.775(16)		169.7(2)
O15–D15a...O6	1.013(8)	2.86(2)	1.871(16)	97.0(2)	165.6(2)
O15–D15b...F3	1.007(8)	2.86(2)	1.869(17)		168.9(2)

The O atoms O14 and O15, from the two interlayer  $\text{H}_2\text{O}$  molecules, are surrounded by an approximately tetrahedral environment of four O,F atoms. Atom O14 interacts with O2, O4, O5 and O15 (via D14a, D4b, D5a and D14b, respectively), and O15 with O6, O13, O14

and F3 (via D15a, D13a, D14b and D15b, respectively). Hydrogen-bonds about O14 range in length from 1.736(18) to 1.907(16) Å, and these about O15 range from 1.674(14) to 1.871(16) Å. Angles subtended at O14 and O15 by the hydrogen-bonding arrangement about each atom are given in Table 4. These hydrogen-bond lengths and angles are consistent with those reported for the coordination environment about  $\text{H}_2\text{O}$  in hydrated inorganic structures (Ferraris & Franchini-Angela 1972).

Atom O14 is the donor in a H-bond to one layer and also to O15; it is the acceptor in a further two H-bonds from the adjacent layer. Atom O15 is the donor in two hydrogen-bonds to one side of the aluminum phosphate layer, and it is also the acceptor of a H-bond from the other side, thereby linking successive layers; it is the acceptor of one hydrogen-bond from O14 (Fig. 5b).

Further cross-linking of the layers occurs through deuterium atoms at O5 and O12 acting as hydrogen-bond donors to F3. Atom F3 acts as an acceptor of three H-bonds, one long contact [D15b...F3, 1.869(17) Å],

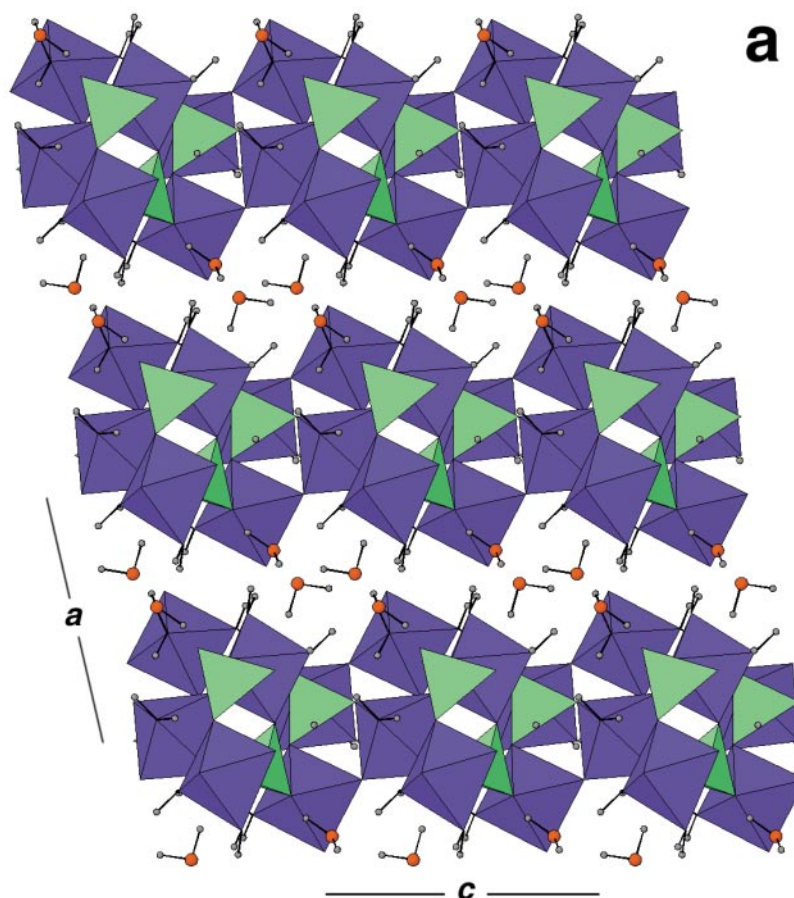


TABLE 4. ANGLES ABOUT F3 AND INTERLAYER MOLECULES OF D<sub>2</sub>O IN DEUTERATED KINGITE

X--O--X	(°)	X--O--X	(°)
D14a - O14 - D14b	112.4(2)	D15b - O15 ... D13a	119.6(2)
D14a - O14 ... D4b	116.9(2)	D15b - O15 ... D14b	114.3(2)
D14a - O14 ... D5a	93.2(2)	D13a ... O15 ... D14b	102.1(2)
D14b - O14 ... D4b	106.1(2)	Al3 - F3 ... D5b	125.3(2)
D14b - O14 ... D5a	112.2(2)	Al3 - F3 ... D12a	122.8(2)
D4b ... O14 ... D5a	115.9(2)	Al3 - F3 ... D15b	109.2(2)
D15a - O15 - D15b	97.0(2)	D5b ... F3 ... D12a	87.0(2)
D15a - O15 ... D13a	117.7(2)	D5b ... F3 ... D15b	91.0(2)
D15a - O15 ... D14b	106.2(2)	D12a ... F3 ... D15b	116.6(2)

