Kidwellite, NaFe$_9^{3+}$(OH)$_{10}$(PO$_4$)$_6$·5H$_2$O, a new species

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SUMMARY. Kidwellite, NaFe$_9^{3+}$(OH)$_{10}$(PO$_4$)$_6$·5H$_2$O, monoclinic, Z = 2, a = 20·61(7) Å, b = 5·15(1) Å, c = 13·75(6) Å, β = 112·64(15)°, space group $A2/m$, Am, or $A2$, is a new species that occurs in moderate abundance as a late-stage mineral associated with rockbridgeite, dufrenite, beraunite, and strengite in novaculite deposits. Colour lively pale chartreuse-green, to greenish-yellow, greenish-white, and bright yellow. H = 3, lustre silky, streak yellow, cleavage {100} perfect, habit acicular elongated parallel to [010], flattened on {100}, biaxial (−), α = 1·787(5), β = 1·800(5), γ = 1·805(5), 2V large, $\beta\|b$, not discernibly pleochroic.

The mineral is moderately widespread as a replacement of rockbridgeite and beraunite from the Ouachita Mountains, Arkansas; Indian Mountain, Alabama; Irish Creek, Virginia; Waldgirmes, West Germany. A related, but apparently distinct, species is also noted from the McMahon pegmatite, South Australia, and the Sapucaia pegmatite, Minas Gerais, Brazil.

A LARGE number of basic ferric and aluminum phosphates have been long recognized as discrete mineralogical entities. Of these, a significant fraction are so poorly crystallized that studies on them, owing to inadequate crystallographic data, still remain in doubt. No less than eighty species have been well-characterized and these represent one of the most extensive families of compounds in the mineral kingdom.

Within this family, certain crystal-chemical principles have been recognized, one of the most characteristic being a subfamily of structures based on linear face-sharing $Me^{2+}-Me^{3+}-Me^{2+}-$ oxygen octahedral trimers. All are fibrous in habit and possess a fibre axis repeat of 5·1–5·2 Å. The octahedral trimers are corner-linked by PO$_4$ tetrahedra and additional Me–O octahedra to form thick sheets with approximate dimension 13·5–14·0 Å × 5·1–5·2 Å. These sheets are then linked in a variety of ways along a third 'variable' axis to generate a number of structure types with complex, but closely related, chemical compositions. Owing to the relative lack of suitable single crystals, the compounds have long resisted studies towards their crystal chemistry and taxonomy. Moore (1970) recognized nine discrete structure types belonging to the subfamily of 5 Å fibre-axis structures: dufrenite, rockbridgeite, beraunite, lipscombite, barbosalite, laubmannite, souzalite, cacoxenite, and 'Mineral A'. Single-crystal structure analysis on the first five compounds has clarified their crystal chemistry in detail, and the structure cell criteria and powder patterns of all nine have established, beyond doubt, the specific status of each (Moore, 1970).

Kidwellite corresponds to 'Mineral A' of Moore and is one of several discrete 5 Å fibre-axis structures heretofore formally unrecorded as specific compounds owing to the extreme difficulty in obtaining suitable single crystals. Six years have passed until sufficient data were at hand to warrant publication of the crystal chemistry of 'Mineral A'.

Occurrences. A detailed account of the phosphate mineral occurrences in the Ouachita Mountains, Arkansas, including their paragenesis and probable modes of origin has been published by Kidwell (1977). These occurrences are confined to the pre-Stanley rocks, near the upper part of the lower divisions of the novaculite. The minerals occur along fractures in these rocks, appearing in a great range of relative abundance from thin films to thick bands and seams, often with botryoidal surfaces. They are particularly abundant where the novaculite has been extensively brecciated and are nearly always associated with earlier formed goethite and variable amounts of manganese oxyhydroxides. Occurrences noted by Kidwell (1977) include Mr. Isom Avants's claims, the Turquoise Pit, Buckeye Mountain, and Coon Creek mine in Polk County, and Fodderstack Mountain in Montgomery County. Kidwell discerned three types of occurrences for kidwellite: as interlayerings with laubmannite and rockbridgeite, as thin, isolated, botryoidal masses, and as sheaves of crystals and small spheres implanted upon goethite.

Many other occurrences have been verified for kidwellite and the conclusion is reached that it is

one of the more abundant basic ferric phosphate species. At the old Irish Creek rockbridgeite locality, Rockbridge County, Virginia, it forms the greater fraction of the dull-brown cap of coarse rockbridgeite fibres; as spheres, sheaves, and replacement upon rockbridgeite and beraunite from Indian Mountain, Cherokee County, Alabama; as epitaxial overgrowth and a replacement rind on rockbridgeite and beraunite crystals from the Rotlaüfchen mine, Waldgirmes, West Germany; and possibly as an alteration product of triplite from the McMahon pegmatite, near Wiperaminga Hill, South Australia (Mineral B; see under Crystallography).