and two of average length [D12a...F3, 1.680(18) Å and D5b...F3, 1.727(18) Å] (Fig. 5b). These, with the covalent bond to Al3, form a distorted tetrahedron about F3 (Table 4).

All other hydrogen-bonding (resulting from deuterium atoms on O4, O5, O9, O12 and O13 acting as bond donors) occurs within the aluminum phosphate layer. Atom O4 takes part in three H-bonds, two donating and

one weak accepting bond [D9b...O4, 2.180(17) Å]. Of the donating bonds, one is weak [D4a...O6, 2.145(17) Å], and the other is of average length [D4b...O14, 1.736(18) Å]. Angles subtended at O4 range from 83° to 131°, including those involving Al.

Angles subtended at O, owing to their covalent bonds to aluminum and deuterium, are listed in Table 5.

#### ACKNOWLEDGEMENTS

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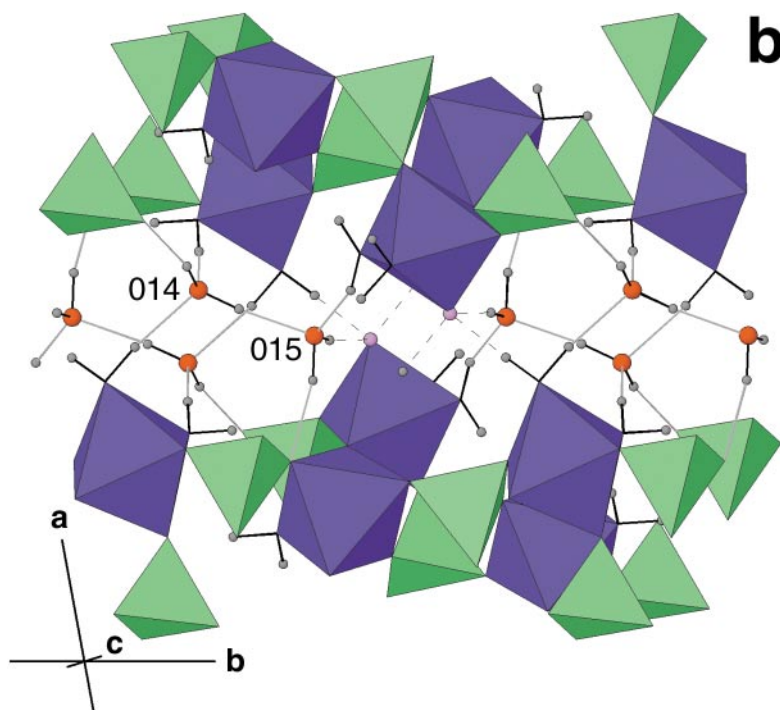


FIG. 5. a) The crystal structure of kingite, refined with neutron-diffraction data, viewed down the  $b$  axis. The  $\text{AlF}_6$  octahedra and the  $\text{PO}_4$  tetrahedra are purple and green, respectively. Interlayer  $\text{D}_2\text{O}$  molecules are shown as red spheres, and D atoms as grey spheres. b) Hydrogen-bonding interactions between the aluminum phosphate layer – interlayer  $\text{H}_2\text{O}$  – aluminum phosphate layer of kingite. Bonds accepted by F3 (pink spheres) are shown by the dashed line(s), and all other H-bonds between the layers and the interlayer  $\text{H}_2\text{O}$  molecules (in red; one pair is labeled) are shown in grey.

TABLE 5. ANGLES ( $^\circ$ ) IN DEUTERATED KINGITE SUBTENDED AT COORDINATING OXYGEN ATOMS BY ALUMINUM AND DEUTERIUM

Al – O – D	( $^\circ$ )	Al – O – D	( $^\circ$ )
Al1 – O4 – D4a	117.3(2)	Al1 – O4 – D4b	132.1(2)
Al1 – O5 – D5a	122.9(2)	Al1 – O5 – D5a	128.7(2)
Al2 – O9 – D9a	124.5(2)	Al2 – O9 – D9b	119.9(2)
Al3 – O12 – D12a	126.7(2)	Al3 – O12 – D12b	125.3(2)
Al3 – O13 – D13a	125.2(2)	Al3 – O13 – D13b	120.9(2)

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