Moore (1970) concluded that kidwellite is one of the latest minerals to form in the ferric phosphate paragenesis. Specimens from all occurrences stated above show the mineral as the last-formed in the parageneses goethite rockbridgeite–kidwellite, goethite–beraunite- kidwellite, goethite–kidwellite. Where kidwellite replaces rockbridgeite crystals, the appearance is particularly spectacular, the bright-yellow rind defining a sandwich-like appearance about the dark-green rockbridgeite owing to crystallographic control of the replacement (see under Crystallography). Fine micromount specimens from the Indian Mountain locality provided by Mr. L. Perloff of Tryon, North Carolina, show that strengite crystals postdate the kidwellite; clear, attractive pink rosettes of this mineral are often implanted upon kidwellite globules, suggesting that the sequence of crystallizing phases observed is a reflection of decreasing pH of the coexisting fluid with time.

Physical properties. Owing to its lively yellow to greenish-yellow colour, kidwellite is easily distinguished from the other 5 Å fibre axis phosphates. When deposited upon other minerals, it occurs as mats and tufts made up of the finest feathery crystals, the individuals rarely exceeding 5 μm in thickness. Upon goethite it occurs as powdery greenish-yellow mats and as small spheroidal knobs of a lively chartreuse colour. The thin greenish-yellow coating commonly observed on the botryoids of rockbridgeite and dufrenite is kidwellite. Rockbridgeite when replaced by this mineral grades from a lustrous greenish-black colour through greenish-yellow to dull yellow, the latter an intimate mixture of kidwellite and goethite. Thick fibrous masses made up of fine needles often fill cavities and fractures in the novaculite rock, especially at the Fodderstack Mountain and Coon Creek localities. The finest specimens from the latter locality show the mineral as rosettes (up to 2 cm in diameter) of feathery matted crystals of a lively greenish-yellow colour although opaque in appearance. At Indian Mountain, it

more frequently occurs as a dust of feathery aggregates implanted upon the other species. The colour ranges from lively pale chartreuse-green, to greenish-yellow, greenish-white, to bright yellow, paler than and easily distinguished from cacoxenite. Confusion may occur in distinguishing the coarser varieties of kidwellite from laubmannite, a species to which kidwellite appears to be structurally closely related.

The lustre is silky and the streak is yellow; hardness = 3. The mineral occurs only as the finest needles, the largest single crystal measuring only 5 μm × 10μm × 50 μm. A scanning electron photomicrograph, kindly provided by A. L. Kidwell, on feathery tufts from a Coon Creek sample shows long stalks of kidwellite loosely connected by rhomboidal crystals growing normal to the stalks, affording a gratelike appearance (fig. 1). These
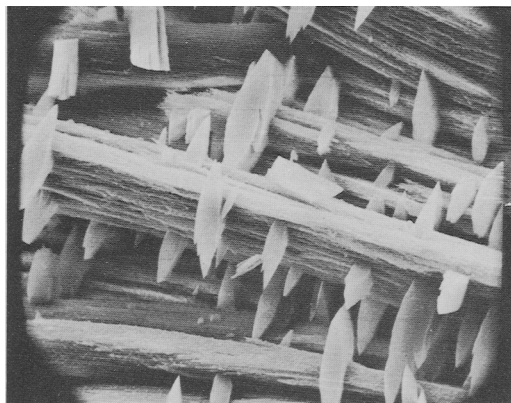

FIG. 1. Kidwellite from the Coon Creek mine. Scanning electron photomicrograph (AP-20, 2000 ×) of tufts. The long stalks are the kidwellite but the wedge-shaped crystals growing normal to the stalks have not been identified.

curious wedge-shaped crystals appear to be twinned and morphologically much resemble stewartite, $Mn^{2+}(H_2O)_4[Fe_2^{3+}(OH)_2(H_2O)_2 (PO_4)_2].2H_2O$, but attempts to further identify them—either by powder diffractometry or optically—have failed. The specific gravity of kidwellite, determined on the Berman torsion balance, was performed on dense fibres of Fodderstack Mountain material and the results ranged between 2·99 and 3·08 (at 23·3 °C). Owing to the impossibility of securing thicker crystals, these values are certainly too low. Some finely crushed fibres eventually sank in methylene iodide; hence the true specific gravity is probably somewhat above 3·3 g cm^{-3}. The cleavage is perfect {100}. Needles are thin prismatic to acicular elongated parallel to [010] and flattened on {100}.

Optically, kidwellite is biaxial $(-)$, $\alpha = 1\cdot787(5)$, $\beta = 1\cdot800(5)$, $\gamma = 1\cdot805(5)$, 2V large, $\beta \parallel b$, colourless in fine needles and not discernibly pleochroic.

X-ray crystallography. Considerable time and effort was expended in obtaining suitable single crystal data. After several dozen fibres were examined, it was concluded that they were in fact composites of many small needles in parallel growth. Although suitable rotation photographs were obtained, all showing the characteristic $5\cdot15$ Å fibre repeat, the Weissenberg photographs were hopelessly cluttered. One crystal, of a mere $5~\mu m$ in thickness, appeared transparent and optically uniform throughout; rotation and Weissenberg photographs each of two weeks exposure, were required to obtain sensible data. Although the b- and c-axes could be established with confidence, selection of the a-axis presented serious problems. Relatively few reflections of the $h0l$ and $h1l$ levels (Cu-K_α radiation) were available for indexing. An earlier study on a different crystal established similar axial data although the crystals were stated as belonging to the orthorhombic system: space group *Pbma*?, $a = 14\cdot0$ Å, $b = 38\cdot3$ Å, $c = 5\cdot14$ Å (Moore, 1970). Closer inspection of the film revealed, however, that intensities related by reflection planes normal to the a^* − and b^* directions were in fact not of equal intensity but consisted of small doublets. Superposition of these films on the more recent film showed coincidence of the reflections but that the earlier data possessed in addition a displacement of the same reciprocal lattice, doubtless arising from the existence of two fibre orientations for the previous crystal.

Extinction criteria are $hkl, k+l \neq 2n$ only; therefore, space group $A2/m$, Am or $A2$, $a = 20\cdot61(7)$ Å, $b = 5\cdot15(1)$ Å, $c = 13\cdot75(6)$ Å, $\beta = 112\cdot64(15)°$. The indexed strong intensities on the single crystal fibres were applied to the powder data and the first nineteen lines, contributed by the $k = 0$- and 1-levels, could be indexed without ambiguity. The powder data (Table I) obtained from a chart diffractometer were used to further refine the raw Weissenberg data to those stated above. We caution readers that the intensity distributions differ somewhat from the previously reported data for 'Mineral A' in Moore (1970) since a rolled sphere mount was employed in the earlier study.

Thick tabular crystals of rockbridgeite when replaced by kidwellite show the latter mineral as a shell of fibres in parallel growth, which are orientated normal to the surface of the broad base, offering the appearance of a sandwich. Thin fibrous masses of rockbridgeite are also capped in the same fashion and X-ray orientation photographs show that the two phases have their $5\cdot1$ Å axes in

common. In fact, Moore (1970) has shown that rhythmic bandings and zonations of sequences of the crystallizing $5\cdot1$ Å phosphates are orientated such that this axis is common to all phases. Noting that these phases all have a plane of dimensions $5\cdot1 \times 13\cdot8$ Å in common, it is likely that solution and

TABLE I. *Kidwellite. X-ray powder data*

1				2		3	
I/I_0	d_{obs}	d_{calc}	hkl	I/I_0	d_{obs}	I/I_0	d_{obs}
						4	13·89
100	9·41	9·51	200	9	9·49	10	9·42
10	6·87	6·86	$\bar{1}02$	2	6·89	2	6·96
30	6·43	6·42	002	4	6·38	3	6·50
5	5·429	5·423	102	1	5·44	—	—
—	—	—	—	5	5·13	2	5·10
12	4·792	4·792	$\bar{4}02$	3	4·79	4	4·86
10	4·541	4·539	$\bar{2}11$	3	4·54	—	—
—	—	—	—	—	—	5	4·31
10	4·141	4·111	$\bar{3}11$	2	4·09	—	—
35	4·017	4·014	$\bar{5}02$	4	4·02	4	3·94
40	3·813	3·810	302	3	3·826	—	—
5	3·634	3·643	$\bar{4}11$	3	3·644	—	—
55	3·413	3·408	$\bar{6}02$	8	3·425	4	3·48
40	3·193	3·210	$\bar{5}11$	10	3·189	7	3·21
35	3·173	3·172	004	—	—	—	—
15	3·078	3·073	113	4	3·086	6	3·11
10	2·943	2·951	$\bar{5}13$	2	2·959	5	2·99
15	2·846	2·842	213	3	2·851	—	—
15	2·831	2·837	$\bar{6}11$	—	—	—	—
15	2·789	2·785	511	2	2·788	3	2·75
10	2·577	2·577	020	3	2·578	3	2·61
15	2·484	—	—	2	2·487	—	—
5	2·424	—	—	2	2·418	—	—
5	2·392	—	—	2	2·400	—	—
5	2·183	—	—	1	2·187	—	—
15	2·050	—	—	2	2·067	—	—
5	2·000	—	—	1	2·003	—	—
—	—	—	—	1	1·952	—	—
—	—	—	—	2	1·909	—	—
5	1·854	—	—	2	1·856	2	1·80
—	—	—	—	1	1·817	—	—
10	1·735	—	—	2	1·737	—	—
—	—	—	—	1	1·712	—	—
5	1·690	—	—	1	1·692	—	—
—	—	—	—	1	1·664	—	—
5	1·643	—	—	2	1·646	3	1·65
5	1·598	—	—	2	1·602	—	—
10	1·587	—	—	3	1·593	4	1·58
5	1·558	—	—	1	1·563	—	—
—	—	—	—	2	1·548	—	—
5	1·522	—	—	1	1·523	—	—

1. Kidwellite. This study. Chart diffractometer, scan speed $1° \min^{-1}$ in 2θ, graphite monochromatized Cu-K_α radiation. Sample from Fodderstack Mountain.

2. 'Mineral A' (= kidwellite). Moore (1970).

3. 'Mineral B.' This study. Sample from the McMahon pegmatite, South Australia. Gandolfi mount, Fe-K_α radiation, 114·6 mm camera diameter.

deposition of successive phases is controlled by this epitaxial relationship with preferential solution occurring along (but not normal to) this plane where chemical bonding in the third direction is relatively weak.

Kidwellite appears to be closely related structurally to souzalite, $(Al, Mg, Fe)_6Al(OH)_6(PO_4)_4.2H_2O$, $Z = 2$, $a = 12.58$ Å, $b = 5.10$ Å, $c = 13.48$ Å, $\beta = 113.0°$, space group $A2/m$, Am, or $A2$. Souzalite, like kidwellite, is a fibrous mineral that replaces another 5.1 Å structure, that of scorzalite $FeAl_2(OH)_2(PO_4)_2$. Eventual structure analysis will doubtless show that all 5 Å fibre axis phosphates are related at least by the existence of linear face-sharing octahedral trimers.

During the course of this study, a bright-yellow fibrous mineral somewhat resembling strunzite was sent to us by Mr. J. E. Johnson of St. Peters, South Australia. The mineral was found as an alteration product of triphylite from the McMahon pegmatite, South Australia. So far, single crystals suitable for study have not been found although the fibre axis repeat is 5.19 Å. The powder data resemble kidwellite to a significant degree (Table I) except for the presence of a 13.89 Å line in that mineral

and differences in relative intensities between the two. An unknown silky white mineral replacing rockbridgeite from the Sapucaia pegmatite, State of Minas Gerais, Brazil, gives a pattern that is indistinguishable from the Australian material suggesting that a new phase is in fact involved. For the time being we have dubbed it 'Mineral B'. It is interesting to note that kidwellite and 'Mineral B' have as their strongest intensity the 9.41–9.51 Å line, which distinguishes these minerals from all other fibrous ferrosoferric phosphates with a 5 Å fibre repeat.

Chemical analysis. Compact masses of fibrous kidwellite from Fodderstack Mountain were examined optically and appeared free from other minerals. Complete wet chemical and analytical results appear in Table II. It reveals a simple composition in excellent agreement with $NaFe_9^{3+}(OH)_{10}(PO_4)_6.5H_2O$. For $Z = 2$ and a unit cell volume of 1347.05 Å^3 the computed density is 3.34 g cm^{-3}, which satisfactorily explains the observations made on finely crushed fibres placed in methylene iodide solution.

Name. We honour Mr. A. L. Kidwell of Houston, Texas who, over the past thirty years of his personal field study in the Ouachita Mountains, has brought much new information on the phosphate occurrences to light. The type specimen is placed in the U.S. National Museum of Natural History, as well as the other specimens that afforded important new information on this species. The species and its name received approval prior to this publication by the International Commission on New Minerals and New Mineral Names, IMA.

TABLE II. *Kidwellite. Chemical analysis and its interpretation*

	1	2	3	4
P_2O_5	31.3 %	31.42	6.00	6
SiO_2	0.27	—	—	—
Al_2O_3	0.98	—	0.26	—
Fe_2O_3	52.3	53.01	8.91	9
MgO	0.01	—	—	—
MnO	0.02	—	—	—
Na_2O	1.60	2.29	0.71	1
H_2O^+	13.3	13.28	20.11	20
H_2O^-	0.3	—	—	—
Total	100.07	100.00	35.99	36

1. Kidwellite (type). Fodderstack Mountain, Arkansas. Jun Ito, analyst.
2. Weight percent compound for ideal $NaFe_9^{3+}(OH)_{10}(PO_4)_6.5H_2O$. For $Z = 2$, $\rho = 3.34$ g cm^{-3}.
3. Cations based on P = 6.00, computed from (1).
4. Ideal number of cations based on (2).

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